LABORATORY MEASUREMENTS OF TRITIUM

IN

NATURAL WATERS

by

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An independent study submitted to the Graduate School as partial fulfillment of the requirements for the degree of Master of Science in Hydrology

New Mexico Institute of Mining and Technology

Socorro, New Mexico

May, 1972

ACKNOWLEDGEMENTS

I would like to thank Dr. G. W. Gross for his valuable advice and guidance without which this study could not have been carried out. I would also like to extend my deepest appreciation to Dr. W. Brutsaert and Dr. R. McGehee for being the members of the advisory committee.

Special thanks to Mr. D. Rabinowitz for his valuable help and close cooperation in carrying out the experiments.

ABSTRACT

In this study the methods of tritium measurements in natural waters used in the New Mexico Institute of Technology tritium laboratory are explained.

The enrichment, conversion, and counting procedures and necessary equipment, especially periodic addition cells are discussed in detail.

The relation between apparent and real enrichment factors are discussed and two computer programs for the calculation of apparent enrichment factors and initial tritium concentrations of enriched samples, and real tritium enrichment factors from the apparent are given.

Labelling and storing of samples and recording the experimental data are also explained within the text.

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1. INTRODUCTION

The nuclei of some elements are unstable and undergo spontaneous changes to attain a more stable nucleus. This phenomenon is called radioactivity and the elements which exhibit this phenomenon are called radioactive elements. The new element which is the product of disintegration may be again a radioactive element or not.

Radioactive decay law states that the rate of decay is proportional to the amount of atoms present. This proportionality can be expressed by using a proportionality constant λ.

$$\frac{dN}{dt} = -\lambda N. \tag{1.1}$$

Integrating this equation and substituting $N = N_o$ when $t = t_o$

$$N = N_o e^{-\lambda t} \tag{1.2}$$

where

N_o = initial number of the atoms.

N = number of the atoms at time t.

λ = disintegration decay constant (T^{-1}).

t = time interval.

The half life of a radioactive element is denoted by $t_{1/2}$ and is an important concept. It is defined as the time interval during which the number of atoms of radioactive element decreases by one-half. The half-life can be calculated by substituting $N = N_o/2$ into the equation (1.2).

$$\frac{N_o}{2} = N_o e^{-t_{1/2}\lambda} \rightarrow t_{1/2} = \frac{\log_e 2}{\lambda} = \frac{0.693}{\lambda} \qquad (1.3)$$

The atoms having the same atomic number but different mass numbers are called isotopes. They have identical chemical properties. However, they may exhibit different radioactive properties. Hydrogen, for example, has two isotopes, deuterium and tritium with mass numbers 2 and 3 respectively. Of these two tritium is unstable and show radioactive properties whereas deuterium is stable and does not. Tritium is transformed into helium by means of a decay process.

$$_1H^3 \rightarrow {}_2He^3 + {}^-\beta$$

This decay process is called beta emmission and the half-life of this disintegration is 12.26 years.

Natural tritium is produced in the stratosphere, under the continuous bombardment of $_7N^{14}$ with high energy particles of cosmic radiation.

$$_7N^{14} + {}_0n^1 \rightarrow {}_6C^{12} + {}_1H^3.$$

The neutrons generated by the spontaneous fission of uranium and by the (α,n) reactions react with lithium traces in the rocks and form tritium. Tritium is also produced in sea water by a similar mechanism. The production of tritium in the earth's crust is a negligible source of tritium for natural waters [12].

There is a balance between the natural tritium and decay. It is reported by Holmes [11] that there are 6 tritium atoms for every 10^{18} hydrogen atoms in the precipitation over the U.S. This very low

concentration of tritium leads to the definition of tritium units (TU) such that

$$1\ \text{TU} = \frac{1\ \text{T atom}}{10^{18}\ {}_1\text{H}^1\ \text{atom}} \quad .$$

Atomic bomb explosions also produce tritium in the atmosphere. The magnitude of tritium concentration which is produced in this way is much higher than that of natural sources. It is clear that concentration of tritium in the atmosphere changes from time to time depending on the number of explosions of atomic bombs.

By observing tritium concentration fluctuations in the atmosphere and in two artesian wells in the direction of ground water flow, the time interval during which water molecules travel from one well to another can be obtained [8]. Hence, ground water flow and the other parameters of ground water problems can be calculated.

If it is necessary, equation (1.2) should be used for time corrections.

2. COUNTING OF TRITIUM IN NATURAL WATERS

Counting the tritium amount of waters which were sampled in the field can be considered mainly in 3 steps.

a. Enrichment of the samples.

The tritium concentrations in natural waters are very low and it is not possible to measure these low concentrations with the counters available. Therefore, it is necessary to enrich the samples before starting to count. That enrichment can be obtained by means of electrolysis. Even after the enrichment, contamination of the counter from the previous count and from the cosmic radiations is a serious problem in counting. The contamination of the counter from the previous counts can be reduced sufficiently by flushing the counter with pure hydrogen prior to the count. It is possible also to prevent the effects of cosmic radiation by keeping the detector in a stainless steel shield. Despite these precautions, counter might still have an ititial background. It is necessary therefore to measure the background of the counter every two weeks, and necessary corrections should be made.

b. Conversion into the gas phase

c. Counting

These steps will be discussed in detail.

3. ENRICHMENT OF TRITIUM IN NATURAL WATERS

3.1 Theoretical background

Enrichment takes place during electrolysis, because the isotopes of hydrogen are discharged more slowly in relation to their atomic weight. The equation which governs the enrichment is

$$\frac{dP}{P} = \alpha\frac{dD}{D} = \beta\frac{dT}{T} \tag{3.1}$$

P, D, and T are the number of the moles of protium, deuterium, and tritium respectively. α and β are the enrichment factors of deuterium and tritium respectively with respect to protium.

If we apply initial conditions to equation (3.1),

$$\int_{P_o}^{P}\frac{dP}{P} = \alpha\int_{D_o}^{D}\frac{dD}{D} = \beta\int_{T_o}^{T}\frac{dT}{T}\,, \tag{3.2}$$

it becomes

$$\frac{P}{P_o} = \left(\frac{D}{D_o}\right)^{\alpha} = \left(\frac{T}{T_o}\right)^{\beta}. \tag{3.3}$$

If we assume $T << D << P$,

and equation (3.3) becomes

$$\frac{V}{V_o} = \left(\frac{D}{D_o}\right)^{\alpha} = \left(\frac{T}{T_o}\right)^{\beta}. \tag{3.4}$$

V_o and V are the initial and final volumes of the sample respectively.

If x indicates the mole fraction,

$$X_d = \frac{D}{D + T + P} = \frac{D}{P} \rightarrow D = X_d \cdot P. \tag{3.5}$$

In the same way

$$D_o = X_d^o \cdot P_o. \tag{3.6}$$

$$T = X_t \cdot P \tag{3.7}$$

$$T_o = X_t^o \cdot P_o. \tag{3.8}$$

Using equation (3.4)

$$\frac{V}{V_o} = \left(\frac{T}{T_o}\right)^{\beta} \rightarrow T_o = T\left(\frac{V}{V_o}\right)^{-1/\beta}$$

and

$$X_t^o = X_t \left(\frac{V}{V_o}\right)^{1-1/\beta}. \quad \text{(from (3.3) and (3.4))} \tag{3.9}$$

If equation (3.9) is solved for β;

$$\beta = \frac{\ln \frac{V}{V_o}}{\ln \frac{X_t V}{X_t^o V_o}}. \tag{3.10}$$

Running at least one standard sample, prepared by diluting a known standard sample, in every batch, β can be calculated, hence for unknown samples X_t^o can be obtained by using equations (3.10) and (3.9) respectively.

A computer program is given for the calculation of β and X_t^o values (see overleaf).

Starting from $V/V_o = (D/D_o)^{\alpha}$ and in the same way as in calculation of β, α can be obtained

$$\alpha = \frac{\ln \frac{V}{V_o}}{\ln \frac{X_d V}{X_d^o V_o}}. \tag{3.11}$$

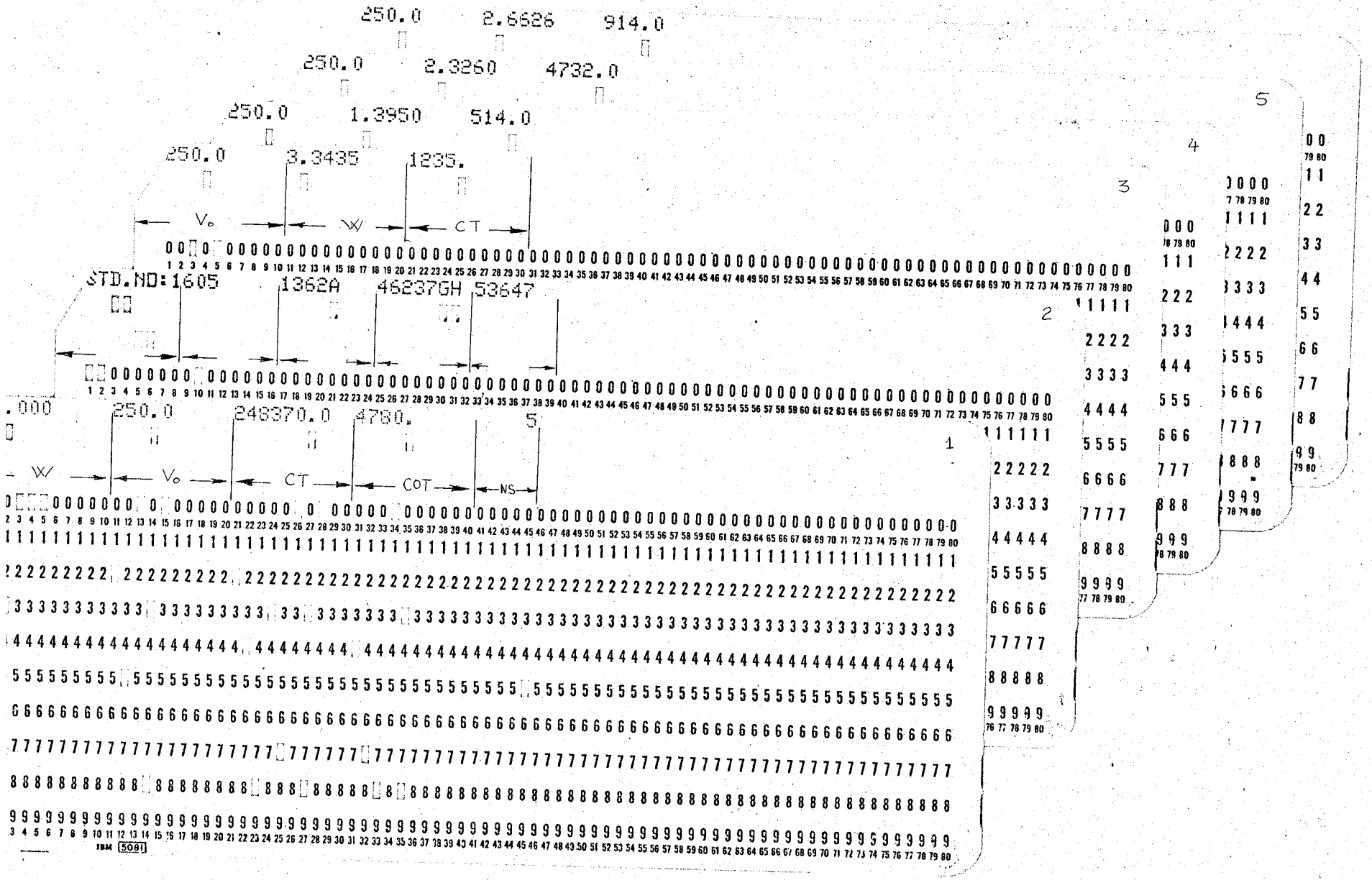
```
C
C
C
C
C               TRITIUM ENRICHMENT(BETA) CALIBRATION
C
C                              AND
C
C             DETERMINATION OF TRITIUM BATCH ENRICHMENT
C               (WITH THE DATA OF PERIODIC ADDITION)
C
C
C
C
C     THIS PROGRAM WAS WRITTEN TO CALCULATE THE APPARENT BETA VALUE FROM THE DA-
C     TA OF THE STANDART SAMPLE AND USING THIS APPARENT BETA VALUE TO CALCULATE
C     THE INITIAL TRITIUM CONCENTRATION OF THE UNKNOWN SAMPLES
C
C
C
C
C     THE TERMS USED IN THE PROGRAM
C
C
C
C     VO    INITIAL VOLUME OF THE SAMPLE                       IN MILLILITERS
C     W     FINAL WEIGHT OF THE SAMPLE(AFTER ELECCROLYSIS)     IN GRAMS
C     COT   INITIAL TRITIUM CONCENTRATION                      IN TRITIUM UNITS
C     CT    FINAL TRITIUM CONCENTRATION                        IN TRITIUM UNITS
C     BETA  ENRICHMENT FACTOR OF TRITIUM OBTAINED WITH
C           THE PERIODIC ADDITION METHOD                       DIMENSIONLESS
C     NS    NUMBER OF SAMPLES TO BE DETERMINE
C     SON   SAMPLE NUMBER
C
C
C
C     THESE TERMS REFERS TO IN THE EQUATIONS (3.9) AND (3.10)
C
C
C
C     VO=VO
C     W=V
C     COT=XO
C     CT=X
C     BETA=BETA
C
C
```

```
C
C
            DIMENSION N(30)
            WRITE(6,2)
  2         FORMAT(1H1,/////,42X,'TRITIUM ENRICHMENT(BETA)  CALIBRATIO
   *N '//,54X,'***********',/////////,18X,'SON',15X,'VO',14X,'W',13X,'C
   *OT',12X,'CT',13X,'BETA'/)
C
C
C
C
            READ(5,1)W,VO,CT,COT,NS
  1         FORMAT(4F10.0,I5)
            L=2*NS
            READ(5,10)(N(K),K=1,L)
 10         FORMAT(20A4)
C
C
C
C     RV    RESIDUAL FRACTION OF WATER
C     RT    FRACTIONAL RECOVERY OF TRITIUM
C
C
C
            RV=W/VO
            RT=W*CT/(VO*COT)
            BETA=(ALOG(RV))/ALOG(RT)
            WRITE(6,3)N(1),N(2),VO,W,COT,CT,BETA
```



```
  3         FORMAT(1X,17X,2A4,F15.2,F15.3,F15.2,F15.0,F15.3)
            WRITE(6,71)
 71         FORMAT(1H0,////////,39X,'DETERMINATION OF TRITIUM BATCH EN
   *RICHMENT',/,53X,'************'/)
            WRITE(6,70)
 70         FORMAT(1H0,/////,18X,'SON',15X,'VO',14X,'W',14X,'CT',12X,'
   *BETA',12X,'COT'/)
```

```
                J=NS-1
      DO 20 I=1,J
                READ(5,4)VO,W,CT
    4           FORMAT(3F10.0)
                RV=W/VO
C
CCC
CCC     RBETA   RECIPROCAL OF BETA VALUE WITH OPPOSITE SIGN
CCC     F       A SUITABLE FACTOR FOR ROUTINE CALCULATIONS
CCC
C
                RBETA=-1./BETA
                F=RV**RBETA
                COT=CT*RV*F
                N1=2*I+1
                N2=N1+1
                WRITE(6,7)N(N1),N(N2),VO,W,CT,BETA,COT
    7           FORMAT(1X,17X,2A4,F15.2,F15.3,F15.0,F15.3,F15.2)
   20   CONTINUE
                END
```



PUNCHING OF DATA CARDS

1. Data card of standard sample
2. Card for sample numbers
   The number of standard sample
3. Data card of sample # 605
4. Data card of sample # 1362A
5. Data card of sample # 46237GH

TRITIUM ENRICHMENT(BETA) CALIBRATION

****

SCN	VO	W	COT	CT	BETA
STD.NO:1	250.00	2.000	4780.00	248370.	5.500

DETERMINATION OF TRITIUM BATCH ENRICHMENT

****

SCN	VO	W	CT	BETA	COT
605	250.00	3.343	1235.	5.500	36.19
1362A	250.00	1.395	514.	5.500	7.37
46237GH	250.00	2.326	4732.	5.500	103.05
5367	250.00	2.663	914.	5.500	22.23

Deuterium is present in normal hydrogen to the extent of one part in 5000 to 7000 in rainwater, hence initial deuterium concentration can be assumed constant and has a value of 0.015%. Final deuterium concentration after the enrichment process X_d can be obtained by means of falling drop technique.[10] Since the variables on the right-hand side of the equation (3.11) are known, α can be calculated.

Experiments of Ostlund and Werner[17] show that the ratio of logarithms of β and α is constant and:

$$\gamma = \log \beta / \log \alpha = 1{,}337 \pm 0.007.$$

3.2 Preparation of standard samples

Standards for our experiments were prepared by diluting the standard samples obtained from U.S. Atomic Energy Commission, at various ratios. The time corrections of these standards can be found from the tables provided. Time corrected standard sample N^{o} 65-3 contained 96.81×10^6 TU on 2nd August 1971.

Standard No 1 for our experiments was prepared from sample No 65-3 by dilution in two steps.

1st dilution $\dfrac{\text{5 ml. of Std \#65-3}}{\text{2000 ml. of Bg + 5 ml. of Std \#65-3}} = \dfrac{1}{401}$

2nd dilution $\dfrac{\text{10 ml. of diluted sample}}{\text{495 ml. of Bg + 10 ml. of diluted sample}} = \dfrac{1}{50.5}$

Total dilution $= \dfrac{1}{401} \times \dfrac{1}{50.5} = \dfrac{1}{20250.5}$

In this case, initial tritium concentration of standard No 1 on 2nd August 1971 is

$$\frac{96.81 \times 10^6}{20250.5} = 4.78 \times 10^3 \text{ TU.}$$

Standard No 2 which has a total dilution 1/57340 and tritium in the amount of 1688 TU was prepared in the same way.

3.3 Equipment

3.3.1 Periodic addition cells

Water samples are enriched in electolyzing cells. These cells may be ordinary cells or periodic addition cells. A desired volume of water sample is put into an ordianry electolyzing cell and electrolyzed to a desired volume. But in periodic addition cells, water samples are electrolyzed by adding a certain volume of water periodically to a cell. Periodic addition cells [17] are now used in the tritium laboratory of New Mexico Tech for the enrichment of water samples.

A picture of a periodic addition cell is shown in Figure 1. A complete periodic addition cell has 3 main parts:

a. Drop funnel,

b. Electrodes,

c. Cell itself.

3.3.1.1 Drop funnels

The volume of the drop funnels used in the laboratory is 250 ml., marked at 25 ml. intervals. They have also a valve to make the additions and Roman numerals on each indicate drop funnel numbers.

3.3.1.2 Electrodes

Iron and nickel electrodes are used as the cathode and anode respectively, having a surface area of 34 cm^2. They are located in the flattened part of the electrolyzing cell and are covered with water when 50 ml. of water is put into the cell. Connection wires are supported by 2 teflon baffle plates.

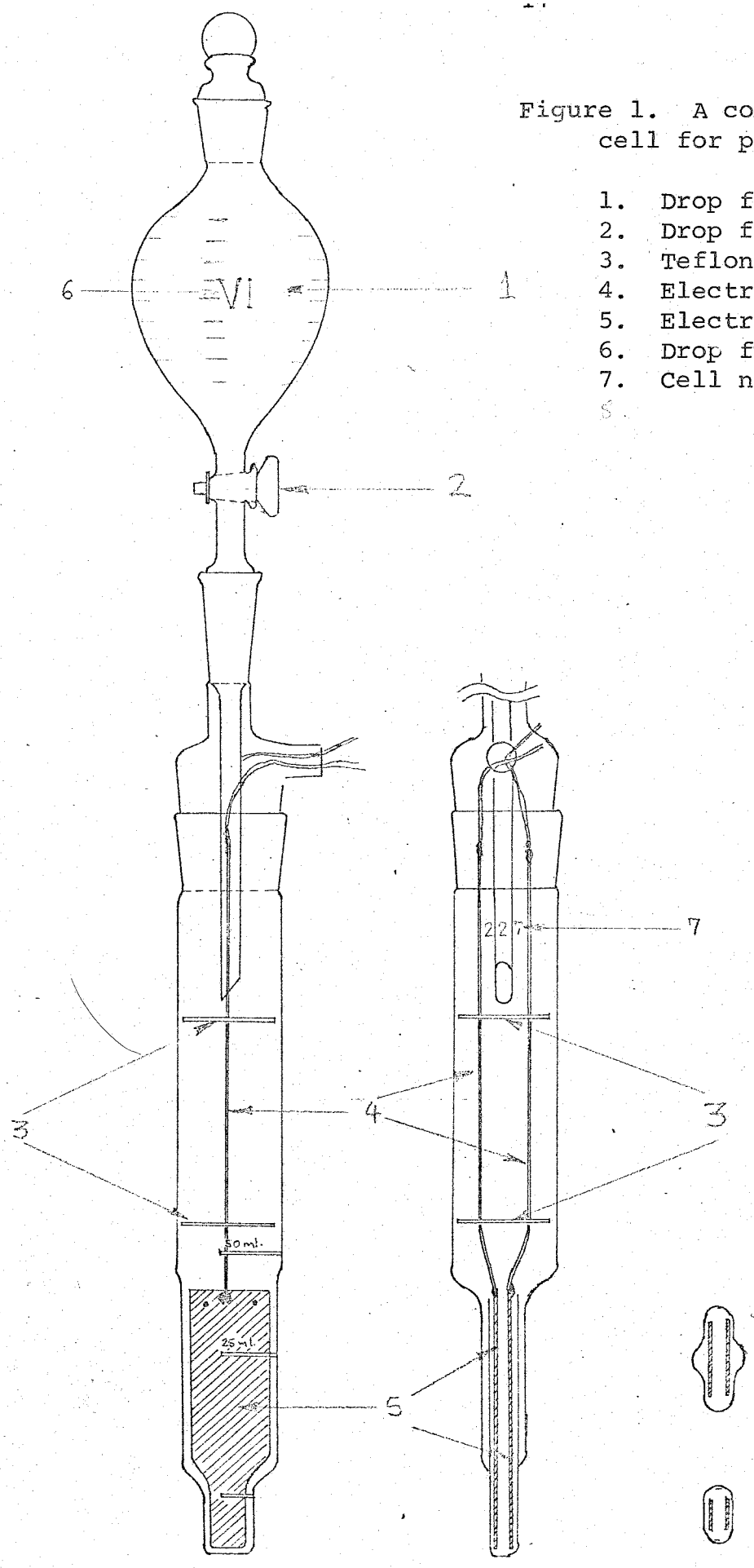


Figure 1. A complete electrolysis cell for periodic addition

1. Drop funnel
2. Drop funnel valve
3. Teflon plates
4. Electrode connection wires
5. Electrodes
6. Drop funnel number
7. Cell number

3.3.1.3 Cell

Since enrichment is faster at points closer to the electrodes, the bottom part of the electrolysis cell is flattened to achieve approximately constant enrichment at every point. There are 3 marks on the cells showing 50 ml., 25 ml., and 2.5 ml., just above the neck of the flattened part, on the middle and narrowest part respectively, The factory printed numbers located at the upper part of each cell are used as a cell number.

3.3.2 Low temperature water bath and power supply

In order to avoid losing large numbers of heavy isotope atoms, electrolysis should take place in a low-temperature water bath with the temperature kept at about 7°C. This temperature is provided by means of a refrigeration unit and kept almost constant by a thermoswitch. There is also a water pump which circulates the water throughout the bath constantly. This provides a constant temperature in every point of the bath.

Hydrogen and oxygen, which are the products of electrolysis, should be disposed of to avoid an explosion. This is done by means of an exhaust pipe, fan, and connection hoses.

The details of the water bath and the power supply are shown in Figure 2.

A maximum of 10 samples can be electrolyzied simultaneously in the New Mexico Tech tritium laboratory.

3.3.3 Vacuum distillation apparatus

Before starting electolysis, electrolyte must be added to maintain the electric current through the sample. After electrolysis the electrolyte must be removed by neutralization and vacuum distillation.

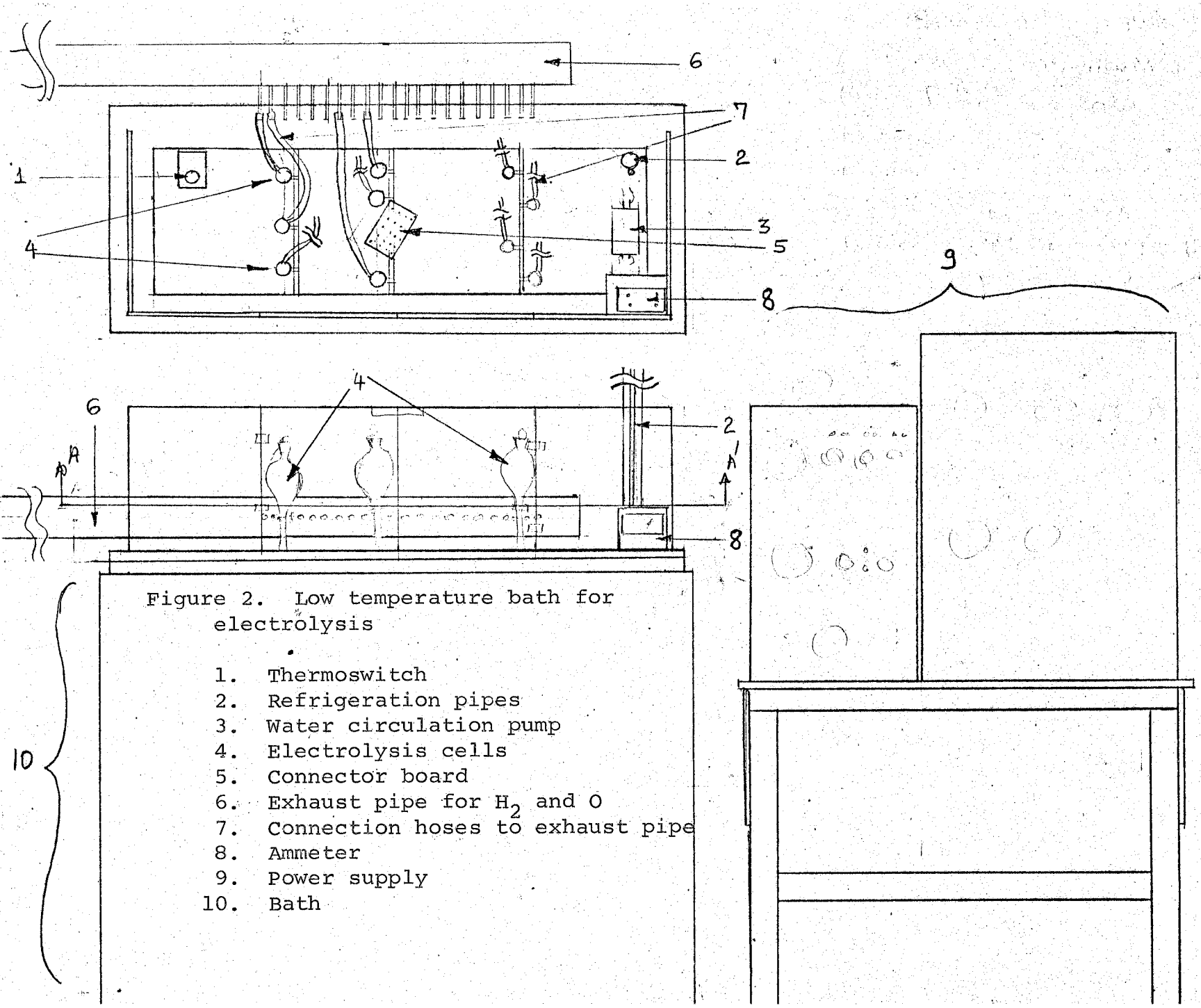


Figure 2. Low temperature bath for electrolysis

1. Thermoswitch
2. Refrigeration pipes
3. Water circulation pump
4. Electrolysis cells
5. Connector board
6. Exhaust pipe for H_2 and O
7. Connection hoses to exhaust pipe
8. Ammeter
9. Power supply
10. Bath

The vacuum distillation apparatus used is shown in Figure 3.

3.4 Experimental procudure

3.4.1 Preparation of the samples for electrolysis

3.4.1.1 Collection of the field data and recording of the samples

The ground water data should be chosen from the artesian wells, and before the sample is taken the well must be pumped to flush the casing.

The samples are put in one gallon bottles. The bottles are carefully labeled with sample number, date of collection and location. Information about the pumpage before the sampling, especially for the wells which are not in use for a long time, should be added. Indication of the owner also might be useful.

In the N.M. Tech laboratory this information is recorded in a "sample register book."

The copy of one page from this book is given as an example. The number at the top left is the page number. The other numbers on the left in a column are the sample numbers. Roswell is the name of the area where the samples on this page were collected. "Date started" means the date on which counting began.

3.4.1.2 Regular distillation

The presence of salt in samples which are collected at the field may cause trouble during electrolysis, therefore it is necessary to remove the salt prior to electrolysis. Hydrogen may also be present related to the salts. But as the sample is not enriched, it is assumed that the error caused in losing hydrogen by means of distillation will stay between the error limits.

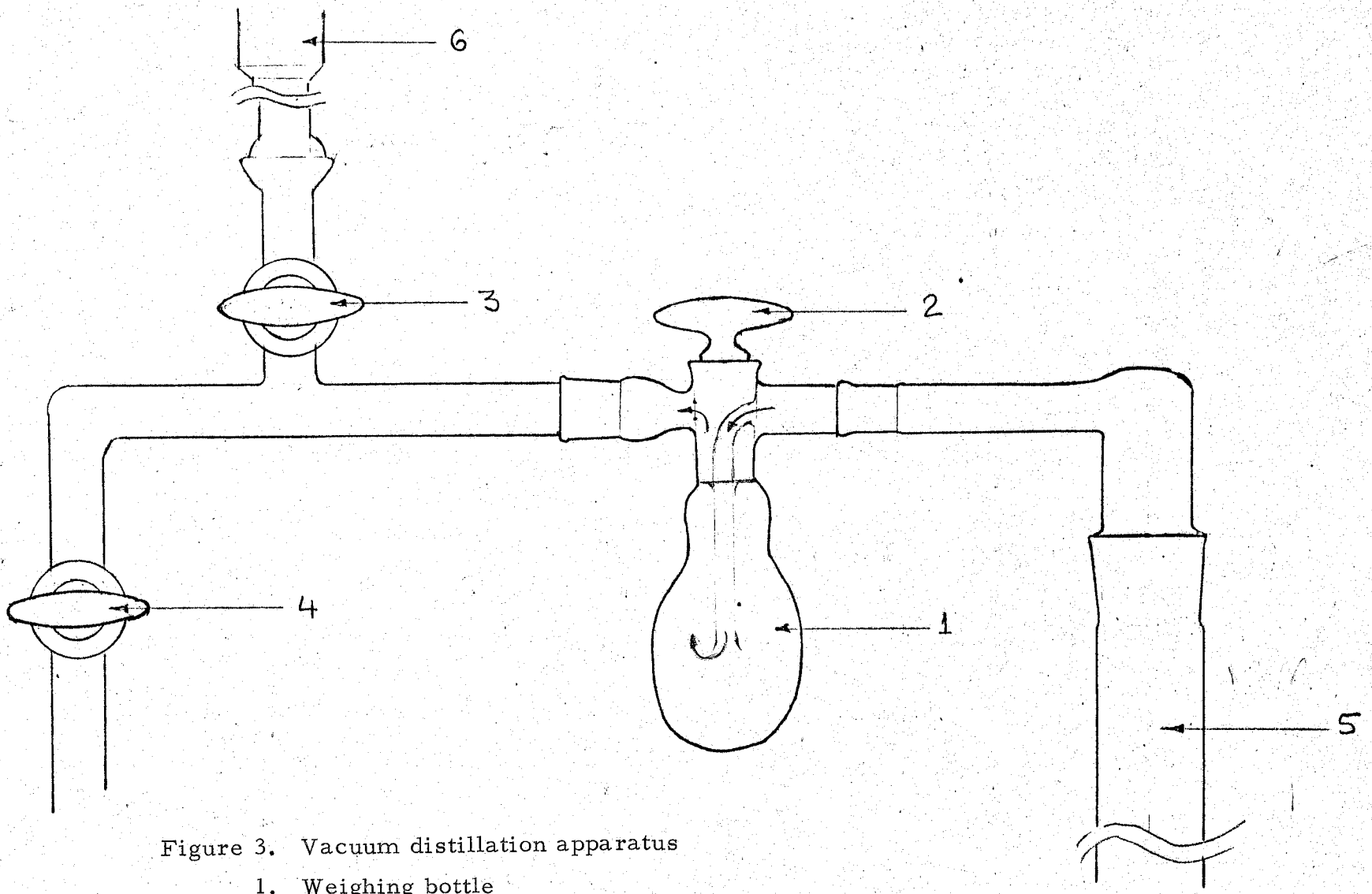


Figure 3. Vacuum distillation apparatus

1. Weighing bottle
2. Weighing bottle valve
3. Pirani gauge valve
4. Pump valve
5. Electrolysis cell
6. Pirani gauge

Arrows show direction of the air during pumpage

#1380 Date collected: May 20, 1968 Roswell
Date started:
Location: Max Wiggins (E. of Dexter) Irr.
Collected after several hrs. pumping

#1381 Date collected: May 20, 1968 Roswell
Date started:
Location: H. B. Pollard (N.E. of Lake Arthur); D.C. Pipe, Irr.
Collected after 5 hrs. pumping

#1382 Date collected: July 15, 1968 Roswell
Date started:
Location: Max Wiggins (E. of Dexter)
Collected after several hrs. pumping

#1383 Date collected: June 17, '68 Roswell
Date started:
Location: Max Wiggins
Collected after several hrs. pumping

#1384 Date collected: July 15, 1968 Roswell
Date started:
Location: ~~H. B.~~ Pollard

#1385 Date collected: June 17, 1968 Roswell
Date started: 10/10/71
Location: H. B. Pollard (N.E. Lake Arthur)

#1386 Date started: July 15, 1968 Roswell
Date started: 10/10/71
Location: Wood Ranch

#1387 Date collected: April 16, 1968 Roswell
Date started: 10/10/71
Location: Max Wiggins

#1388 Date collected: June 17, 1968 Roswell
Date started: 10/10/71
Location: Elk #1 (pumped 5 min., Flow)

#1389 Date collected: Aug. 6, 1968 Roswell
Date started: 10/10/71
Location: Clardy Farms, Oasis

#1390 Date collected: Aug. 6, 1968 Roswell
Date started: 10/10/71
Location: Wood Ranch (@hydrant)

After distillation, each sample is put into a drop funnel. Sample and drop funnel numbers are recorded in a daily record book.

250 ml. of previously distilled sample is electrolyzed.

3.3.2 Addition of electrolyte

0.6 gr. Na_2O_2 is dissolved in 50 ml. of each sample.

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2 + Heat.$$

3.4.2 Electrolysis

50 ml. of a sample which contains 0.6 gr. of Na_2O_2 and 200 ml. of the same distilled sample is put into each of the periodic addition cells and its funnel, respectively. One of the samples must be a known sample in order to be able to calculate the enrichment factor β. The electrolysis is made at a constant current of 3.0 A. 50 ml. of a sample will reduce to 25 ml. after 24 hours. Every 24 hours 25 ml. of sample should be added to the cells from the funnels. At the end of the ninth day there will be only 25 ml. of sample in each cell. At that time the current should be reduced to 0.3 A. Approximately 6 days after the current is reduced, only 3 ml. of sample will remain in the cells and the electrolysis is complete. After electrolysis is over electrolysis cells should be cleaned with soap and rinsed carefully.

Black coating on the electrodes offers a rapid way to constancy of β. Therefore the electrodes are removed carefully and rinsed in running water. Only if their black coating is too thick, they are brushed gently with a soft bottle brush or pipe cleaner.

Both electrodes and cells are left to dry.

Equations (3.10) and (3.9) apply when the volume of the sample is reduced directly to a certain ratio of the initial volume by electrolysis.

However in the method which is the subject of this study the samples are electrolyzed by adding a certain volume of the sample periodically into electrolysis cells which were explained in detail previously. Certainly the β value obtained in the latter will differ from the previous one. An equation can be given simply $f(\beta, \beta') = 0$

where

β value obtained by electrolysis of the sample directly to a certain volume.

β' value obtained by periodical addition of certain amount of the sample into the electrolysis cell.

3.4.3 Neutralization of enriched sample

To avoid losing a large amount of hydrogen which is bonded in the NaOH, it is necessary to neutralize the enriched sample. CO_2 is added to the enriched sample before vacuum distillation. A hose, one end of which is connected to a CO_2 tank, can be used for this purpose. The other end of the hose is connected to a pipet, which is submerged in the enriched sample in the cell. By experiments it is found that addition of CO_2 at a pressure of 10 lbs. to the enriched sample for about half an hour is enough for neutralizing.

$$2NaOH + CO_2 \quad Na_2CO_3 + H_2O.$$

3.4.4 Vacuum distillation

It is necessary to get off the Na_2CO_3 which was formed in the liquid during the neutralization. This must be done before conversion and since the sample is measured in the amount of 2-3 milliliters, after the electrolysis, vacuum distillation should be chosen for this purpose.

The main part of the vacuum distillation apparatus is a weighing bottle. It is specially manufactured with a valve provided to pump air

in the cell through the bottle. As it is seen in the figure, this valve also provides a long circulation of the vapor inside the bottle. This and -200°C provided by liquid nitrogen prevent the water passing through wighing bottle. The system should be pumped below 2000 μs, as measured by Pirani gauge. After reaching 2000 μs or less, the pump is stopped. Pirani gauge and pump valves are closed and the weighing bottle is submerged into liquid nitrogen, thus initiating vacuum distillation. Distillation will continue until the cell is completely dry. After that, the sample is weighed and pipetted into a bottle of 4-5 cc. This bottle must be labelled with the sample, batch, and cell number.

3.5 Recording of enrichment

Table 1 is given as an example of how to keep the records of enrichment.

The first five columns are used to indicate funnel numbers, sample numbers, cell numbers, total volume of the samples, and the amount of Na_2O_2 added to the cells respectively. On the sixth column, the initials of the person who started to electrolyze, the date, and the time should be recorded. The columns from 7 through 14 show the additions made every day. On those columns, also, the initials of the person who made the additions, the date, and the time should be noted.

As it is mentioned before, at the end of the ninth day the samples reduce to 25 ml. At that time the electric current also should be reduced to 0.3 A. This is shown on column 15. The columns under the titles "power off" and "vac. dist." indicate the end of electrolysis and

TABLE 1

Batch Number 3

Funnel No.	Sample No.	Cell No.	Initial volume V_o (ml.)	Na_2O_2 added gr.	3.0A power on YB	ADDITIONS								Power reduced to 0.3A YB	Power off	Vac. dist.	Recovered gr.	Remarks
						1st By YB	2nd By YB	3rd By DR	4th By YB	5th By DR	6th By YB	7th By YB	8th By YB					
I	1373	226	250	0.6	8/9/71 0940	8/10/71 0950	8/12/71 1000	8/13/71 1000	8/14/71 1040	8/15/71 0950	8/16/71 1020	8/17/71 1300	8/18/71 1305	8/19/71 1600	8/28/71 0530DR	9/11/71 0940JW	2.5387	
II	1375	30	"	"	"	"	"	"	"	"	"	"	"	"	8/27/71 0630 DR	9/10/71 1600 YB	.6287	Lost in distill.
III	1374	24	"	"	"	"	"	"	"	"	"	"	"	"	8/27/71	9/10/71	3.1722	
IV	911	23	"	"	"	"	"	"	"	"	"	"	"	"	8/27/71 2100DR	9/12/71 1030JW	3.0876	
V	Std. #2	227	"	"	"	"	"	"	"	"	"	"	"	"	8/26/71 2110DR	9/12/71 0930JW	2.5089	
VI	1370	27	"	"	"	"	"	"	"	"	"	"	"	"	8/28/71 1700YB	9/11/71 1040JW	1.7160	not much sample to begin w/
VII	1367	228	"	"	"	"	"	"	"	"	"	"	"	"	8/27/71 2100JW	7/13/71 1225JW	1.5155	
VIII	1371	225	"	"	"	"	"	"	"	"	"	"	"	"	8/28/71 0530DR	9/13/71 1630JW	2.6340	
IX	1364	28	"	"	"	"	"	"	"	"	"	"	"	"	8/26/71 2110DR	9/13/71 1140JW	2.3856	
X	1372	25	"	"	"	"	"	"	"	"	"	"	"	"	8/28/71 0530DR	9/12/71 1135JW	2.2440	

Electrolysis off 1550 8/10/71 1550 8/11/71 because of strong wind.

Electrolysis off 1150 - 1430 because of power failure.

vacuum distillation. Also on those columns the date, the thime and the initials are important. The amount of sample which is recovered at the end of the enrichment is shown on column 18.

If there is something wrong with any one of the samples during the enrichment, the result can be mentioned under the "remarks" on the row which belongs to that sample. Any other unusual happenings during the electrolysis can be mentioned below the table by indicating the time and cuase.

3.6 Discussion of periodic additions and computation procedure of real enrichment factor.

As it was mentioned before, enrichment factors obtained by using periodic addition cells are not real. The following development is from Ostlund[17].

Let

β real enrichment factor

β' apparent enrichment factor

T_o initial number of the moles of tritium in 250 ml. sample

$T = T_o \left(\frac{V}{V_o}\right)^{\frac{1}{\beta}}$ from the equation (3.4).

Since, in the periodic addition method only 50 ml. sample is electrolyzed, V/V_o is constant and equal to one-half, the number of moles of tritium in the reacting liquid at the end of the first day;

$$T_1 = 0.2\ T_o(1/2)^{\frac{1}{\beta}}$$

at the end of the second day

$$T_2 = 0.2\ T_o(1/2)^{\frac{1}{\beta}} + 0.1\ T_o(1/2)^{\frac{1}{\beta}}$$

and so on

$$T_9 = 0.2\ T_o(1/2)^{\frac{1}{\beta}} + 0.1\ T_o \sum_{i=1}^{8} (1/2)^{\frac{1}{\beta}}$$

The tritium recovery at the end of the 9th day

$$r = \frac{T_9}{T_o} = 0.2(1/2)^{\frac{1}{\beta}} + 0.1 \sum_{i=1}^{8} (1/2)^{\frac{1}{\beta}}$$

Over all recovery when the electrolysis is over

$$R = r\ (\frac{V}{25})^{\frac{1}{\beta}} \qquad (3.5.1)$$

where

V final volume of the liquid

R value was given by Ostlund[17]

$$R = r(\frac{V}{25})^{\frac{1}{\beta}} = (\frac{V}{250})^{\frac{1}{\beta'}} \qquad (3.5.2)$$

Substituting the value of r and arranging the equation

$$2[(1/2)^9 \frac{V}{25}]^{\frac{1}{\beta}} + \sum_{i=1}^{8} [(1/2)^i \frac{V}{25}]^{\frac{1}{\beta}} - 10(V/250)^{\frac{1}{\beta'}} = 0.$$

After calculation of β', the obove equation can be solved for β numerically. A computer program is given for this purpose. In this program β values were calculated by using the data of standard samples of batch number 1.

```
C
C
C
C
C     THIS PROGRAM WAS WRITTEN TO SOLVE THE VALUE FOR BETA FROM THE EQUATION
C     BELOW BY USING NEWTON ITERATIVE METHOD
C
C
C
C                                                  8
C     F(BETA)=2*((A**9)*(V/25))**(1/BETA)+SUM((A**I)*(V/25))**(1/BETA)-
C                                                 I=1
C           10*(V/250)**APBETA=0
C
C
C
C     WHERE
C
C
C     A   =     (0.5)**I)(V/25)       I=1,9
C     V         FINAL VALUME OF THE SAMPLE                        IN MILLILITERS
C     APBETA    APPERANT BETA VALUE WHICH IS OBTAINED BY
C               USING PERIODIC ADDITION CELLS                     DIMENSIONLESS
C     BETA      REAL ENRICHMENT FACTOR TO BE CALCULATED           DIMENSIONLESS
C
C
C
C     MAIN PROGRAM WHICH HAS ONE SUBROUTINE READS THE DATA,SETS UP THE ABOVE
C     EQUATION,CALLS THE SUBROUTINE,CALCULATES THE BETA ITERATIVELY AND PRINTS
C     OUT THE RESULTS RESPECTIVELY.
C     SUBROUTINE FONK: TAKES THE DERIVATIVES WITH RESPECT TO BETA AND CALCULATES
C     F(BETA) AND DERIVATIVE OF F(BETA) FOR A CERTAIN VALUE OF BETA AND
C     RETURNS TO THE MAIN PROGRAM
C
C
C
      DIMENSION A(10)
C
C
C
C     TOL       TOLLERANS OF CALCULATION ERROR IN BETA
C     NM        NUMBER OF THE SAMPLES
C
C
C
```

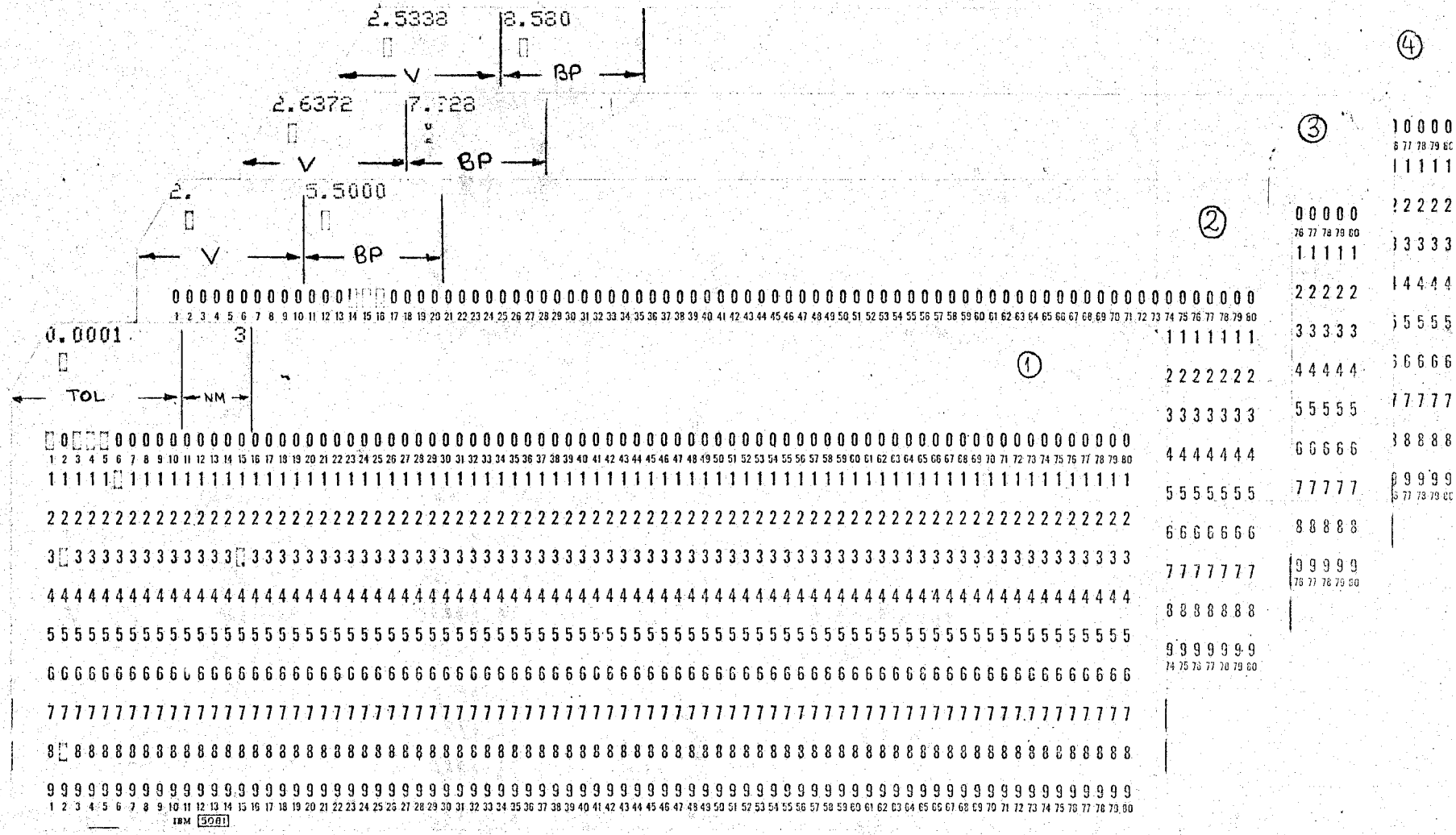
```
      READ(5,12)TOL,NM
   12 FORMAT(F10.0,I5)
C
CCCCC
C     DF1       A DUMMY VALUE
CCCCC
C
      DF1=10000.
      WRITE(6,45)
   45 FORMAT(////////////)
      DO 40 J=1,NM
C
CCCCC
C     BP        APPARENT BETA
CCCCC
C
          READ(5,1) V,BP
    1     FORMAT(2F10.0)
  100     BETA=BP
          DO 10 IJ=1,9
             A(IJ)=((0.5)**IJ)*(V/25.)
   10     CONTINUE
          DO 20 JJ=1,100
C
```



```
C
CCCCC
C     FB        F(BETA)
C     FBP       DERIVATIVE OF FUNCTION BETA WITH RESPECT TO BETA
CCCCC
C
```

```
C
            CALL FONKS       (V,BP,A,BETA,FBP,FB)
            D=FB/FBP
            BETA=BETA-D
            DF=ABS(D)
            IF(DF.LT.TOL) GO TO 30
            DIFFER=DF1-DF
            IF(DIFFER.LT.0.) GO TO 41
 20       CONTINUE
 41       WRITE(6,19)
 19       FORMAT(10X,'DOES NOT CONVERGE')
          GO TO 40
 30       WRITE(6,31)V,BP,BETA
 31       FORMAT(20X,'V=',F7.4,10X,'APPARENT BETA=',F8.4,10X,'BETA=',F8.
     *4////)
 40    CONTINUE
       END
```

```
      SUBROUTINE FONKS(V,BP,A,BETA,FBP,FB)
      DIMENSION A(10)
      B=1./BETA
      FBP=0.
      FB=-10.*(V/250.)**(1./BP)
      DO 10 I=1,8
          FB=FB+A(I)**B
          FBP=FBP-(ALOG(A(I)))*(A(I)**B)/(BETA**2)
 10   CONTINUE
      FB=FB+2.*A(9)**B
      FBP=FBP-2.*(ALOG(A(9)))*(A(9)**B)/(BETA**2)
      RETURN
      END
```



Arrangement of the data cards.

V= 2.0000	APPARENT BETA= 5.5000	BETA= 6.8423
V= 2.6372	APPARENT BETA= 7.9280	BETA= 10.1282
V= 2.5338	APPARENT BETA= 8.5800	BETA= 10.9657

3.7 Error analysis

Let for simplicity

$$X = X_t$$

$$X_o = X^o_t$$

$$y = \left(\frac{X}{X_o}\frac{V}{V_o}\right)^{\beta}$$

Then equation (3.9) can be written in the form

$$y^{\beta} = \frac{V}{V_o}$$

and

$$\frac{\Delta(y^{\beta})}{y^{\beta}} = \frac{\Delta V}{V} - \frac{\Delta V_o}{V_o} \qquad (3.7.1)$$

$$\Delta(y^{\beta}) = \Delta\left[\left(\frac{X}{X_o}\frac{V}{V_o}\right)^{\beta}\right] = \beta y^{\beta-1}\frac{\Delta X}{X_o}\frac{V}{V_o} + \beta y^{\beta-1}\frac{X}{X_o}\frac{\Delta V}{V_o}$$

$$-\beta y^{\beta-1}\frac{X}{X_o^2}\frac{V}{V_o}\Delta X_o - \beta y^{\beta-1}\frac{X}{X_o}\frac{V}{V_o^2}\Delta V_o + (y^{\beta}\ln y)\Delta\beta$$

$$= \beta y^{\beta}\frac{\Delta X}{X} + \beta y^{\beta}\frac{\Delta V}{V} - \beta y^{\beta}\frac{\Delta X_o}{X_o} - \beta y^{\beta}\frac{\Delta V_o}{V_o} + (y^{\beta}\ln y)\Delta\beta$$

$$\frac{\Delta(y^{\beta})}{y^{\beta}} = \beta\frac{\Delta X}{X} + \beta\frac{\Delta V}{V} - \beta\frac{\Delta X_o}{X_o} - \beta\frac{\Delta V_o}{V_o} + \Delta\beta\ln y \qquad (3.7.2)$$

Equating the equations (3.7.1) and (3.7.2) and by solving for $\frac{\Delta X_o}{X_o}$

$$\frac{\Delta X_o}{X_o} = \left(\frac{\Delta V}{V} - \frac{\Delta V_o}{V_o}\right)\left(1 - \frac{1}{\beta}\right) + \frac{\Delta X}{X} + \frac{\Delta\beta}{\beta}\ln\left[\frac{X}{X_o}\frac{V}{V_o}\right] \qquad (3.7.3)$$

Since the sign of ΔV, ΔX, etc. is unknown, then the equation (3.7.3) is written as

$$\pm\frac{\Delta X_o}{X_o} = \pm\left(\frac{\Delta V}{V} + \frac{\Delta V_o}{V_o}\right)\left(1 - \frac{1}{\beta}\right) \pm \frac{\Delta X}{X} \pm \frac{\Delta\beta}{\beta} \ln\left[\frac{X}{X_o}\frac{V}{V_o}\right] \qquad (3.7.4)$$

The equation (3.7.4) also can be used for the calculation of error in β, by solving for $\frac{\Delta\beta}{\beta}$

Error in X can also be calculated with the formula below. The terms will be explained in detail in the following chapters.

$$\pm\frac{\Delta X}{X} = \pm\frac{\Delta T}{T} \pm \frac{\Delta C_r}{C_r} \pm \frac{\Delta P}{P} \pm \Delta(EV) \qquad (3.7.5)$$

$$\frac{\Delta C_r}{C_r} = \frac{1}{\sqrt{C_r}} \qquad (3.7.6)$$

where

T Absolute temperature of the tube

C_r Net count

P Actual pressure of hydrogen

EV Effective volume of the counter.

The factor $\ln\left[\frac{X}{X_o}\frac{V}{V_o}\right]$ shows the importance of counting and electrolysis techniques. Improvements in electrolysis techniques will increase the tritium recovery $r = \frac{X}{X_o}$ and improvements in counting techniques will not be necessary for low V/V_o ratios. The improvements in these techniques will make the factor $\ln\left[\frac{X}{X_o}\frac{V}{V_o}\right]$ tend to zero.

Equation (3.7.6) also shows that long counting times will decrease the error in X.

The other errors come from ordinary measurements, like volume, temperature, etc. If there is need, more precise instruments can be used.

It also should be remembered that the β value was concerned in this chapter is the real enrichment factor.

3.8 Maintenance of the equipment

a. Glasswares: After each article is used, it is cleaned with tap water, dried and kept in a drawer.

Drop funnels might be rinsed with alcohol for quick drying.

b. Electrodes: After the electrolysis, electrodes are removed carefully and rinsed in running water, and then let to dry. Only if their black coating is too thick, they are brushed gently with a soft bottle brush or a pipe cleaner.

c. Pipets: Each pipet is used only once and they are collected in a container full with tap water, afterwards they are rinsed, dried in the oven, and kept in a drawer.

d. Electrolyzed samples: After the vacuum distillation each sample is pipetted into a bottle of 4-5 cc., labelled with the sample, batch, and cell numbers on it and stored in a box until counting.

4. CONVERSION INTO GAS PHASE

4.1 Theoretical background

Hydrogen must be separated from oxygen before counting. In order to do this, water vapor is forced through a magnesium column heated to 600°C.

$$Mg + H_2O \xrightarrow{600°C} MgO + H_2.$$

The hydrogen we get in this way may be H_2, T_2, or HT. The second step is to collect hydrogen in charcoal by freezing it at -200°C by means of liquid nitrogen. A cold trap is used between those steps to catch water vapor which has not reacted with the magnesium.

4.2 Equipment

The equipment used for the conversion experiments consists mainly of two parts, oven and gas assembly as shown in Figure 4.

The oven is used to heat the magnesium column to 600°C. The magnesium insert details and the installation of the magnesium insert into the oven are shown in Figures 5 and 6 respectively. After every two or three conversions the magnesium column should be changed. To avoid leakage the O ring at the bottom of the magnesium insert should be greased.

There are two cold traps on the glass assembly. One of them is used to catch the unreacted water vapor with magnesium. Hydrogen is collected on the charcoal. After a sample is transferred into the counter, the charcoal of this sample should be cleaned by pumping. A good cleaning is obtained by submerging the charcoal cleaning cold trap into the liquid nitrogen.

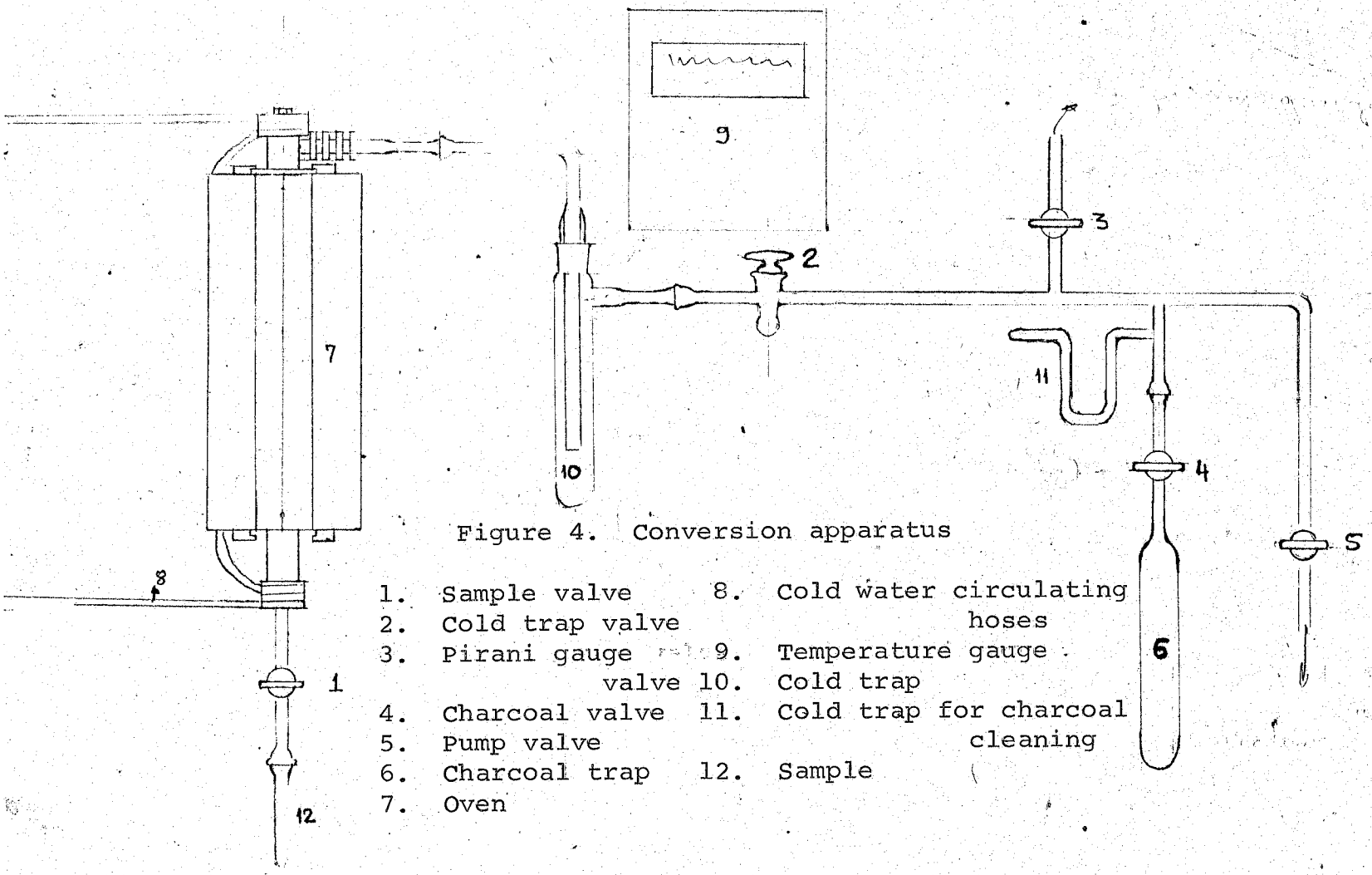
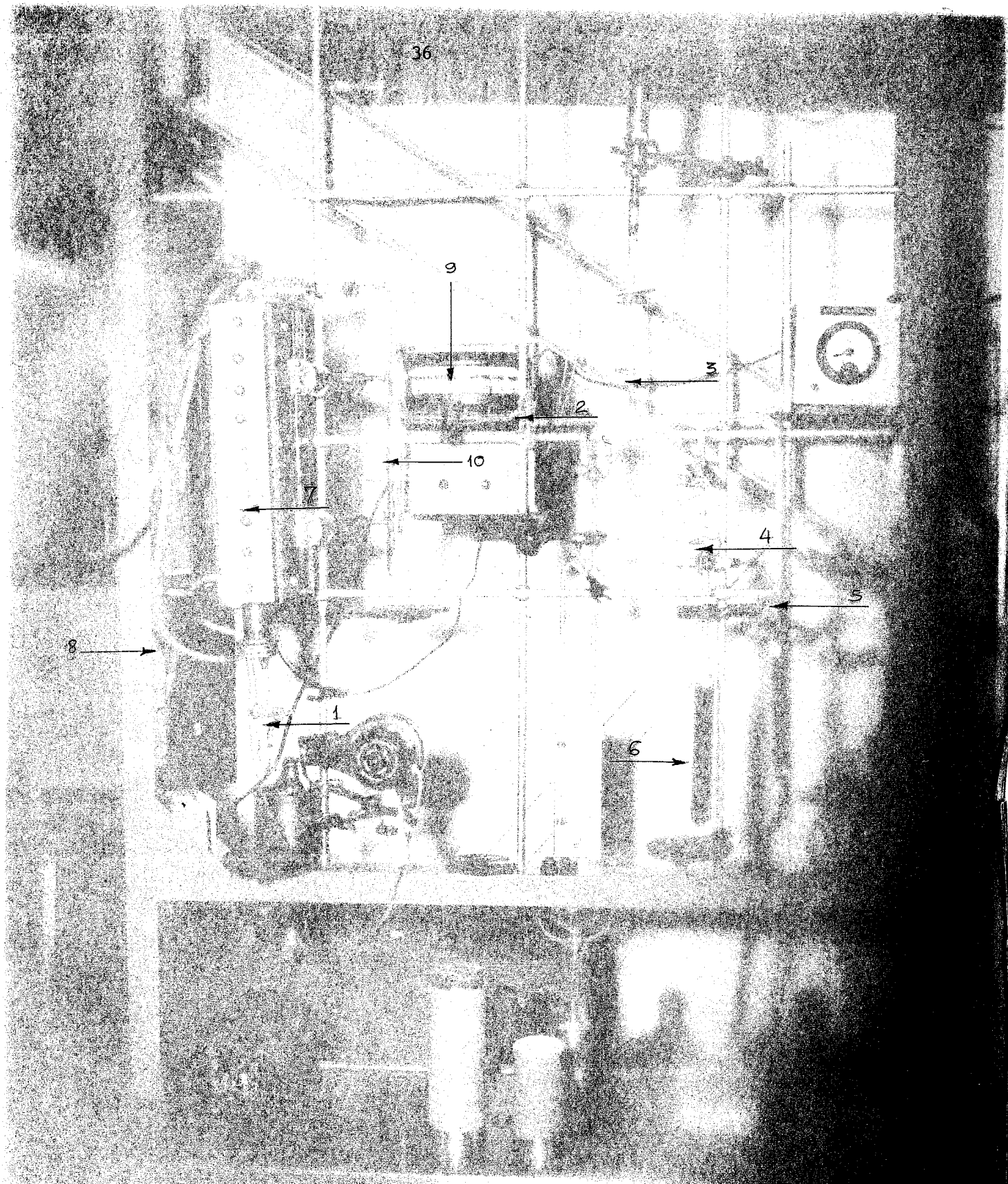


Figure 4. Conversion apparatus

1. Sample valve
2. Cold trap valve
3. Pirani gauge valve
4. Charcoal valve
5. Pump valve
6. Charcoal trap
7. Oven
8. Cold water circulating hoses
9. Temperature gauge
10. Cold trap
11. Cold trap for charcoal cleaning
12. Sample



PICTURE 1

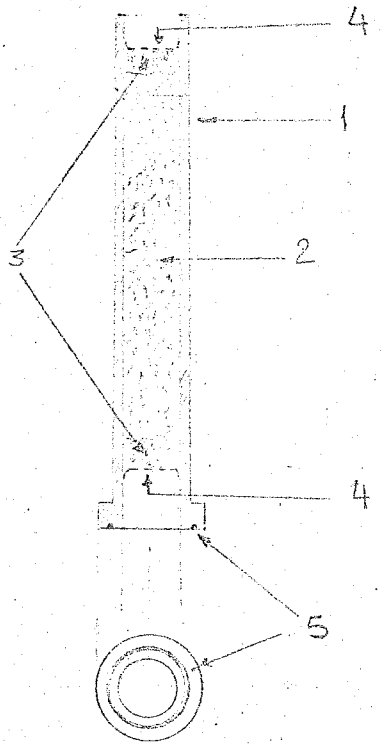


Figure 5. Magnesium insert details

1. Magnesium insert
2. Magnesium grains
3. Glass wool
4. Stainless steel screens
5. O ring

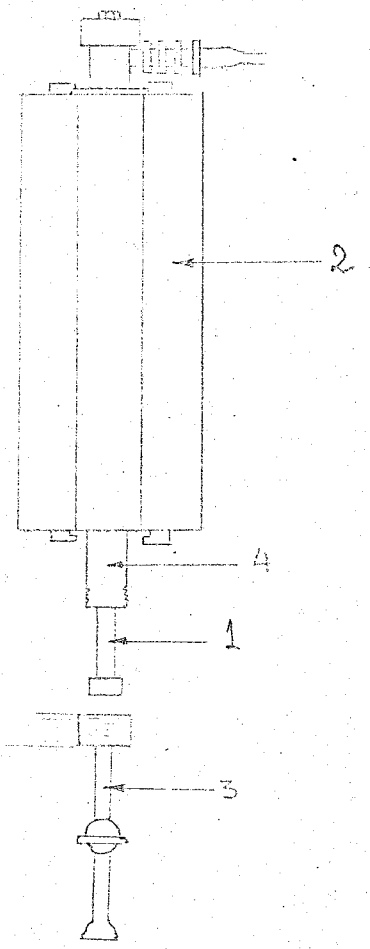


Figure 6. Placing the magnesium insert in the oven

1. Magnesium insert
2. Oven
3. Sample assembly
4. Pipe connected to the oven

4.3 Preparation of enriched sample for conversion

Prior to the preparation of a sample, the sample tube should be cleaned carefully with tap water and rinsed with distilled water. If a background sample is to be prepared, acetone should be used after rinsing the tube with tap water.

1.15 ml. of sample is measured and placed into the sample tube by means of a pipet and the tube is clogged with glass wool as shown in Figure 7. Special pipets are used for background samples.

4.4 Experimental procedure

The oven is heated by means of a time switch. Starting time can be chosen depending on work and aim. It takes about an hour to reach 600°C and the system should be pumped - without charcoal - at least 20 minutes before conversion starts. It is useful therefore to adjust the time switch to a time which is one and a half hours before starting work in the morning. It is also important to switch the water pump and vacuum pump on, closing all the valves except cold trap and vacuum pump valves, and to insert a clean magnesium column into the oven the evening before.

A list is given below to show how to use this equipment step by step during the conversion. The numbers in brackets refer to the numbers in Figure 4.

1. Put the sample on and freeze it with liquid nitrogen. [12]
2. Pump the air off sample.
3. Submerge charcoal in liquid nitrogen. [6]
4. Check the vacuum by using Pirani gauge. Wait until vacuum crips below 40 μs.

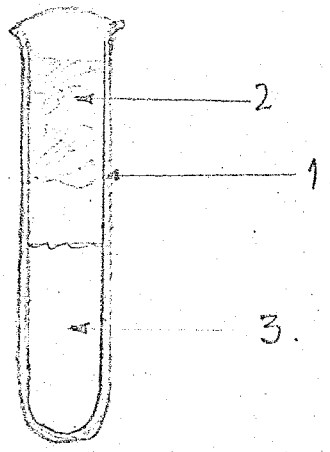


Figure 7. Preparation of a sample

1. Sample tube
2. Glass wool
3. Water sample

5. Put the cold trap on and wait until vacuum drops below 20 μs.

6. Start the conversion.

6.1. Close the Pirani gauge valve. [3]

6.2. Close the pump valve. [5]

6.3. Open the charcoal valve. [4]

6.4. Remove the liquid nitrogen surrounding the sample. [12]

6.5. Turn the pump off.

7. After the sample liquifies start to heat it.

8. After all the sample is evaporated put the pump on.

9. Check the vacuum.

9.1. Close the charcoal valve. [4]

9.2. Open pump valve. [5]

9.3. Open Pirani gauge valve. [3]

If it is not below 2000 μs, continue conversion by closing Pirani gauge valve and pump valve, and opening charcoal valve respectively.

If it is below 2000 μs, conversion is complete.

10.1. If we are going to do another conversion:

10.1.1.1. Close cold trap [2], Pirani gauge [3], and pump valve [5].

10.1.1.2. Take the charcoal with liquid nitrogen off [6].

10.1.2. Put the clean charcoal with liquid nitrogen on [6].

10.1.3. Take the cold trap off.

10.1.4. Start to pump the oven in the following steps:

10.1.4.1. While charcoal valve is closed, open the valves in this order:

a. Pump valve [5].

b. After pressure in the system is low - this can be determined by listening to the noise of the pump - open Pirani gauge valve [3].

c. After vacuum reaches 50 μs or less, open cold trap valve [2].

10.1.5. Put the new sample in and freeze it.

10.1.6. Pump the air off the sample.

10.1.7. The sample is now ready for counting right away, or the charcoal with liquid nitrogen may be kept in a freezer.

10.1.8. Return to step 4 and continue as before.

10.2. If conversion is complete:

10.2.1. If we have a charcoal to be pumped.

10.2.1.1. Turn the power off.

10.2.1.2. Take the charcoal with liquid nitrogen off and put the charcoal to be pumped on.

10.2.1.3. Take the liquid nitrogen surrounding cold trap off.

10.2.1.4. Close the sample valve [1].

10.2.1.5. Pump the oven until pressure drops below 50 μs.

10.2.1.6. Close cold trap [2] and Pirani gauge valve [3] and open charcoal valve [4].

10.2.1.7. When the system drops below 50 μs, submerge the charcoal cleaning cold trap [11] in the liquid nitrogen and pump for 2 hours.

10.2.1.8. After 2 hours check the pressure, close the charcoal trap [4] and Pirani gauge valve [3], and take the liquid nitrogen surrounding the cold trap off.

10.2.1.9. Pump the system until the cold trap is dry, close the pump valve [5] and turn the pump off.

10.2.1.10. If the temperature in the oven is lower than 100°C, turn the water pump off..

10.2.2. If we don't have a charcoal to be pumped.

10.2.2.1. Turn the power off.

10.2.2.2. Take the charcoal with liquid nitrogen off and put a closed ball point joint in place of the charcoal.

10.2.2.3. Take the liquid nitrogen surrounding the cold trap off.

10.2.2.4. Close the sample valve [2].

10.2.2.5. Pump the oven until pressure drops below 50 μs.

10.2.2.6. Close the cold trap [2], Pirani gauge [3], and pump valves [5], and turn the pump off.

10.2.2.7. When the temperature in the oven is below 100°C, turn the water pump off.

4.5 Maintenance of the equipment

a. Mg insert: Mg insert is taken out of the oven after 2 conversions. Then proceed as follows:

a1. Take all Mg out of the insert.

a2. Rinse with tap water.

a3. Close the bottom side with a rubber cork.

a4. Submerge vertically into water which is 3-4 inches deep.

a5. Put diluted HCl and wait until gas bubbles subside.

a6. Throw away the HCl, rinse with tap water.

a7. Repeat the procedure, rinse with tap water, let it dry and keep in a drawer.

b. For not mixing clean and used charcoal traps, the used charcoal traps are kept in a special place, separated from the clean ones, after transferring the hydrogen into the counter. If there is no conversion on the apparatus, the following procedure should be done for cleaning of charcoal.

Numbers in brackets refer to Figure 4.

b1. Put the charcoal on [6].

b2. Pump the oven until pressure drops below 50 μs. [Sample valve [1] is closed.]

b3. Close cold trap [2] and Pirani gauge valve [3] and open charcoal valve [4].

b4. When the system drops below 50 μs, submerge the charcoal cleaning cold trap [11] in the liquid nitrogen and pump for 2 hours.

b5. After 2 hours check the pressure, close the charcoal trap [4] and Pirani gauge valve [3], and take the liquid nitrogen off surrounding the cold trap.

b6. Pump the system until the cold trap is dry, close the pump valve [5] and turn the pump off.

b7. Take the charcoal trap off, close with a cork and keep in a freezer.

4.6 Procedure for multiple conversions.

When a conversion is complete do these in order.

a. Take the charcoal with liquid nitrogen off in the following steps.

a1. Close cold trap [2], Pirani gauge [3], and pump valve [5].

a2. Take the charcoal with liquid nitrogen off [6].

b. Put the clean charcoal with liquid nitrogen on [6].

c. Take the cold trap off.

d. For pumping the oven open the valves in this order, while charcoal valve is closed.

d1. Pump valve [5]

d2. After pressure in the system is low, open Pirani gauge valve.

d3. After vacuum reaches 50 μs or less, open cold trap valve.

e. Put the new sample to be converted on and freeze it.

f. Check the vacuum by using Pirani gauge. Wait until vacuum drops below 40 μs.

g. Put the cold trap on and wait until vacuum drops below 20 μs.

h. Start the conversion as explained before.

5. RADIATION MEASUREMENTS

5.1 Theoretical background

After the sample is enriched and collected in the charcoal in the gas phase, then it is ready for counting. For counting, a mixture of ethylene and argon is used as a quenching gas. This mixture prevents multiple discharges and cascading. Partial pressures of argon and ethylene are 34 and 83 mm Hg, respectively. Pure ethylene corrodes the wires of the detector and makes it inoperable after a few runs. To avoid the corrosion, ethylene is frozen in the cold trap at first and then put into the detector after argon and hydrogen. Ethylene also corrodes easily the Pirani gauge.

The formula which is used to calculate tritium concentration after the count is:

$$X_t = \frac{T \times C_r}{Ph_{act} \times EV} \times 481 \text{ TU.}$$

X_t = tritium concentration in tritium units when the sample was counted.

T = absolute temperature of tube

Cf = Corrected net count Cr = Net count - Background*

$P_{h_{act}}$ = Actual pressure of hydrogen

EV = Effective volume of the counter**

* Background: Memory contamination of detector. This should be measured every two weeks.

** Effective folume of the counter is assumed nearly constant and equal to one.

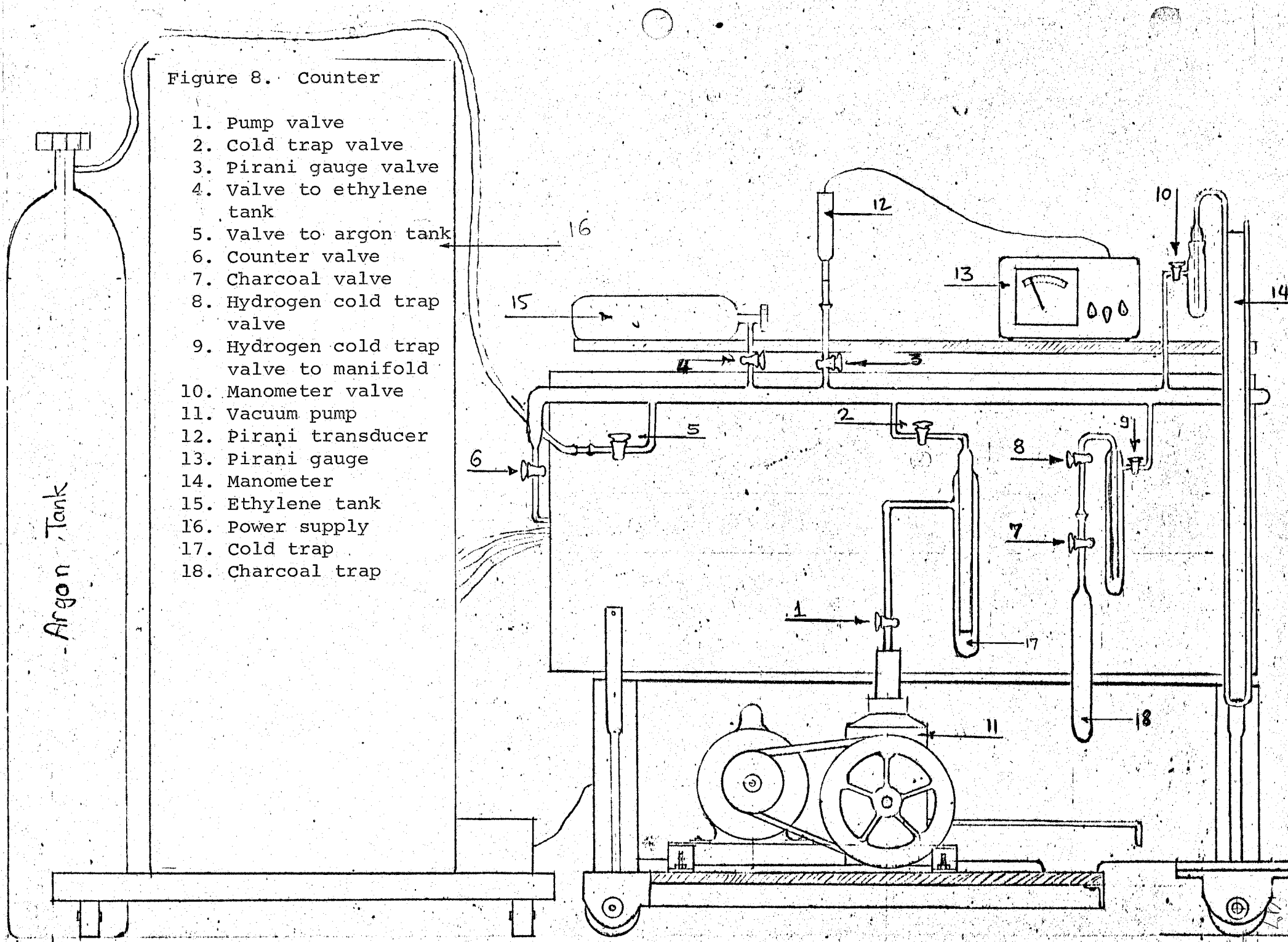


Figure 8. Counter

1. Pump valve
2. Cold trap valve
3. Pirani gauge valve
4. Valve to ethylene tank
5. Valve to argon tank
6. Counter valve
7. Charcoal valve
8. Hydrogen cold trap valve
9. Hydrogen cold trap valve to manifold
10. Manometer valve
11. Vacuum pump
12. Pirani transducer
13. Pirani gauge
14. Manometer
15. Ethylene tank
16. Power supply
17. Cold trap
18. Charcoal trap

If β is known, then X_t^o can be obtained from equation (3.10).

5.2 Equipment

The set up of the Geiger counter is shown in Figure 8 and 9. A photograph is also attached. The counter consists of a stainless steel shield and an empty space where the detector is placed.

The background due to cosmic radiation will be in the magnitude of 500 cpm* in an unshielded counting tube of one liter volume. Stainless steel shielding surrounding the detector reduces this naturally present cosmic radiation. However, even if the detector is enclosed inside a stainless steel shield, the background due to cosmic radiation will still remain over 100 cpm. It is possible to reduce this contamination to less than two counts per minute with the detector construction details of which are shown in Figures 10 and 11.. The connections of guard electrodes, anitcoincidence circuit, screen wires and center wire are made in a special way. These connections are not shown in the Figures.

Effective volume of a counter occupies the center of the counter. This volume changes with time. In the counter used in the New Mexico Tech tritium laboratory, this volume is assumed to be constant and equal approximately to 1 liter.

Since the detector is not infinite length, electric field is not uniform specially at the end of detector. The effect due to this non-uniformity of the electric field inside the detector is called end effect.

Very large counters have high background rates due to the large surface area for secondary production from previous count and cosmic

* cpm - counts per minute

PICTURE 22

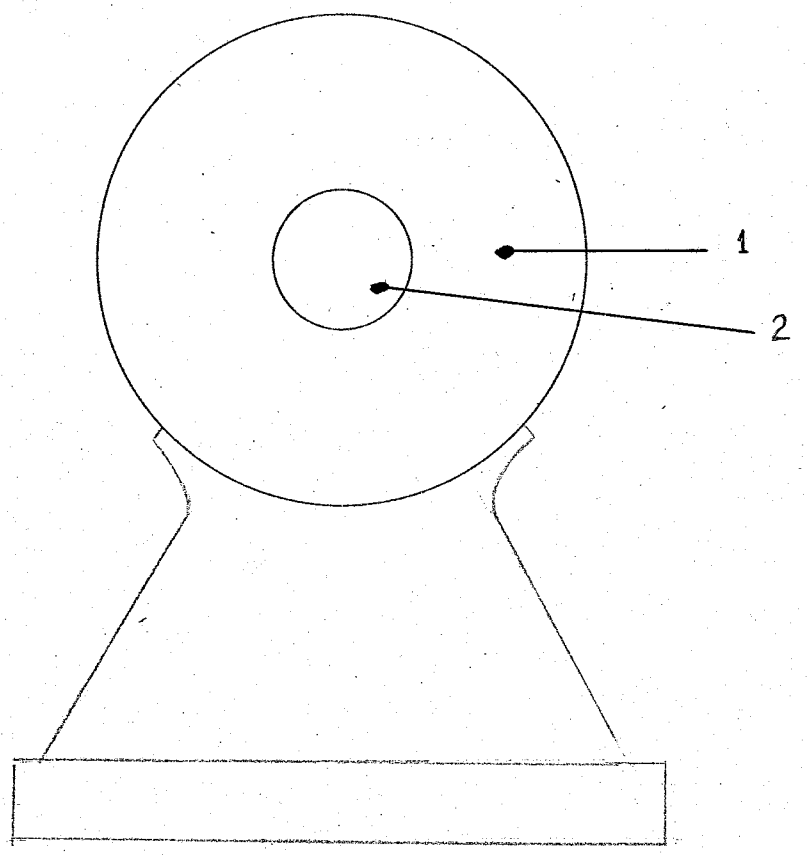


Figure 9. Counting array

1. Stainless steel shield
2. Detector

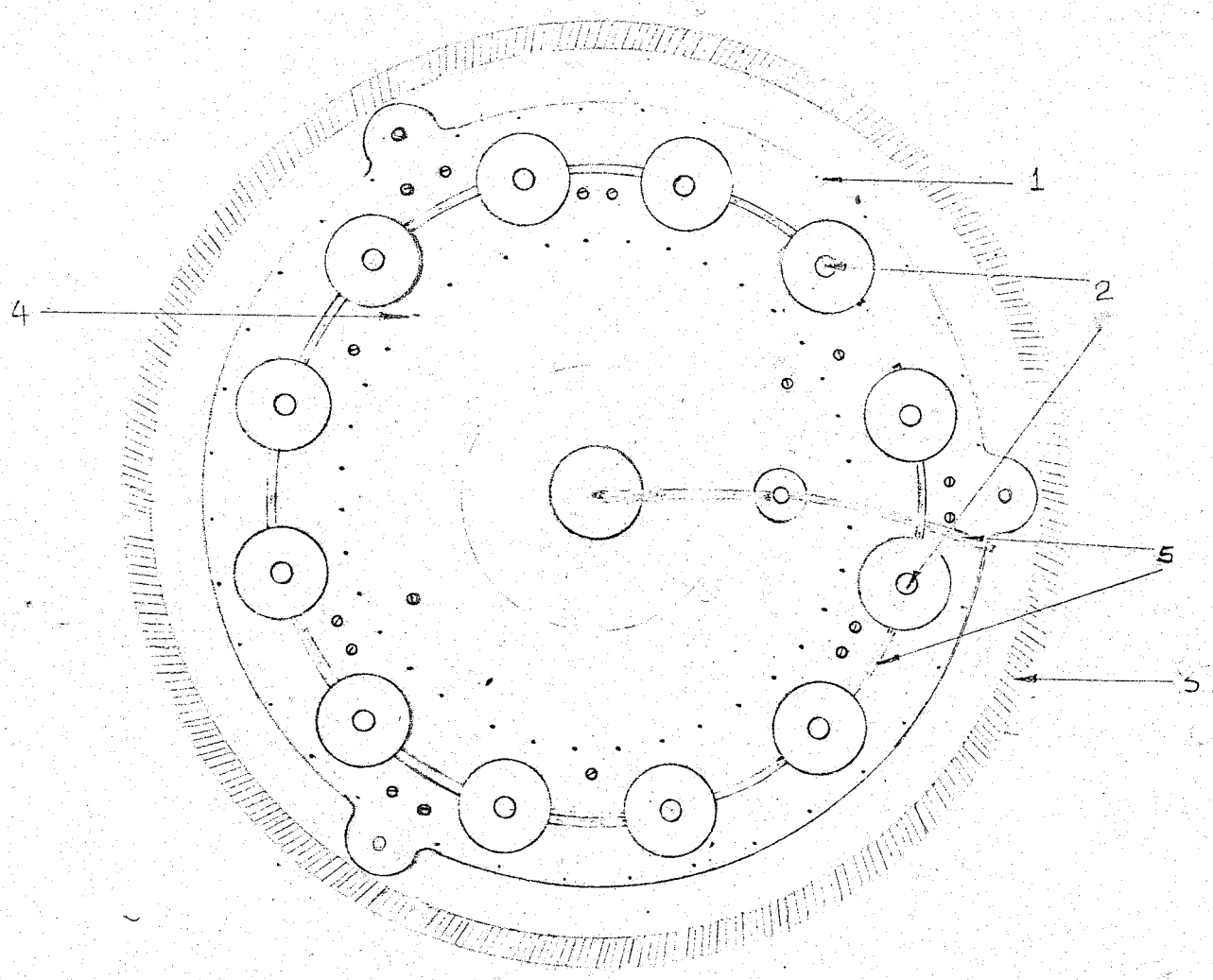


Figure 10. Cross section of the detector

1. Guard electrodes
2. Anticoincidence circuit
3. Vacuum tube
4. Screen
5. Connection wires

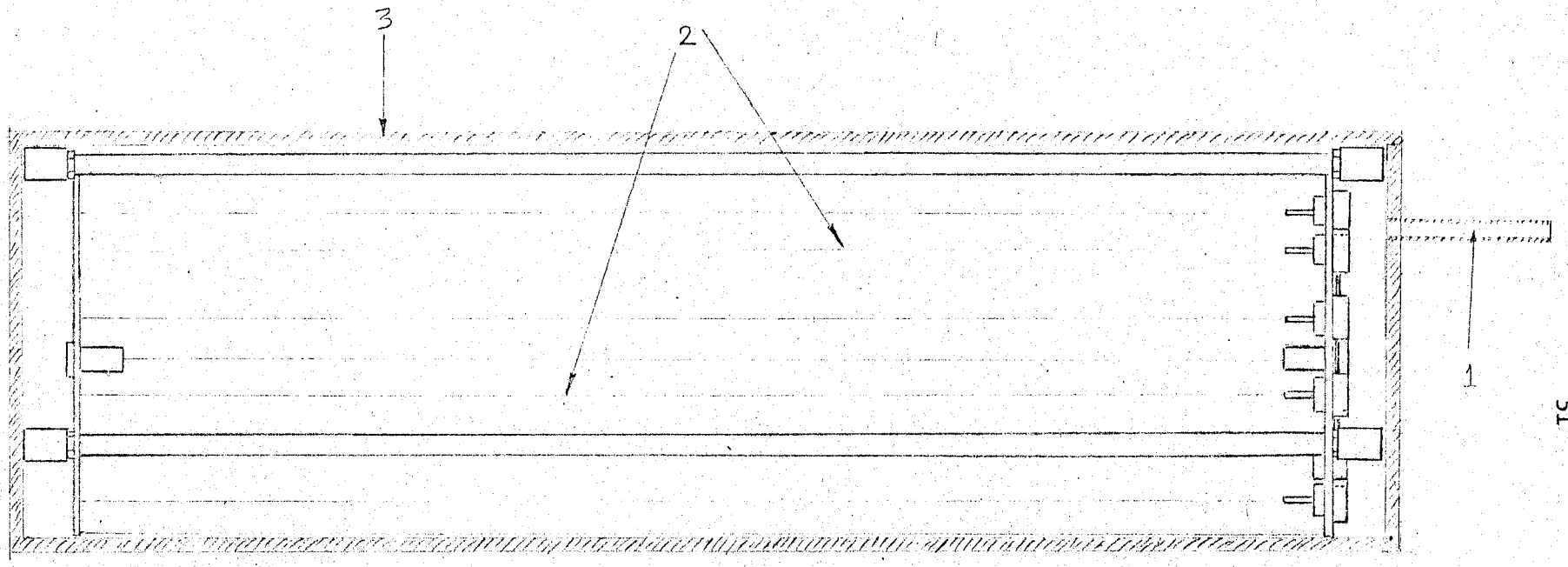


Figure 11. Longitudinal section of detector

1. Gas inlet
2. Anticoincidence screen and guard electrode wires
3. Vacuum tube

radiation. This is called wall effect.

5.2.1 Practice of operation

A photograph of the control panel is given (Picture 3). For the operation of the counter, do these in order, before starting to count. The numbers in brackets refer to picture 3.

1. While the switches [1] and [2] are on the Th* positions apply 300 volts to the screens (switch [3]) and put anticoincidence circuit and center count switches on. [4] and [5]

2. Apply 1500 volts to center wire and anticoincidence circuit with coarse adjustment knobs. [6] and [7]

3. Wait about half an hour.

4. Find approximate thresholds as follows.

a. Increase the voltages of center wire and anticoincidence circuit until center and anticoincidence count indicators just start to count by using coarse adjustment knobs.

b. By using fine adjustment knobs, [8] and [9], find the voltages which give 6 to 10 cpm on center count indicator [10] and 20 to 30 cpm on anticoincidence count indicator [11]. In finding the right voltages it might be necessary to repeat the same process several times. Stop switch [12] and reset switch [13] can be used for this purpose.

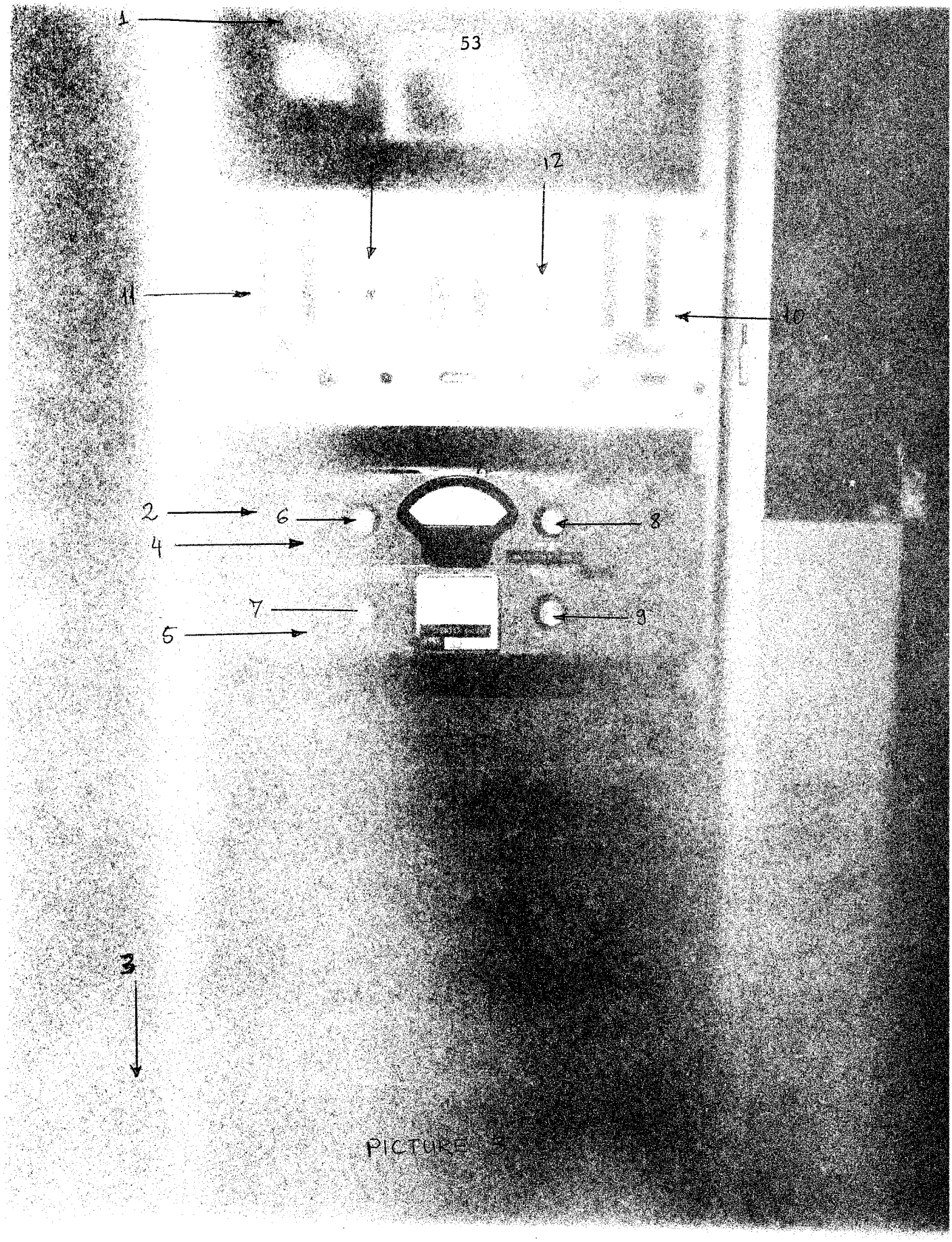
c. Put the switches on OP**positions and start to count.

d. Record the operating voltages on the anticoencidence circuit and center wire and starting time to count into the register book.

5. Wait about 1 hour.

* Th - Threshold voltage

** OP - Operating voltage



PICTURE 3

6. Take the count in such a way:

a. Stop the count and put the counter on threshold voltages.

b. Read the counts on CC*, AC**, and Net count*** indicators and record the time and the counts into the register book.

c. Calculate the counts per minute.

7. Find the real thresholds which the same way done before.

8. Wait until at least 100 count is read on the net count indicator.

9. Take the count and if it is necessary repeat the same process.

10. When counting is over, switch off anticoincidence circuit, center wire and screen.

5.2.2 Calibration of the counter

a. Background checks

Background checks are made at least every two weeks.

b. Plateau determination

Consider simple Geiger counter. (Figure 12).

If it is started to apply potential to that system and increase gradually, it will be observed that no signals at the low potentials will be taken. After a certain potential the counting rate will increase very fast within a small range of potential. If it is continued to increase the potential, counting rate will stay almost constant within a certain range; after a certain range it will increase very fast again (Figure 13). The potential difference at which counting starts is called the threshold potential, and this flat region as plateau. At the end of

* CC - center count
** AC - anticoincidence count indicator
*** The counts of AC and CC cancels each other inside electronic circuit in such a way that it gives the net count.

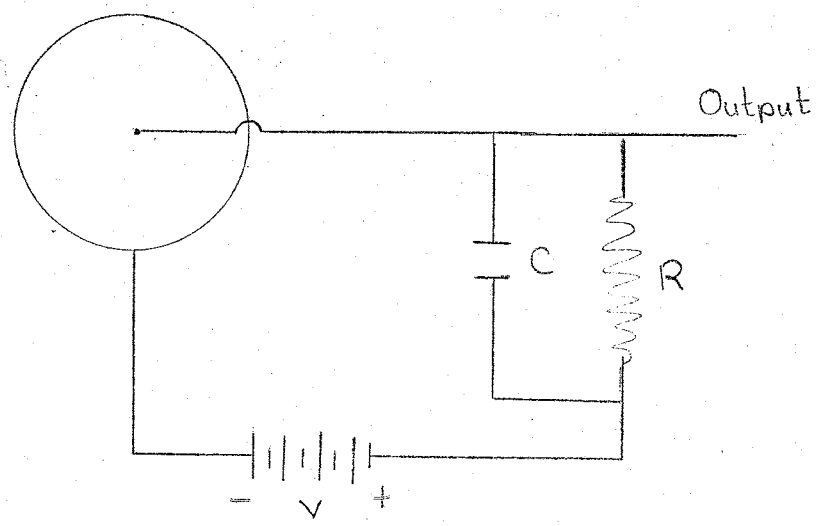


Figure 12: Fundamental counter circuit
(After KORFF, S.A., 1957)

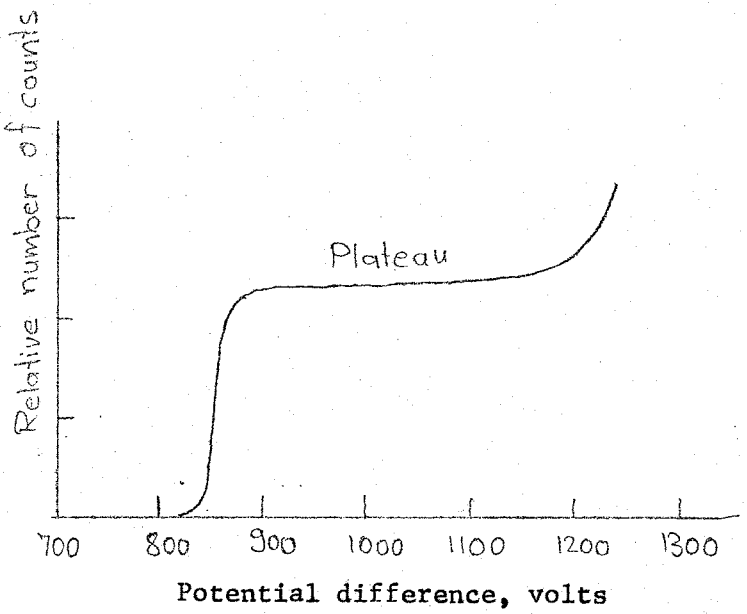
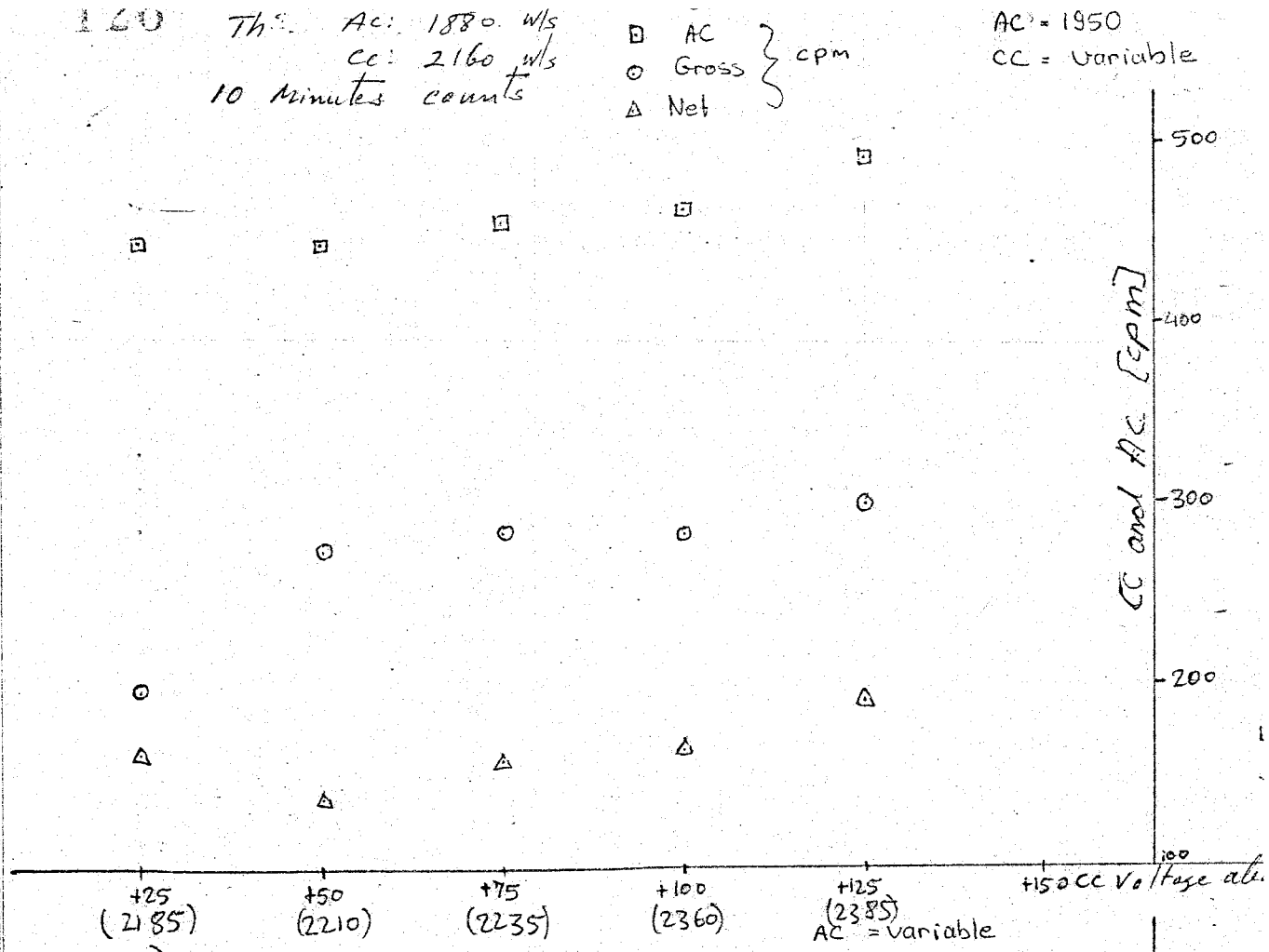
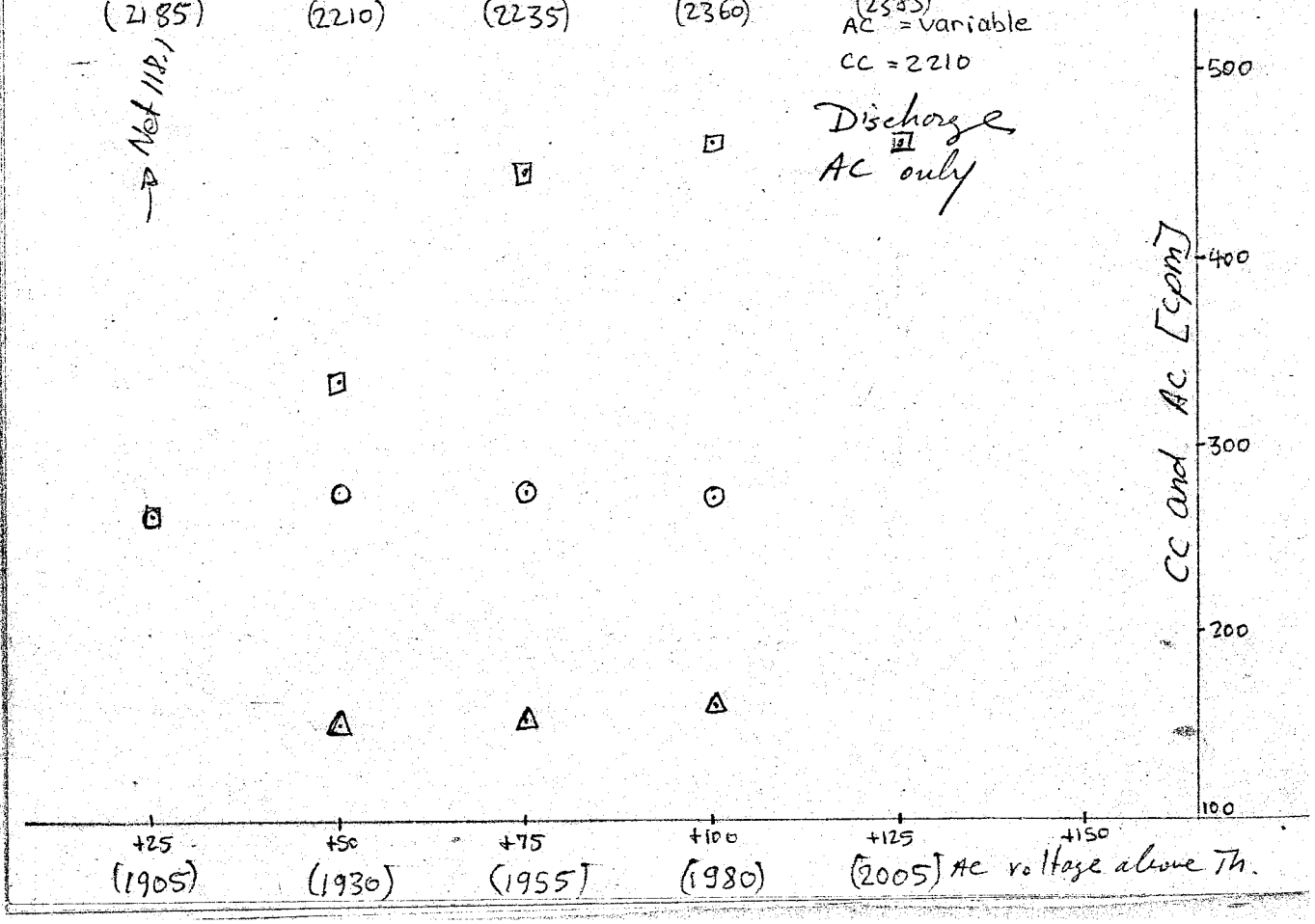


Figure 13: A typical plateau of a Geiger Muller counter.
(After ARYA, A.P., 1966)


Th: AC: 1880 w/s
CC: 2160 w/s
10 Minutes counts
AC
Gross
Net
cpm
AC = 1950
CC = Variable
500
400
300
200
100
CC and AC [cpm]
+25 (2185)
+50 (2210)
+75 (2235)
+100 (2360)
+125 (2385)
+150
CC voltage above Th.


AC = Variable
CC = 2210
Discharge
AC only
Not 118.)
500
400
300
200
100
CC and AC [cpm]
+25 (1905)
+50 (1930)
+75 (1955)
+100 (1980)
+125 (2005)
+150
AC voltage above Th.

plateau, high electric field near the central wire causes multiple ionizations and very fast increasing counting rate. That means a complete discharge is set up along the whole length of the electrode. It is desireable therefore to take the counts in plateau region.

For the plateau determination of the counter in New Mexico Tech tritium laboratory, do these in order.

1. Fill the tube with background sample.

2. Find the threshold potentials.

3. Keep either AC or CC potential constant and increase the other by 25 volts every 10 minutes and take the count on each indicator. Write down the results.

4. Now keep the potential of the other circuit constant and do the same things.

5. Draw voltage versus counts (AC,CC, Net) graphs for both experiments.

6. From these graphs the range of plateau can be determined. Figure 14 is attached as an example.

5.3 Statistical fluctuations

The following development is from Hoag[9].

Tritium has a considerably long half life, 12.5 years. If the measurements of the substances such as tritium are made over a very long time interval, the number of the atoms which disintegrate each second is found to be constant. But when measurements are made over a comparatively short time interval, it will be found that the number of disintegrated atoms is sometimes greater and sometimes smaller than the average. The distribution of the observed number around the average

can be determined from probability considerations and is represented by the Gaussian error curve.

A counter has a background activity due to contaminations, cosmic radiations, etc., which is a subject of statistical fluctuations. It can be shown[13] that

$$bT = \bar{b}T \pm 0.67\sqrt{\bar{b}T} \qquad (5.2.2.1)$$

where

b background count, measured over a comparatively short time interval T.

$\bar{b}$ average background.

The activity of a radioactive substance including the background, over the time period T.

$$aT = \bar{a}T \pm 0.67\sqrt{\bar{a}T} \qquad (5.2.2.2)$$

or

$$aT = (\bar{a} - \bar{b})T + 0.67\sqrt{(\bar{a} + \bar{b})T} \qquad (5.2.2.3)$$

First term of the equation (5.2.2.3) gives the average activity and the second term gives the probable error which will be made in a single observation. The limit of the observation is given.

$$\bar{a}T < 0.67\sqrt{\bar{b}T}$$

Relative probable error is

$$r = \frac{67}{S\sqrt{T}}$$

where

$$S = \frac{\bar{a} - \bar{b}}{\sqrt{\bar{a} + \bar{b}}}$$

S is called relative sensitivity of the instrument.

5.4 Experimental procedure

The order of transferring the gases into the detector is hydrogen, argon, and ethylene respectively. Hydrogen can be transferred by removing the liquid nitrogen surrounding the charcoal trap, and followed by argon. Ethylene, which was previously measured and frozen in the cold trap, is transferred by removing the liquid nitrogen surrounding the cold trap. After the mixtrue of hydrogen, argon, and ethylene is prepared in the detector, hydrogen can be counted. In that case a complete procedure of counting hydrogen can be considered in two main steps, namely, preparation of the gas mixture and counting.

The procedure is given below. The numbers in brackets refer to the parts of the equipment shown in Figure 8.

5.4.1 Preparation of the gas mixtures

The procedure for preparation of the gas mixtures can be described in 5 steps:

I. Preparation of the counter

Before the gases are transferred into the counter, the counter must be cleaned carefully. In order to do this:

a. Place the sample [18]

b. Turn the pump on.

c. Open the valves in the following order:

c1. Pump valve [1]

c2. Cold trap valve [2]. Wait until the pressure in the manometer is almost zero.

c3. Hydrogen trap valves [8] and [9]

c4. Counter valve [6].

d. Flush the tube with argon twice. If the previous count was low (1 or 2 cpm), flushing once is enough.

e. When the pressure in the manifold is less than 25 μs, place the liquid nitrogen around the cold trap [17].

f. When the pressure in the manifold is less than 10 μs, pump off the air trapped in the valves.

g. Pump the system with the cold trap for one and a half hours.

h. Close counter valve [6], hydrogen cold trap to manifold [9], and cold trap valve [2], and evacuate the cold trap by pumping while heating.

i. Wait until cold trap gets cool [17].

II. Transferring the ethylene into the manifold and freezing it in the cold trap.

This is accomplished in the following order:

a1. Open the cold trap valve to the manifold [9].

a2. When the pressure in the system is less than 10μs, close the Pirani gauge valve [3].

a3. Close the pump valve [1].

b. Ethylene is admitted into the manifold by gradually opening the valve to the ethylene tank [4] until the right-hand side column of the U tube reads 798 mm. and the valve is closed. The pressure difference between the columns of the manometer is noted.

c. Freeze ethylene in the cold trap [17] by using liquid nitrogen and wait 2 minutes.

d. Open the pump valve [1] and pump off the impurities for 5 minutes.

e. Check the pressure in the system. If it is lower than 10 μs, open the hydrogen cold trap valve to the manifold [9], and after a while open the counter valve [6] and wait until the pressure drops below 10 μs.

f. Close Pirani gauge [3], cold trap [2], and pump valve [1] respectively, and turn off the pump.

III. Transferring the hydrogen into the manifold.

a. Open hydrogen cold trap valves [8] and [9] and charcoal valve [7] respectively.

b. Take off liquid nitrogen surrounding the charcoal [18].

c. Heat charcoal for 5 minutes.

d. Close hydrogen cold trap valves [8] and [9] and charcoal valve [7] respectively and take the charcoal [18] off.

e. Write down the observed amount of hydrogen ($P_{h_{obs}}$) in mm. of mercury pressure.

IV. Transferring the argon into the manifold

a. 34 mm. of mercury is admitted by gradual opening of the valve to the argon tank [5].

b. Write down the amount of the mixture of hydrogen and argon and calculate the exact amount of argon.

V. Mixing the gases in the manifold

a. Replace acetone dry ice bath* with liquid nitrogen.

b. Open cold trap valve [2].

* In order to keep frozen water vapor in the cold trap, if there is some, and let ethylene into the manifold, acetone dry ice bath is used. This mixture keeps the cold trap at - 80°C.

c. Wait 15 minutes.

d. Close cold trap valve [2].

e. Take off acetone dry ice bath.

f. Wait one hour and put the power on.

g. Wait half an hour.

5.4.2 Counting

a. Close counter valve [6] and note the temperature of the counter.

b. Find approximate thresholds and start to count.

c. While counting is going on, write down amounts of mixture by reading the manometer. This is called observed amount of mixture (P_{obs}).

d. Calculations

$$P_{ctd} = P_h + P_a + 83.$$

P_{ctd}, P_h, and P_a are calculated pressure of the mixture, hydrogen, and argon respectively.

83 is the theoretical amount of ethylene in mm. of mercury pressure which is transferred into the counter.

$$H_2 \text{ correction} = P_{ctd} - P_{obs}.$$

$$P_{h_{act}} = P_{h_{obs}} - H_2 \text{ correction}$$

e. After approximately one hour take the count, find real thresholds and start to count again. Next count must be taken after reaching at least 1000 counts in net.

If it is necessary, this count can be repeated several times.

f. After the last count turn off the power.

5.5 Discussion of counting

Gas counting is much more sensitive that the liquid scintillation technique, however, an experienced technician is needed to carry out the counting process.

Two sets of samples were enriched and counted. The results are given in tables 3 and 4. The β' values obtained are very low when compared to Ostlund's results. Although tap water was used to break the electrodes before unknown samples were run, these low values may be a result of using new electrodes.

Batch N° : 1
Background : 2.35
NS : 5
Initial volume V_o (ml.) : 250

TABLE 2

cell N°	Sample N°	Date coll.	Date Count.	* X_t^o TU's	W gr.	Count cpm.	Tupe Tempe. °C	Tupe Tempe. °K	H_2 Pressure torr	Count-Bg cpm.	TU's Counter time corr.	Computer Results. β or X_t^o	Remarks
I	Std. #1		7/26/71	4780 at 8/2/71	2 ml.	366.9	25	298.16	210.5	364.55	248370	$\beta_3 = 5.500$	cell cracked during vac. distillation. Recover 2 ml by vac
II	Std. #1												Lost in vac. dist.
III	Bg (dis. H_2O)		7/14/71		2.2150	3.5	26	299.16	208.5				Need falling drop to complete enrichmnt cal. with old sys.
IV	Std. #2		7/26/71	1688 at 8/2/71	2.6372	134.	25	298.16	209.5	131.65	90122	$\beta_1 = 7.928$	
V	Std. #2		8/3/71	1688 at 8/2/71	2.5338	147.	24	297.16	212.	144.65	97525	$\beta_2 = 8.580$	
VI	605	10/8/70	7/23/71		3.3435	4.12	25	298.16	205.5	1.77	1235	$X_{t2}^o = 27.31$	cell cracked in dist. possible too much water recovered.
VII	767	5/21/71	8/3/71		1.3950	3.1	24	297.16	208.5	0.75	514	$X_{t2}^o = 5.25$	cell dry 7/15/71 vac. dist. whatever left in the cell
VIII	901	11/7/70	7/29/71		2.6626	3.65	24.5	297.56	203.5	1.30	914	$X_{t2}^o = 16.53$	
IX													Lost sample
X	801	3/4/71	7/16/71		2.3260	8.9	25	298.16	198.5	6.55	4732	$X_{t2}^o = 75.94$	

X_{t1}, X_{t2}, X_{t3} are obtained by using β_1, β_2, β_3 values respectively.

NS : Number of samples to be run in computer.

* For standard samples only.

Batch N° : 2
Background ; 2.35
NS : 6
Initial volume V_o : 250 (ml.)

TABLE 3

ell N°	Sample N°	Date coll.	Date Count.	*X_t° - TU°	W gr.	Count cpm.	Tupe Tempe. °C	Tupe Tempe. °K	H_2 Pressure torr	Count-Bg cpm.	TU° Counter time corr.	Computer Results. β or X_t°	Remarks
[(27)	1365	7/6/71	8/11/71		2.6270	3.10	24	297.16	208.5	0.75	514	X_t° = 8.63	
[(23)	1363	7/7/71	8/20/71		3.2425	2.83	25	298.16	209.5	by 2.23 0.60	411	X_t° = 8.33	
[(30)	1369	7/7/71	8/9/71		2.9911	3.69	24	297.16	207.5	1.34	923	X_t° = 17.41	
/(25)	1368	7/7/71	8/10/71		2.7572	2.93	24	297.16	190.5	0.58	435	X_t° = 7.63	
'(28)	1366	7/6/71	8/12/71		2.7153	2.94	24.5	297.56	166.5	0.59	507	X_t° = 8.77	
I(24)	Std. #2		8/7/71	1688 at 8/2/71	3.0981	130.9	24	297.16	211.5	128.55	86875	β = 9.723	

NS : Number of samples to be run in computer.
* For standart samples only.

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