NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

FORCED EXCHANGE OF TRITIATED WATER WITH NATURAL CLAYS

by

D. DAN RABINOWITZ

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ABSTRACT

This study shows that under forced exchange of ions between tritiated water and clays the rate of exchange depends on the type of clay and the hydrogen ion concentration in the clay-water mixture. Ion exchange between the tritiated water and clay sample was stimulated by a process of electrodialysis under constant ambient conditions. No significant exchange between solution and clay is found under electrodialysis for an illite clay. Similar experiments on kaolinite clay samples show an apparent constant rate of exchange between sample and solution. With the illite clay the pH in the clay-water mixture remained basic during most of the experiment, but with the kaolinite clays, the pH changed from neutral to acidic after equilibrium in tritium concentration was reached. The constant rate of loss of tritium to the kaolinite clays occurs in coincidence with the change in pH of the solution. A fraction of the tritium was recovered in the hydroxyl water of all of the clays. The amount of tritium recovered in the hydroxyl water of each clay is proportional to the cation exchange capacity of the clay, but for the kaolinite clays it is only a small fraction of the tritium lost from solution.

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INTRODUCTION

Background

Isotopes (radioactive and stable) are used extensively in studying the hydrological characteristics of underground fluid reservoirs. Isotope techniques offer, in most cases, a supplement rather than a substitute to the known conventional methods [Harpaz, et al. 1963]. With present day knowledge and instrumentation, isotopes can be readily detected in very minute concentrations.

The presence of isotopes in groundwater can be divided into three categories as follows:

(a) Naturally produced and circulated throughout the hydrologic cycle.

(b) Artificially produced but naturally introduced into the groundwater.

(c) Artificially produced and
   1. injected into the aquifer as groundwater tracers.
   2. An unintentional seepage of highly radioactive wastes into groundwater.

We can further classify (a) and (b) as uncontrolled injections, whereas (c) is controlled.

Tritium as a Groundwater Tracer

Of all available isotopes, tritium, the radioactive isotope of hydrogen, is preferred as a groundwater tracer. The ideal groundwater tracer should depict but not modify the transmission characteristics of the system [Kaufman and Orlob, 1956a]. It is important that the tracer be detectable in low concentration in order to prevent locally contaminated water. Detection should be possible even though the tracer has been hydrodynamically dispersed and consequently diluted. A further requisite is that the tracer (in pure form or as a chemical compound) not be retained on the solid phase of the medium by adsorption; nor should it react through ion exchange. Thus, tritium, which is directly incorporated into the water molecule, provides a nearly perfect tracer for groundwater as well as surface water and all forms of precipitation.

Natural tritium was first identified by its radioactivity in rain water [Grosse, et al. 1951]. Its detection in all forms of natural water became possible [Kaufman and Libby, 1954], and it was evident that tritiated water would be a useful tool in following the path of groundwater movement. The determination of some hydrological characteristics such as the origin of groundwater, dispersivity, mixing and dispersion patterns, can only be achieved by isotopic or tracer methods.

Tritium is usually designated by the symbol T or by the chemical symbol $_1H^3$. Tritium has a half-life of 12.26 years [Jones, 1955] and emits a beta particle with a principal energy of 0.018 Mev, and thus produces a stable helium isotope of mass 3. The reaction is

$$_1H^3 \longrightarrow {}_2He^3 + {}_{-1}\beta^o + 0.018 \text{ Mev.} \qquad (1)$$

Tritium is produced in nature by cosmic rays and by solar flare accelerated particles. One reaction is due to the flux of secondary neutrons. The reaction is [Libby, 1946]

$$_7N^{14} + {}_on^1 \longrightarrow {}_6C^{12} + {}_1H^3 + \text{energy} \qquad (2)$$

or

$$_7N^{14} + {}_on^1 \longrightarrow 3\ {}_2He^4 + {}_1H^3 + \text{energy.} \qquad (3)$$

Sorption in Clay-Liquid System

Definitions. Clay minerals have the property of sorbing certain anions and cations and retaining these in an exchangeable state; i.e., these ions are exchangeable for other anions or cations by treatment with such ions in a water solution [Grim, 1953]. Furthermore, and in more general terms, one should distinguish between absorption and adsorption. The phenomenon by which the solid takes an ion into its structure is called absorption, and the one by which the ion is retained on the solid's surface, adsorption. The total phenomenon is designated as sorption.

Ion exchange mechanism and capacity. In natural water flow, or when a liquid solution is brought in contact with a solid surface, ion retention or exchange will occur. Ion exchange in clays is dependent on the crystalline structure of the clay mineral and on the chemical composition of the solution in contact with the solid surface. The attached ion will retain all its ionic properties, including the requirement that there be a counter-ion in the near vicinity. The adsorbed ion can be removed only by a method which preserves the electroneutrality of the system. The chemical reactions in ion exchange follow the law of mass action, but the reactions are restricted by the number of exchange sites on the mineral and by the strength of the bonding of the exchangeable cations to the edges of the mineral surface [Carroll, 1959].

Ion exchange capacity is measured in chemical equivalents of base adsorbed at pH = 7. The exchange capacity is reported in terms of milliequivalents per 100 grams of clay. Anion exchange takes place at a site of an exposed hydroxyl group, $(OH)^-$, either on a planar surface or on an edge of the broken mineral [Carroll, 1959]. The anion-exchange capacity in kaolinite is similar in amount to the cation-exchange capacity. The study of hydroxyl ion exchange presents a complex problem since it is difficult to trace the hydroxyl ion from solution to its exchange position. One such attempt was carried out by Halevy [1964] using HTO and H_2O^{18}, in a double tracer method.

The common metallic cations found in exchange positions in clay minerals, in the order of replacability, are found to be [Carroll, 1959]:

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ and $Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$.

At low pH values, H^+ replaces other cations.

All aquifers have the capacity of adsorption or ion exchange, depending on the amount of clay present. Should either adsorption or ion exchange take place between a tracer in solution and the medium, the tracer will be lost to the medium.

Electrodialysis Process

Electrodialysis is an electrolytic process by which positive metal ions fixed on the clay are stripped off and replaced mostly by hydrogen ions. This process is carried out in an electrodialysis cell [Vacquier, et al. 1957]. The clay is placed into the central compartment of the cell and separated by membranes from the end compartments. The semi-pervious membranes permit ions to pass through, but confine the clay particles to the center compartment. The transport of ions through the membranes is accomplished electrically by means of a D.C. electric potential imposed across platinum electrodes placed in end compartments of the cell. Electrodialysis is widely used among soil scientists [Puri, 1949] and is also used for demineralization of saline water [Wilson, 1960].

Objective and Scope

Even though tritium is considered an ideal tracer for groundwater flow, some preferential retardation and possible differential absorption within the clay lattice is possible when it is used in a system of high clay content [Kuntsson and Forsberg, 1967].

When tritiated water is used in a clayey aquifer, one should be able to apply a quantitative correction for the tracer which is delayed by adsorption or lost as a result of ion exchange with the medium.

The objective of this work is to study ion exchange processes which are artificially stimulated by means of electrodialysis. The purpose is twofold. First, to try to obtain the rate of cation exchange. This will be done by monitoring the rate at which tritium activity is depleted from the liquid phase versus the appearance of exchangeable cations. Second, by the proper treatment, to extract the tritium from the clay and measure its concentration in order to determine its exchange position with respect to the solid surface, or lattice structure.

Previous Work on the Exchange of Tritiated Water with Clays

Very little experimental work has been done on the exchange between HTO and clays. Each of the investigators had a different objective in studying the problem.

Kaufman and Orlob [1956b], in a laboratory evaluation of groundwater tracers, observed that tritiated water lagged the chloride ion under the same flow conditions. The flow column was packed with sandy loam and some clay minerals. Their conclusion was that one of the following may have occurred:

(a) The tritiated water molecules entered the media granules, replacing water adsorbed on the surface of clay minerals present.

(b) Exchange occurred between the tritiated water and water adsorbed as dipoles on the exchangeable cations sorbed on the clay minerals.

From the data presented it appears that once the flow breakthrough of the tracer occurred, the tritiated water returned to its initial concentration.

Halevy [1964] studied the mechanism of anion exchange and adsorption in kaolinite using water tagged with tritium and heavy oxygen (HTO and H_2O^{18}). Halevy used portions of 200 mg clay with 1 ml of tritiated water. He studied the exchange as a function of particle size, pH, heating and agitation time. The analysis was done on the lattice water. Halevy found the same per cent exchange for H_2O^{18} as for HTO and thus concluded that the tritium exchange is by

hydroxyl group rather than hydrogen ion replacement. The per cent exchange found was below 1 per cent.

Burns [1965] studied the preferential adsorption of tritiated water by kaolinite, illite, bentonite and vermiculite. Burns was seeking a new method for tritium enrichment. His procedure is very much like Halevy's. The analysis for the adsorption determinations was done on the liquid phase. Burns concluded no preferential adsorption in kaolinite and illite (of unknown sources).

Stewart [1967] investigated tritium and deuterium fractionation with kaolinite, illite and montmorillonite. Stewart also attempted to study rate of exchange by storing the sealed clay-water containers over various time periods and temperature ranges. The analysis was done on the adsorbed and lattice water. Stewart showed some correlation between exchange and time of contact; most of the exchange taking place in a very short time. Tritium and deuterium fractionation was of the same order for the initial exchange only. With time, tritium exhibited higher fractionation. In his work, Stewart defines the isotopic effect of fractionation in a two-phase system as follows[1]:

$$E = {}^{R_1}/_{R_2} \qquad (4)$$

where R_1 = tritium-to-protium ratio of hydroxyl water released at oven temperature.
and R_2 = tritium-to-protium ratio in pore and adsorbed water.

[1]Units and symbols are defined where they first appear, and are all compiled in Appendix I.

(The above formulation will be adopted in the present work and will be discussed further with the presentation of results.)

MATERIALS, APPARATUS AND PROCEDURE

Preparation of Materials Used in the Experiments

Standard clays. Clay mineral standards were used in this investigation (Kerr, et al. 1949 and 1950). These clays are: kaolinite from Macon, Georgia (API No. 4), kaolinite from Mesa Alta, New Mexico (API No. 9) and illite from Fithian, Illinois (API No. 35).

All of the clays were pulverized and sieved between 53 and 74 microns (270 mesh < clay < 200 mesh). The clays were oven heated at about 100°C from twelve to twenty-four hours. 100 gram portions of the clay were used in the experiments.

Tritiated water. Distilled Socorro tap water (No. 1196 std.) was used as the basic dilution and addition water. The content of tritium was measured and found to be negligible. Two liters of tritiated water (No. 1195 std.) were prepared by diluting a 126.7×10^6 T.U. standard sample.

The tritium concentration in sample No. 1195 was determined from 9 measurements during the experiments' duration to be 284500 ± 4700 T.U., where a tritium unit is defined as

$$1 \text{ T.U.} = 10^{-18}(T/H). \qquad (5)$$

Tritium concentration in this work is expressed in terms of picocuries per milliliters:

$$1 \text{ T.U.} = 3.24 \times 10^{-3} \text{ pc/ml} \quad (6)$$

or

$$1 \text{ pc/ml} = 309 \text{ T.U.} \quad (7)$$

Sample No. 1195, by the above relations, has a tritium concentration which is equal to 917.4±15.6 pc/ml. The maximum permissible concentration (MPC) of tritium in drinking water is 3000 pc/ml.

Description of Apparatus

Electrodialysis Cell. Figure 1 shows the electrodialysis cell in some detail. The walls were glued with a special lucite compound. The three compartments were equally spaced by parchment paper which was held by a lucite frame. The lucite frame allowed maximum membrane surface area to be exposed. (The parchment paper was of 40 weight and was obtained from the Dixon Paper Co.) The membranes' frames were fixed inside the cell with silicone rubber (RTV-102, produced by General Electric). After each clay was electrodialyzed, the frames were removed and a new set of membranes was put in place. The parchment paper kept very well even during a long run; see Fig. 3. The cell's cover was fastened with four stainless steel-screws. A thin layer of cured silicone rubber, which served as a seal, provided a pad between the top and the cell.

Two platinum electrodes, 1 cm^2 in area, mounted on platinum rods, were inserted through small holes, 14 cm

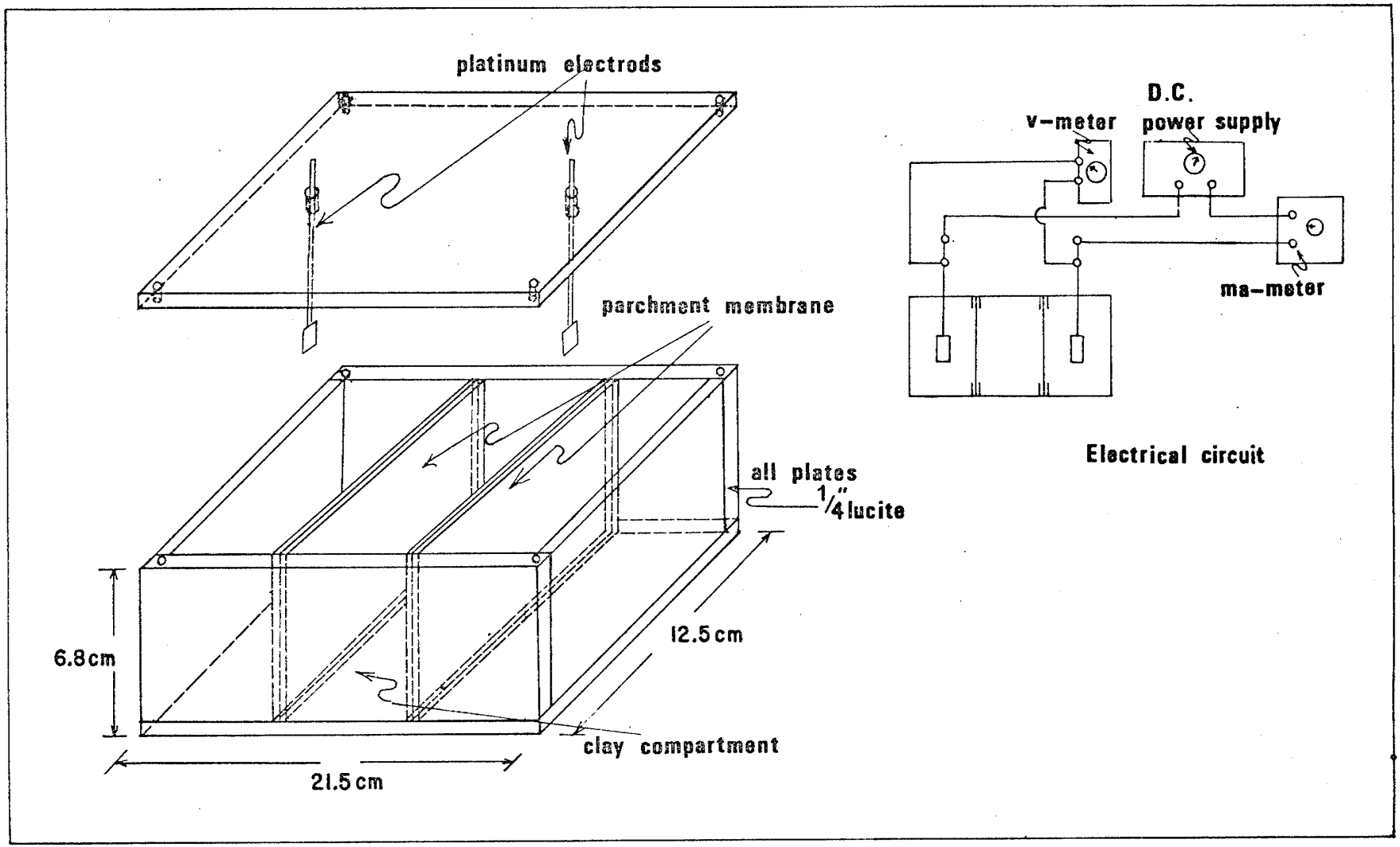

Fig.1 Details of electrodialysis cell and electrical circuit

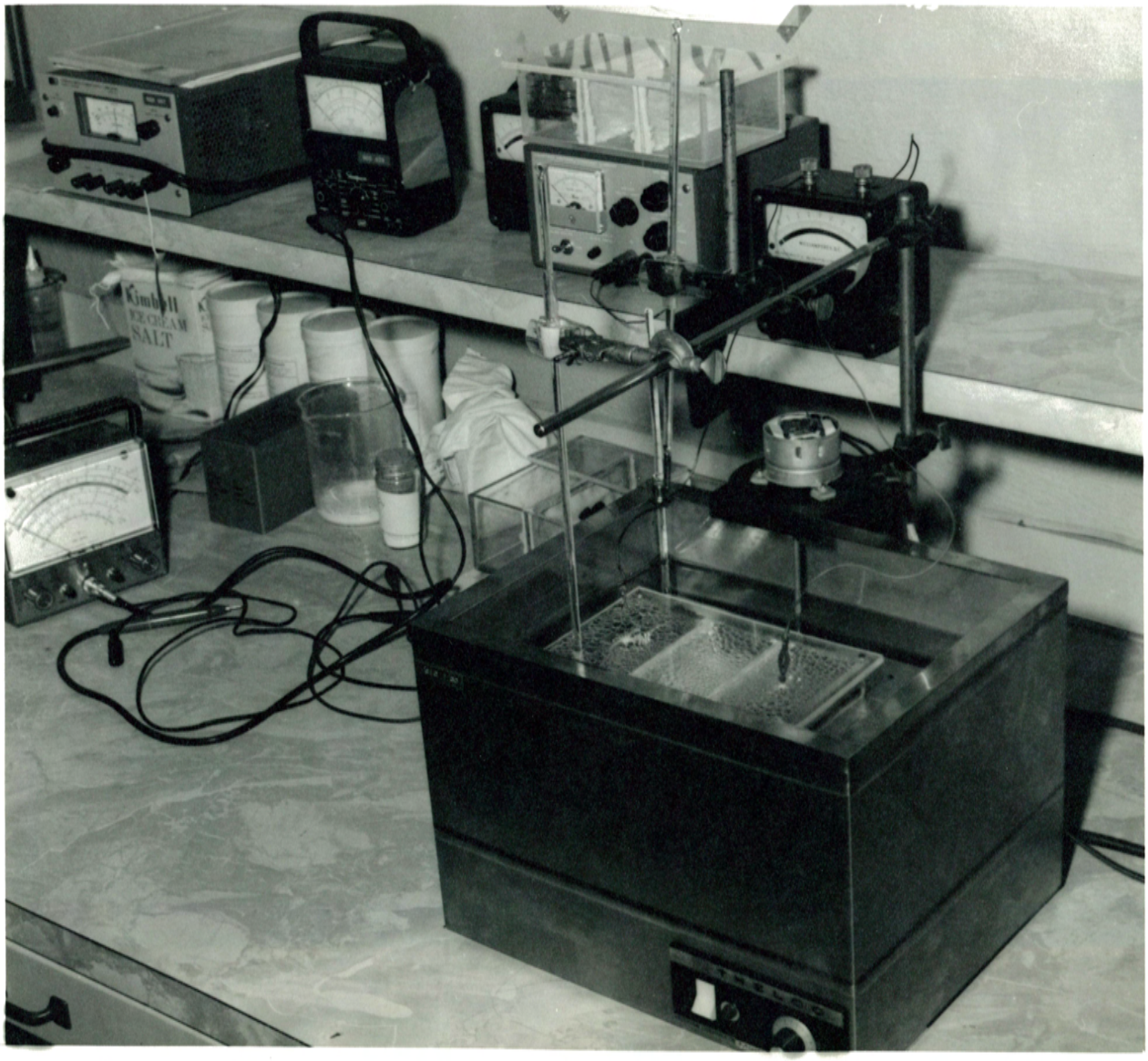

Fig. 2 Photographic view of the electrodialysis experiment

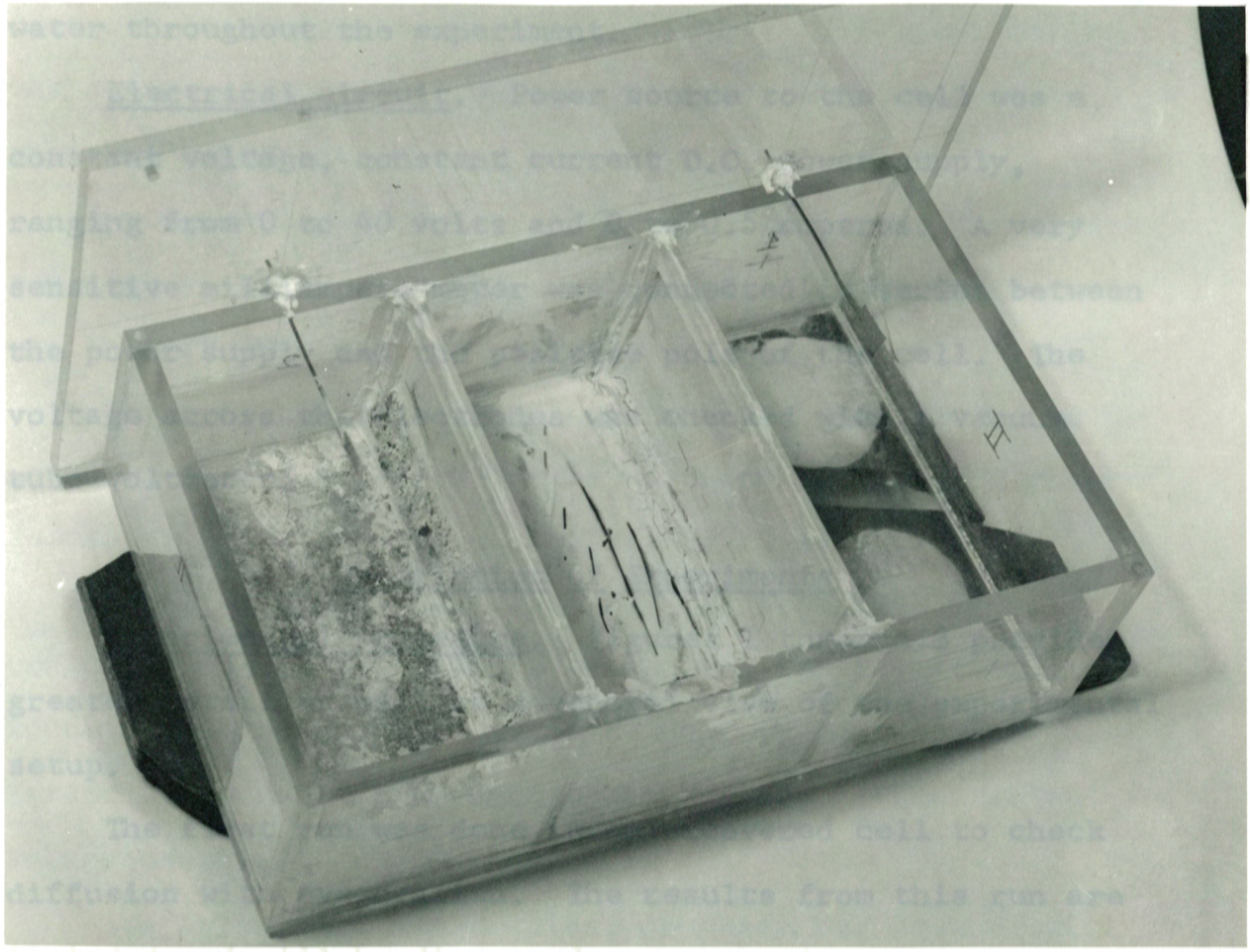

Fig. 3 Photographic view of an electrodialysis cell after 1290 hrs. run

apart, in the cell's top. The electrodes were held to the top with silicone rubber which prevented them from rotating. The electrodes were long enough to stay submerged in the water throughout the experiment.

Electrical circuit. Power source to the cell was a constant voltage, constant current D.C. power supply, ranging from 0 to 40 volts and 0 to 0.5 amperes. A very sensitive milliampere meter was connected in series between the power supply and the positive pole of the cell. The voltage across the electrodes was checked with a vacuum tube voltmeter.

Description of Experiments

Experimental procedure. Figures 1 through 3 provide greater detail as well as a general view of the experimental setup.

The first run was done in an uncovered cell to check diffusion with evaporation. The results from this run are included and will be discussed.

All of the electrodialysis runs were conducted under the same experimental conditions. The center compartment of the cell was loaded with 100 grams of clay. 250 ml of HTO was added to the end compartment containing the positive electrode, 200 ml of distilled H_2O to the center and 250 ml of distilled water to the end compartment containing the negative electrode. Under these conditions, the clay was saturated and below the water surface.

The volume-height relation was calibrated by an experimental procedure. This calibration was done by evaporating water out of the cell while carefully weighing the cell's contents and measuring the water height. The water height was always measured at the same position with respect to the cell's geometry.

Once a cell was ready, it was placed inside a constant temperature bath. The temperature for all the experiments was kept at $30.5^{\circ}C$.

The voltage gradient inside the cell was limited to not more than 3 volts/cm. This was done in order to prevent decomposition of the clay mineral [Grim, 1953].

Sampling Procedure. Each run is identified by an ordinal number. Each sample in a given run is, in addition, identified by a compartment position (-, CT or +), and a letter corresponding to a time of sampling. (See tables in Appendix II.)

Two two-milliliter samples, one each for both tritium and ion analysis, were pipetted out of each compartment. The object was not to extract any sample larger than needed. Cation analysis was done on selected samples for Na^{+}, K^{+} and Mg^{++} ions. The residue water was analyzed, after completion of the experiment, for the Ca^{++} ion concentration. Any precipitates in the compartments were dissolved and analyzed. (All the results from the analysis of the final sample are tabulated at the end of each corresponding table in Appendix II.) From time to time the sampling of the

center compartment for tritium was done in two steps; first, sampling the water above the clay (e.g. 1257A CT), and second, sampling the well stirred clay-water mixture (e.g. 1257A' CT). The distinction is important since, in most cases observed, the tritium concentration of the second sample was higher than that of the first.

The height of the water was measured before and after each sampling. The hydrogen ion concentration was measured more often than the regular sampling periods. The pH meter was calibrated before each measurement with buffer solutions.

Possible experimental errors. Small size samples of high tritium activity were pipetted. Distilled water was used as the rinsing agent for the pipettes and the pH probe. The largest source of error could have been in unintentionally diluting the samples with this distilled water. Another possible source of a measurement error was the water height in each compartment.

MEASUREMENT TECHNIQUES

Tritium Analysis

General. Tritium counting was done with a shielded Geiger-Muller internal gas counter (the counter). The counter's total volume is 4.45±0.03 liters, with a sensitive volume (effective volume) of 1.07 liters and a counting efficiency of about 100 per cent. The sensitive volume of the counter is defined by and separated from the volume of the tube occupied by the anti-coincidence ring counters by an electrostatic field. The initial concentration of tritium in the water sample was chosen on the basis of the counter resolving time and the statistical accuracy of the count for short counting intervals. Sample activity was well below maximum permissible concentration (3000 pc/ml). Not all of the 200 samples analyzed are included in this report. About 50 of the samples were standards of known activity analyzed in order to check for consistency in the conversion and counting procedures.

Gas preparation and counting procedure. Figure No. 4 is a diagrammatic representation of the conversion system which provides for the preparation of more than one sample at a time without interference with the counting procedure. The water sample is converted into hydrogen by reaction with magnesium at 600°C in an evacuated stainless steel oven according to the relation

$$HTO(l) + Mg(s) \xrightarrow{600^{\circ}C} MgO(s) + HT(g). \qquad (8)$$

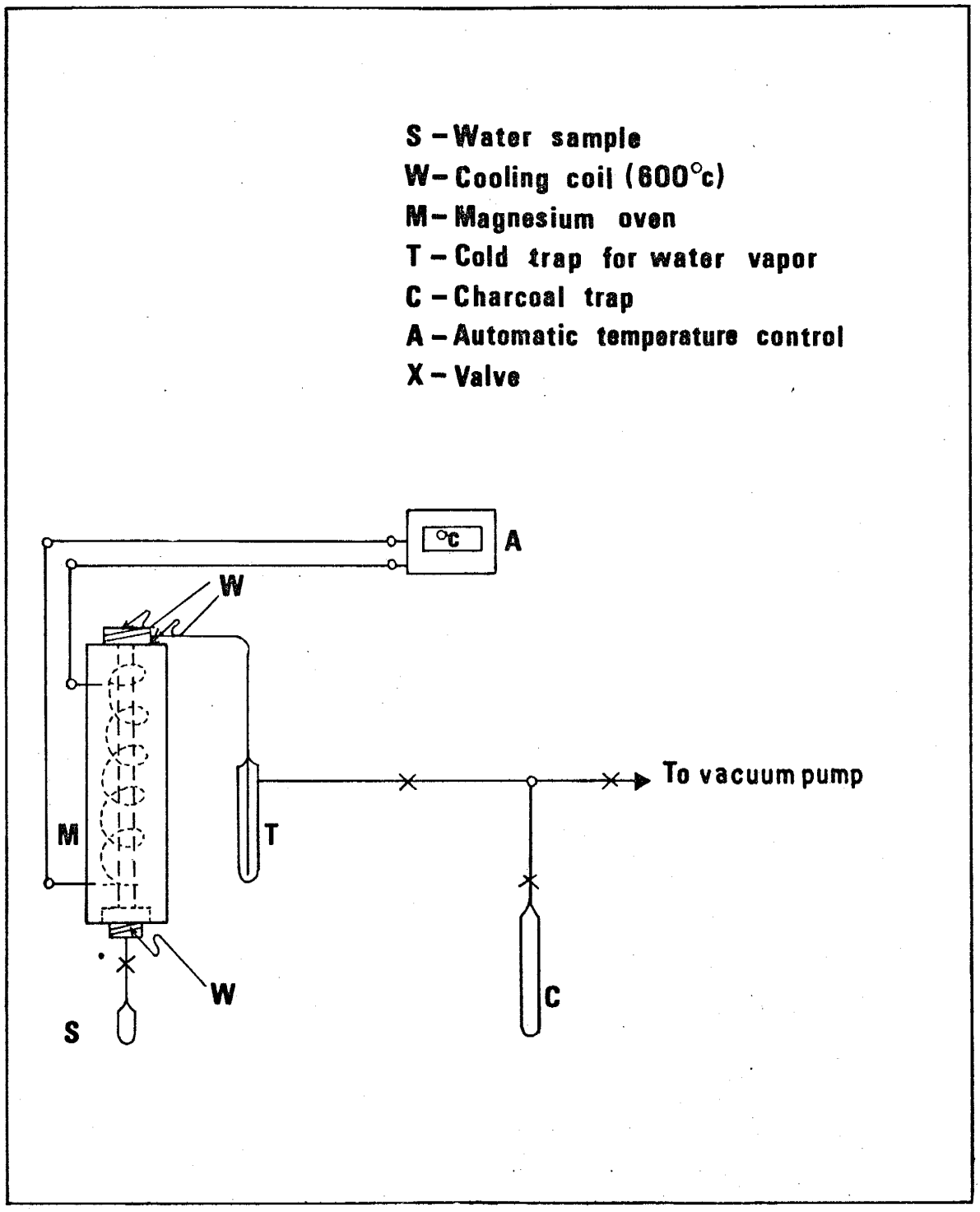

Fig. 4 Details of conversion system

The evolved hydrogen was trapped by adsorption on activated charcoal at liquid nitrogen temperature. The water sample used was pipetted by two micropipettes in two steps for a total of 1.150 ml. When a sample was too small, water of zero tiritum content was added in order to make up for the lack of sample. This called for very careful pipetting since a dilution correction was to be made on the final result. An indication of the completeness of conversion is given by the consistency of hydrogen pressure from one conversion to the next. As many as three samples per day were converted with the same filling of magnesium. With the activity range used, no memory effect in the Mg was observed.

Once a conversion was completed the charcoal trap was removed from the conversion system and transferred to the counting system. The hydrogen gas was then released from the charcoal trap into the evacuated counter. Hydrogen pressure inside the counter varied between 205 and 215 torr. The quenching gas, ethylene (C_2H_4), and the control gas, aragon (Ar) were then added successively. Total pressure in the counter varied between 325 and 335 torr. The three gases were allowed a uniform mixing time of 90 minutes before counting. A total of 10,000 counts was obtained for most samples.

Counter standardization. Periodic checks on the counter's performance were made with hydrogen gas converted from water which had zero tritium concentration in order to determine

the system's background rate (cpm). The same procedure, done with a sample of high known activity of tritium, calibrates the counter's effective volume (liters). Both conversion and gas filling of the standard samples were done under exactly the same conditions as the unknown samples. Figure No. 5 shows the variations in the effective volume and background rate for the counter between December, 1967 and May, 1969. The present work started during April, 1968.

The counter's sensitivity is 2.0 ± 0.2 pc/ml per 1 cpm above background count.

The detailed description of calibration calculations and the procedure for calculations of the unknown samples with error analysis are given in Appendix III.

Chemical Analysis of the Water

Ion concentrations in the water samples as determined by the Metallurgy Laboratory, New Mexico Bureau of Mines, are tabulated in Appendix II and reported in milliequivalents (meq). The samples were analyzed on the Atomic Absorption Spectrophotometer (Perkin-Elmer 303). Most of the samples had to be diluted because of the instrument's sensitivity. The dilutions were done by the investigator with micropipettes.

Water conductivity and pH were measured by the investigator.

Clay Analysis

X-ray diffraction measurements of the clays also were done before and after an electrodialysis run in order to

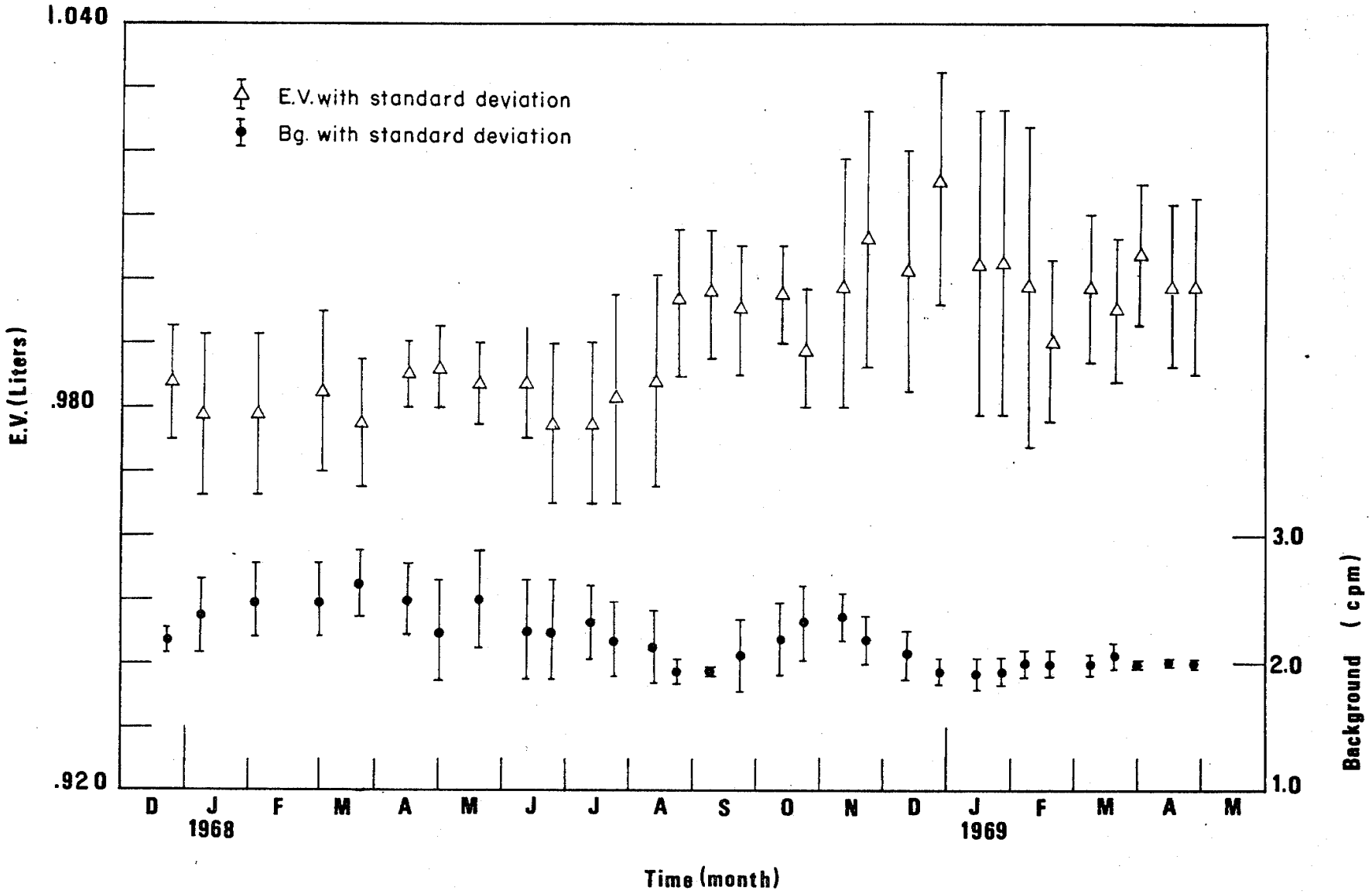

Fig. 5 Effective volume background variations over the experiment's duration

determine any shift in lattice spacing by decomposition of clay minerals under electrodialysis.

After completion of a run adsorbed water was removed from the clay sample by distillation at a temperature up to 200°C. This process determines the final water volume in the center compartment. The extracted water was measured for tritium concentration.

The lattice water was recovered from portions of the clay samples by heating up to 630°C in the conversion oven. See Fig. 4. Since the clay had already been distilled at 200°C, the oven was heated up to 350°C with the vacuum pump connected to the oven in order to remove all adsorbed water. The water evolved between 350°C and 630°C was collected with a liquid nitrogen trap below the oven. After extraction, the tritium concentration of the lattice water was measured.

Two clay samples (API No. 9 and API No. 35) of about 2 grams each, were treated with 48% HF acid, in order to try to liberate any additional free hydrogen and tritium ions that may have been attracted and held, by their electric charge in the clay lattice. After two hours the remaining acid-clay mixture was neutralized and distilled. The recovered water was measured and checked for its tritium concentration.

EXPERIMENTAL DATA

Presentation

Although all runs were conducted under similar conditions, there are essential distinctions between the experiments that affect the analysis of the results. The initial, individual discussion of each experiment which follows will develop the pertinent differences between the experiments and provide the necessary background for the analysis to follow.

All of the experiments were conducted in identical cells under similar initial conditions except for type of material in the center sample compartment. The specific activity of tritium 917.4±15.6 pc/ml was the same for each run, and each experiment was begun with tritiated water in the + compartment only.

Each experiment will be discussed in parallel fashion in terms of the plot which graphically represents the data tabulated in Appendix II for each run.

Run Number 1254 (1 and 2). These experiments were run without clay samples in the center cell compartment and without power and were conducted to ascertain the accuracy of the procedure used in all experiments for correction for tritium losses by exchange to the cell material and by fractionation under evaporation.

Figure 6 illustrates the results of each run. The open symbols show the change in specific activity in each cell as a function of time for runs No. 1 and No. 2. The solid symbols similarly illustrate the change in total activity with time.

The first experiment was done with an open cell at room temperature and was continued for 120 hours. The second experiment with a different covered cell was continued inside a constant temperature bath for 1800 hours. Corrections for tritium losses by evaporation, under the assumption of evaporation without fractionation, were calculated by multiplying an average concentration, in each compartment, times the volume lost. The average concentration was determined for each period between two successive samplings. A correction was also made for the amount of activity extracted with the sample itself. The accuracy in the measurements is 2%.

The plot of total activities represents values corrected for evaporation and sampling losses. The accuracy of determination of the total activity is of the same order as for the specific activity since only errors associated with the counting and calibration of the counter are significant. The accuracy of 2% does not hold true when absolute losses are calculated, due to the introduction of significance error.

Figure 6 shows that equilibrium in specific activities was reached in run 1 below the theoretical dilution value (the calculated equilibrium value depending upon initial

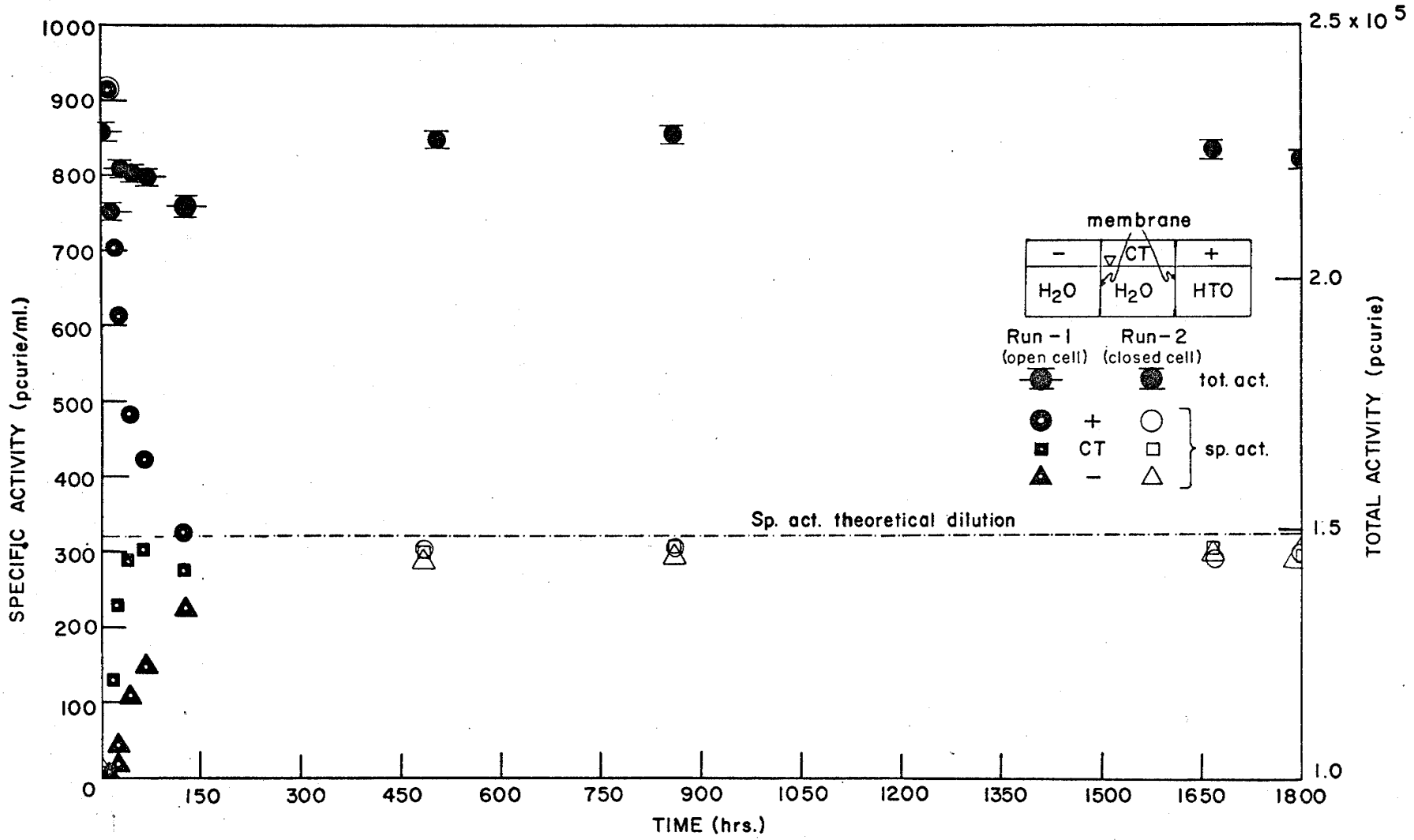

Fig. 6 Activities versus time. No clay, self-diffusion

specific activity and water volume for each run). This is an indication of tritium loss which can not be recovered and and represents a maximum loss since the cell was uncovered thus allowing additional dilution of the water sample with water vapor from the ambient atmosphere.

The drop in total activity after 12 hours is most likely an experimental error which should be rejected. The drop in total activity between 60 and 120 hours also indicates that for large volume losses the simple, linear averaging of specific activities between successive samples has to be modified under rapidly changing concentrations. The total water loss after 120 hours was 100 ml of water from each compartment. The total activity loss was 15501±4032 pc.

Run 2 (constant temperature, covered cell) corresponds to the environmental conditions under which the clay samples were electrodialized. Evaporation and sample dilution by water vapor from the atmosphere is minimized by the closed cover. The loss in total activity is only 2414±4595 pc after 504 hours and 6524±4446 pc after 1800 hours. Even though the cell was opened only three times during the course of this run, the rate of water loss compares well with the experiments run on the clays and indicates that the frequency of cell opening is not significant. The cell used in this run had not been used previously, hence, the total loss in activity of 2.8±1.9% of the initial total activity represents the total unaccounted losses to be expected by fractionation under evaporation and to the cell material.

Run Number 1201 (Kaolinite API No. 4). This was the only experiment run to completion in which an electrolyte (0.7 meq/ml $LiClO_4$) was added to the sample water. The results are presented in Fig. 7.

Equilibrium in specific activity between the three compartments occurs (after 330 hours) below the theoretical dilution value. Fig. 7 also shows the trend followed by the specific activity in the center compartment which first builds toward the activity value in the anode section and only then begins to approach equilibrium with the water in the cathode compartment. This departure from an asymptotic equilibrium trend represents the retarding effect of the clay on the tritium concentration front.

The first sampling, after 24 hours, shows an apparent total activity higher than the initial total activity in the sample, and was not used in the total activity calculations. Total loss was 27349±4067 pc which is 11.9±1.8% of the initial total activity.

After completion of the electrodialysis experiment the clay was heated to 630°C in the oven and the lattice water was recovered. The water color was green and had a strong chlorine odor. After an additional distillation the tritium concentration was measured and found to be 26.3±1.0 pc/ml. The water collected between 200°C and 350°C showed an activity of about 6 pc/ml. Lattice water from the reference clay that was not electrodialized, was

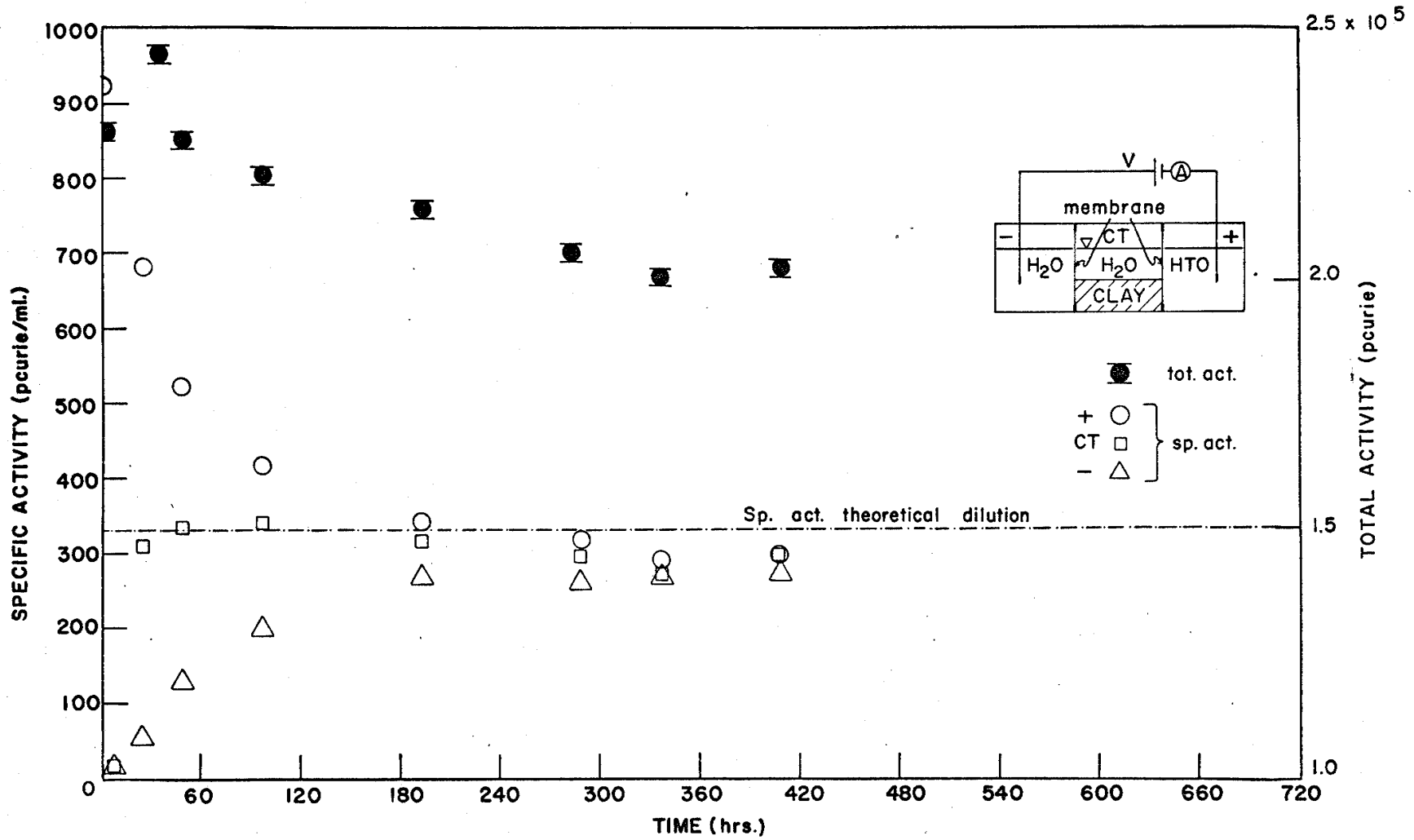

Fig. 7 Activities versus time. Kaolimite API No. 4
($LiClo_4$ electrolyte added)

measured for tritium. The count rate was identical to the background rate.

Run Number 1257 (Kaolinite API No. 4). This experiment, Fig. 8, represents a rerun of run No. 1201 in which the clay sample and cell membranes were replaced and run without the addition of electrolyte to the sample water. The total water lost by evaporation (205 ml after 1288 hrs.) was almost identical to the water loss of run 1254 which was run simultaneously in the same constant temperature bath. A check of the water in the constant temperature bath showed no loss of tritium to the bath.

Equilibrium concentrations in specific activity for the three compartments occurred close to the theoretical dilution value after only 124 hours. Run 1257 shows the most rapid approach of any toward equilibrium values. Since this was a rerun of 1201, only one sample was taken between 0 and 124 hrs.

Once equilibrium in tritium concentration was reached tritium disappeared from the liquid sample at a constant rate. Total loss was 59156±4147 pc which is 25.8±1.8% of the initial total activity.

The lattice water collected at 630°C shows a tritium concentration of 36.2±1.0 pc/ml.

Runs Number 1199 and 1245 (Kaolinite API No. 9). Fig. 9 represents activity determinations of the sample waters as a function of time for both experiments. Run 1199 was made with (0.20 meq/ml NaCl) added to the sample water as

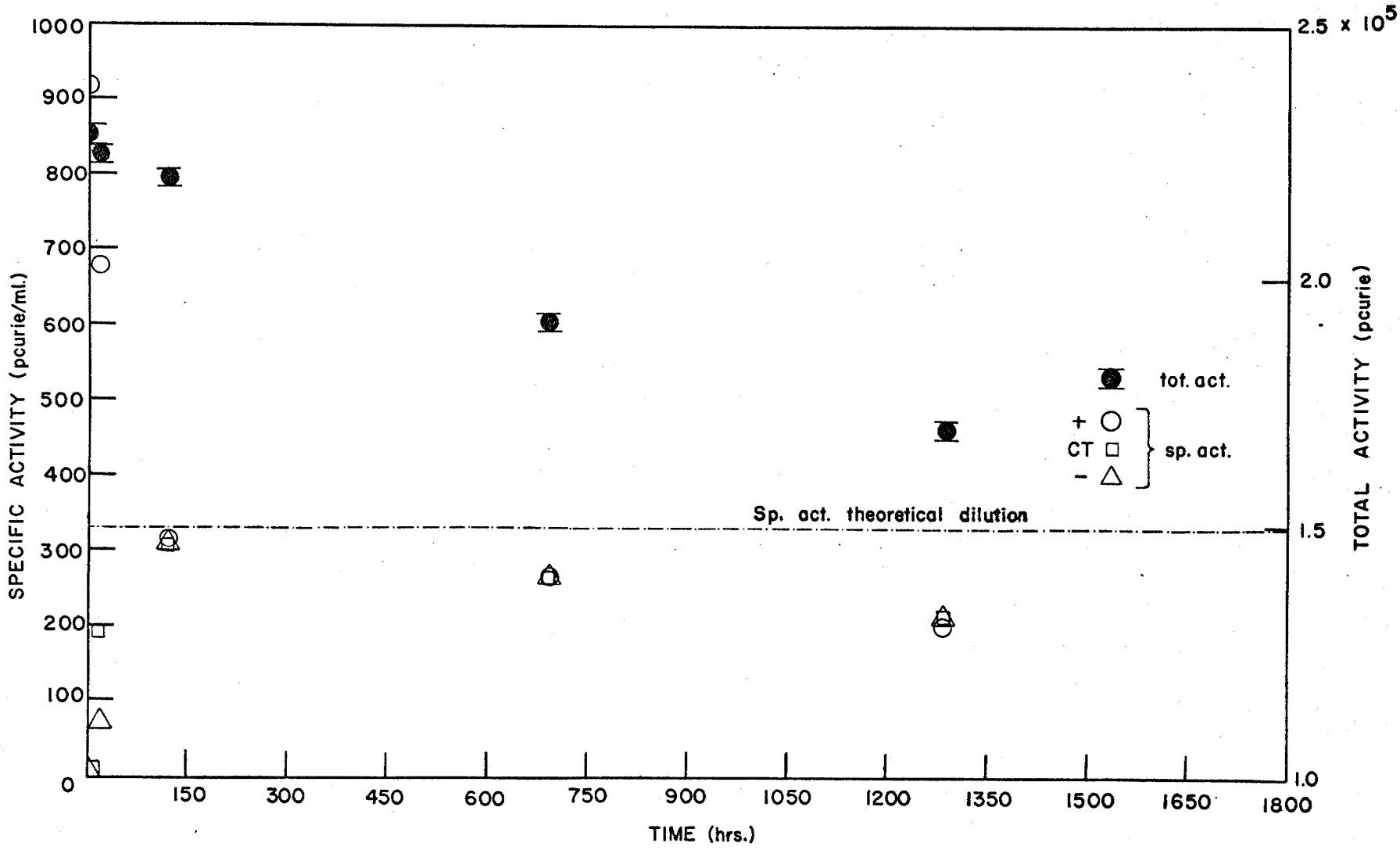

Fig. 8 Activities versus time. Kaolimite API No. 4

an electrolyte and was terminated after 72 hrs. because of membrane disintegration. Run 1245 was a rerun of 1199 made with new membranes and a fresh clay sample without electrolyte. The data for run No. 1199 is presented only for the purpose of comparison of the diffusion of tritium through the same clay under different conditions. The determination of total sample water activity is presented only for run No. 1245.

Equilibrium was reached after 182 hours and at the theoretical dilution value. The pH value at that time was 7.5 in the center compartment, Table VI (Appendix II). The tritium disappearance from the water did not begin until 60 hours after equilibrium had been reached at which time the pH measured in the center compartment was still 7.5. The drop in specific activity at 342 hours is accompanied by a pH drop in the center compartment to 5.3.

The total tritium lost in run 1245 after 228 hours was 9591±4544 pc and after 342 hours the loss increased to 18247±4444 pc. Total loss was 28235±4324 pc which is 12.3±1.9%.

The lattice water showed a tritium concentration of 11.9±0.5 pc/ml.

The clay was treated with HF acid, neutralized with NaOH, and the mixture was distilled and measured for tritium. The count rate of the sample was equal to the background rate. The tritium may have been removed completely with the hydroxyl water or possibly as free hydrogen at 650°C.

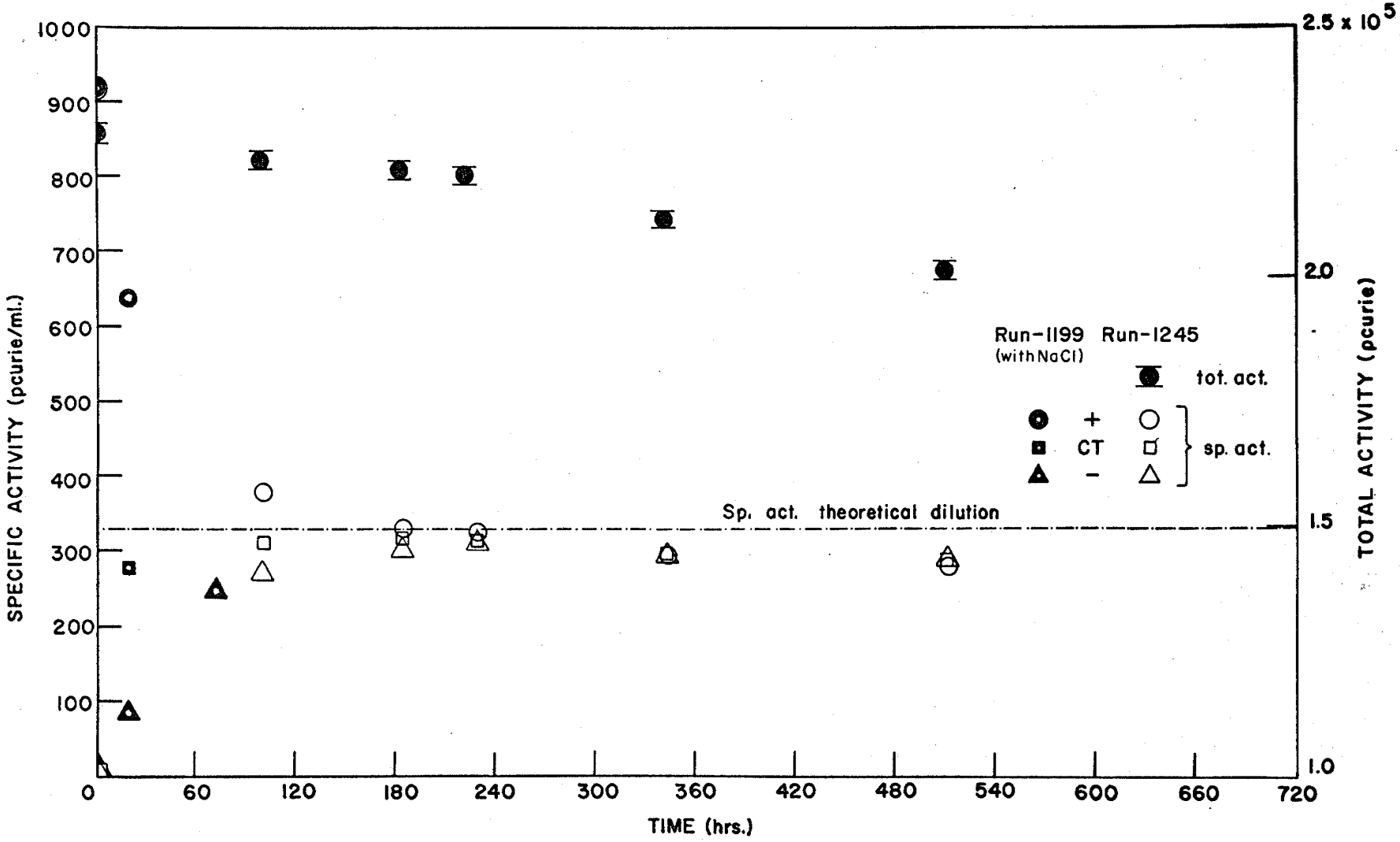

Fig. 9 Activities versus time. Kaolimite API No. 9

Run Number 1271 (Illite API No. 35). This electrodialysis run was carried out in a new cell. Equilibrium in specific activity between the anode and center compartments was reached after 120 hours and was well above the theoretical dilution values as shown in Fig. 10. Total equilibrium was not reached even after 684 hours.

In the previous experiments the trend of the specific activity curves indicated very clearly the trend in the total activity. In this experiment the total activity plot shows a significant variation at 63 hours. There is a drop in total activity of 13168±4137 pc and a corresponding drop of pH in the center compartment to 3.6, Table VII (Appendix II), with two short plateaus between 8 and 12 hours and again between 24 and 48 hours. From 63 hours to the end of the experiment there is a steady return of activity to the solution and a rise of pH in the center compartment to 6.5. The negative peak at 63 hours may be an indication of a strong retention of tritium by the clay until equilibrium is reached between the tritium concentration in the center compartment and the tritium concentration in the anode compartment. Total loss was well within the experimental error.

Lattice water at 630°C had a tritium concentration of 92.9±2.0 pc/ml.

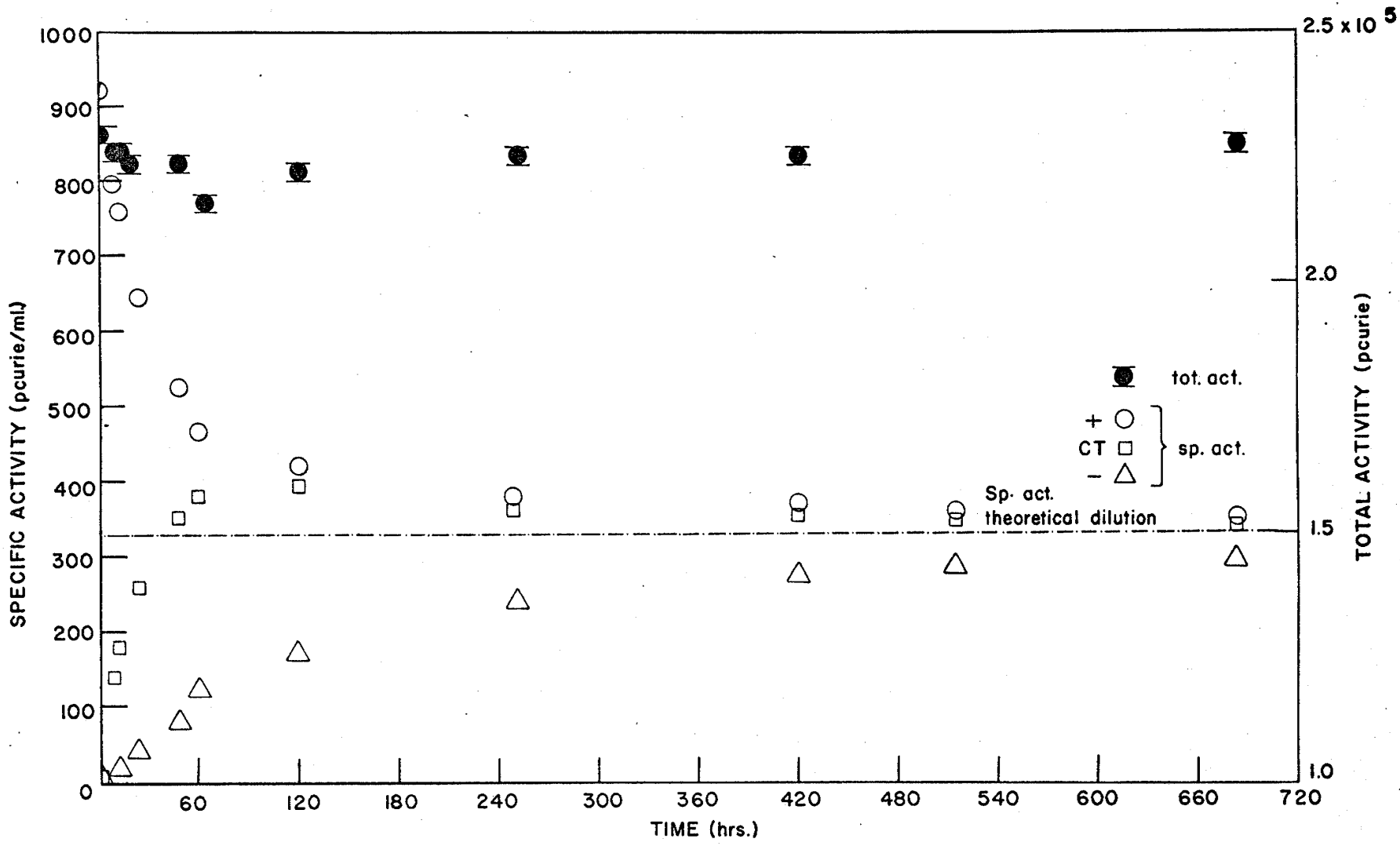

Fig. 10 Activities versus time. Illite API No. 35

Analysis

Even a casual comparison of Figs. No. 8, 9, and 10 reveals that the loss in total activity with time differs strikingly for three standard clays which were electrodialyzed under similar conditions. The total loss varies from almost 26% of the initial total activity for the Georgia kaolinite (run 1257) to less than the error of determination for the illite (run 1271). Although the acid treatment was negative and no significant fraction of the tritium lost to the kaolinite clays was identified as hydroxyl-water recovered by thermal release from the lattice structure, there can be no doubt that the unrecovered tritium must have been lost by exchange to the clay structure, and held there by strong electrostatic forces. The loss in activity from the solution by evaporation or to the material of the containing cell is insignificant. The cell in which the illite sample was electrodialyzed had not been used previously, and since there was no loss in total activity in this run (1271), there can be no significant loss to the cell material for the electrodialysis runs made over shorter time durations on the other clay samples. Table II shows that the rate of evaporation (0.12 ml/hr) after corrections for the illite sample is the same as that for the self-diffusion experiment without clay (Run 1254 part 2 was also run in a new cell). The best fit to the total activity data for the latter run, Fig. No. 6 is a straight

line with a total loss well within the significant error value of ±2%. In addition, checks on water of the constant temperature bath show no tritium has been exchanged from the cells. The specific activity in both kaolinite samples run without electrolyte approached equilibrium values under self-diffusion rapidly. The specific activity was in equilibrium in all compartments after less than 180 hours for the New Mexico clay, Fig. No. 9, and in less than 120 hours for the Georgia clay, Fig. No. 8. The best fit to the total activity data for both clays, after equilibrium has been reached, is a straight line showing a constant rate of loss of tritium from the solution to the clay.

Table I gives the average rate of loss of total activity between samplings for the four clay sample runs which were completed. The loss rates show a considerable variation from sample to sample until equilibrium under self-diffusion is reached. The variation in rate loss before equilibrium results largely from the retardation of the concentration front by the clays. The delay of diffusion of tritium by the clay, shows clearly only in the specific activity plot for the center compartment for the illite, Fig. No. 10 and for the kaolinite sample run with electrolyte, Fig. No. 7. In each of these experiments equilibrium under self-diffusion was not reached with the cathode compartment by the end of the run.

Retardation of the diffusion front by the kaolinite clays run without electrolyte is significant only in that

TABLE I: TRITIUM LOSS RATE (pc/hr)

1201 series Kaolinite API No. 4 with electrolyte	1257 series Kaolinite API No. 4	1245 series Kaolinite API No. 9	1271 series Illite API No. 35
$\frac{19\pm92}{(0\text{-}48)}$[1]	$\frac{289\pm316}{(0\text{-}16.5)}$	$\frac{63\pm47}{(0\text{-}99)}$	$\frac{443\pm549}{(0\text{-}8)}$
$\frac{155\pm125}{(48\text{-}96)}$	$\frac{45\pm56}{(16.5\text{-}124)}$	$\frac{30\pm72}{(99\text{-}182)}$	$\frac{521\pm400}{(48\text{-}63)}$
$\frac{71\pm63}{(96\text{-}192)}$	$\frac{51\pm10}{(124\text{-}694)}$	$\frac{19\pm130}{(182\text{-}228)}$	$\frac{+(110\pm105)}{62\text{-}120}$
$\frac{93\pm63}{(192\text{-}288)}$	$\frac{35\pm10}{(694\text{-}1288)}$	$\frac{76\pm53}{228\text{-}342}$	$\frac{+(23\pm46)}{(120\text{-}252)}$
$\frac{110\pm125}{(288\text{-}336)}$		$\frac{59\pm36}{(342\text{-}510)}$	$\frac{+(3\pm35)}{(252\text{-}420)}$
$\frac{+(29\pm83)}{(336\text{-}408)}$[2]			$\frac{14\pm63}{(420\text{-}516)}$
			$\frac{+(25\pm36)}{(516\text{-}684)}$

[1] The numbers in parentheses, below the line, are hours over which rate was determined.

[2] Gain in total activity.

it contributes to the variability in the rate loss calculations before equilibrium under self-diffusion was reached. An apparent preferential affinity of the clay for the tritiated polar water molecule prior to equilibrium was determined by the experiments on the Georgia kaolinite (run 1257) in which the water was first stirred above the clay and then stirred with the clay in the center compartment. The water sample taken before the clay-water mixture was stirred was consistently lower in activity than the sample of water taken above the clay surface after the clay suspension had settled. This effect, Table V (Appendix II), is apparent only before equilibrium values of specific activity were reached. The total activity rate losses for kaolinite clays were calculated from water samples taken before stirring, and were not corrected for tritium returned to the water sample by stirring the clay. Thus, rate loss values determined before equilibrium are apparent values only. This effect is not significant in the determination of the rate losses between samplings after equilibrium under self-diffusion had been reached or in the determination of the total tritium lost to the clays.

Table II shows the specific activity of the tritium held in the lattice waters of the clays. The conversion to total activity was done by multiplying this value by the number of milliliters of lattice water recovered per gram of clay times the total weight of clay. In all cases the total recovered is less than 600 pc and accounts for only

TABLE II SUMMARY OF RESULTS AND CALCULATIONS

SAMPLE NUMBER	TOTAL TIME (HRS.)	PREDOM-INANT CLAY PH	REPORTED CEC[3] (MEQ/100g)	TOTAL CATION RECOVERED (MEQ/100g)	TOTAL TRITIUM LOST (%)	$\frac{(T/H)\ clay\ 630^{o}C}{(T/H)}$ equilibrium (%)	TOTAL TRITIUM EXCHANGED ($pc/ml \times H_2O^{+}$) (FICOCI)
1254 series self-diffusion with evaporation	120	-	-	-	6. 8±1.8	-	-
1254 series self-diffusion without evaporation	1800	-	-	-	2. 8±1.9	-	-
1201 series[1] Kaolinite API No. 4 with electrolyte	408	UK[2]	12.2	4.2[2]	11. 9±1.8	8.03±0.30	340.0±12.9
1257 series Kaolinite API No. 4	1288	ACIDIC	12.2	10.5	25. 8±1.8	11.20±0.30	466.0±12.9
1245 series Kaolinite API No.9	510	BASIC TO ACIDIC	6.8	2.2	12. 3±1.9	3.63±0.02	161.0± 6.8
1271 series Illite API No. 35	684	BASIC	25.0	34.6	0.30±1.8	28.40±0.60	557.0±12.0

[1] 1201 series through 1271 series: electrodialysis.
[2] 1201 total Ca^{++} and PH were not measured.
[3] Cation exchange capacity.

TABLE II (cont'd) SUMMARY OF EVAPORATION LOSSES AND RATE, SAMPLING AND CELL USE

SAMPLE NUMBER	TOTAL TIME (HRS.)	TOTAL TRITIUM LOST (%)	CELL NUMBER	ORDER BY WHICH CELL USED	SAMPLING POINTS PER RUN	TOTAL WATER LOST BY EVAPORATION (ML)	EVAPORATION RATE (ML/HR)
1254 series self-diffusion with evaporation	120	6.8±1.8	1	1	4	243.0	2.0
1254 series self-diffusion without evaporation	1800	2.8±1.9	3	1	5	209.0	0.12
1201 series Kaolinite API No. 4 with electrolyte	408	11.9±1.8	2	2[1]	7	86.0	0.21
1257 series Kaolinite API No. 4	1288	25.8±1.8	2	3	4	197.0	0.15
1245 series Kaolinite API No. 9	510	12.3±1.9	1	2	5	68.0	0.13
1271 series Illite API No. 35	684	0.3±1.8	4	1	10	83.0	0.12

[1]Cell was used for the first time with NaCl for 1199 series.

an insignificant fraction of the tritium lost to the lattice structure of the kaolinite clays.

The pH of the water in the center compartment is the only parameter which shows strong correlation with the loss of tritium to the clays. The pH of the water in the center compartment for the Georgia kaolinite (run 1257) dropped to 5.0 at equilibrium and remained below 5.0 for the remainder of the run.

The pH of the water for the New Mexico kaolinite (run 1245) did not become acidic until after 200 hours when a drop to 5.3 was observed. Loss in total activity to the clay was small until this time and then increased to 65 pc/hr.

The only significant loss in tritium to the illite (run 1271) occurred in coincidence at 63 hrs. with a drop in pH from 6.4 to 3.6. After 120 hrs. the pH in the center compartment had returned 6.6 and tritium was returned to the solution from the clay. The exact relation of exchange to pH remains to be determined. This correspondence has also been noted by Hamid and Warkentin (1967) for Iodine-131, who found that I^{131} adsorption could be prevented if the pH value remained above 7.

No evidence was found that the pH change in the center compartment was related to any physical or chemical changes in the system other than the exchange property of the clay. X-ray diffraction measurements of the reference clays before

and after the electrodialysis indicated no shift in lattice spacing which means no alternation of the basic structure of the clay minerals occurred under electrodialysis.

SUMMARY AND CONCLUSIONS

The stated objective of this study, the determination of any possible exchange of tritium from water to a clay lattice structure, is obtained by monitoring the rate of appearance of cations into the liquid phase against rate of loss of tritium from the liquid under the influence of an electric field. Since the water in the cell was analyzed while the experiment was in progress the cation rate of appearance in the water was determined only for soluble ions. The pH conditions in the end compartments caused precipitation of the Ca^{++} ion in the cathode compartment. Ca^{++} ion exchange could only be determined at the end of each run. As a result, the metal ion exchange rates are apparent values only. The useful result of the analysis for the cations is in the comparison of the total amount recovered (meq) to the reported cation exchange capacity of these standard clays, see Table II.

The exchange of tritium with respect to the clay lattice, expressed as an isotopic fractionation effect, is also listed in Table II. The equilibrium tritium to protium ratio (T/H), provides the basis for comparison of the results obtained for the different clays. One should note that the values for the isotopic fractionation determined from the tritium found in the lattice waters are proportional to the known cation exchange capacities of the clays. In

terms of total activity, however, the fractionated tritium as listed in Table II amounts to only a small fraction of the total activity lost from the liquid except for the illite (run 1271).

The presence of tritium in the lattice water, indicates that some of the tritium is moving as $(OT)^-$, and that the tritium preferentially undergoes hydroxyl exchange.

According to Kelly and Jenny [1936], however, the exchange power of kaolinite is directly traceable to the H^+ ions of the crystal lattice. An important feature of the lattice structure is a subsurface OH plane, covered by a network of O^{-2} ions, in which the H^+ ions of the OH planes are accessible through the meshes of the oxide (O^{-2}) lattice. Absorption of tritium would depend on differential displacement of H^+ ions with T^+ ions. If some of these H^+ ion sites, exposed by breaks across the octahedral layer, were originally occupied by metal ions, then in the cation replacement of the metal ion under electrodialysis fractionation by preferential replacement of the tritium ion could occur. Although the exact location of the exchange site is indefinite, the cation exchange is probably on the surface of broken lattices of the crystals.

The discrepancy between the apparent loss of tritium to the kaolinite clays and the amount of tritium recovered from the lattice water of these clays is not resolved. The experimental procedure provides a self consistent set of statistically valid data that indicate that the tritium

must have been lost to the clay. The agreement between rate of loss and pH after equilibrium conditions have been reached appears to be real. The acid condition of the center compartment requires a complex chemical reaction. If this relation is true, the application to the problem of groundwater tracing is clear. Appreciable losses of the tritium isotope will occur only in an acid environment.

The application to the problem of disposal of radioactive wastes is equally understood i.e, maintain an acid environment in the disposal aquifer.

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APPENDICES

APPENDIX I: UNITS AND FORMULAS

Units

Tritium units (T.U.). Tritium units is the number of atoms per 10^{18} hydrogen (protium) atoms

$$1 \text{ T.U.} = (T/H)\ 10^{-18} \tag{1}$$

or

$$1 \text{ T.U.} = 7.2 \times 10^{-3} \text{ dmp/ml} \tag{2}$$

or

$$1 \text{ T.U.} = 3.24 \times 10^{-3} \text{ pc/ml} \tag{3}$$

where pc (picocurie) = 10^{-12} c

To calculate the fractionation factor ,E, the following was used:

$$E = {}^{R_t}/_{R_{eq}} \tag{4}$$

where R_t = isotopic ratio of tritium to protium in water extracted from the clay at temperature t.

R_{eq} = Isotopic ratio of tritium to protium at theoretical equilibrium in the electrodialysis cell

When using T.U., E is readily determined by

$$E = (\text{T.U.})_t/(\text{T.U.})_{eq}. \tag{4a}$$

APPENDIX II: OBSERVED AND CORRECTED DATA

TABLE III DATA FROM EXPERIMENT USING NO CLAY, SELF-DIFFUSION[1]

SAMPLE NO.	COMPART-MENT	ELAPSED TIME (HRS.)	RESIDUE VOLUME (ML)	SPECIFIC ACTIVITY (PICOCI/ML)
1196 std.	-	0	250.0	0. ± 0.
1196 std.	CT	0	250.0	0. ± 0.
1195 std.	+	0	250.0	917.4±15.6
1254A	-	12	239.1	12.6± 0.9
	CT	12	239.1	132.4± 2.4
	+	12	241.1	707.8± 6.9
1254B	-	24	228.2	42.7± 1.5
	CT	24	228.2	229.0± 1.9
	+	24	230.2	615.6± 4.6
1254C	-	48	206.4	113.0± 1.7
	CT	48	206.4	294.0± 3.2
	+	48	208.4	477.3± 4.8
1254D	-	60	195.5	156.0± 2.5
	CT	60	195.5	301.5± 4.3
	+	60	197.5	424.9± 4.3
1254E	-	120	154.5	226.0± 2.8
	CT	120	154.5	274.4± 3.2
	+	120	155.5	325.1± 3.4
1254F	-	504	232.8	296.9± 6.1
	CT	504	229.2	300.7± 5.8
	+	504	230.0	308.5± 6.2
1254G	-	864	218.5	303.0± 5.6
	CT	864	212.3	300.4± 5.5
	+	864	213.7	308.2± 7.1

[1]This table is a combination of two experiments:
a) 0-120 hrs. self-diffusion with free evaporation, and
b) 0-1800 hrs. self-diffusion with the cell covered.

TABLE III (cont'd)

SAMPLE NO.	COMPART-MENT	ELAPSED TIME (HRS.)	RESIDUE VOLUME (ML)	SPECIFIC ACTIVITY (PICOCI/ML)
1254H	-	1668	189.0	296.3± 6.5
	CT	1668	177.1	302.0± 6.8
	+	1668	179.9	296.2± 6.8
1254I	-	1800	180.0	294.1± 6.9
	CT	1800	167.0	294.8± 6.9
	+	1800	170.0	295.9± 7.1

TABLE IV DATA FROM EXPERIMENT

USING KAOLINITE API NO.4

Weight of clay 100 gms.
Mesh size 53-74 microns
Voltage gradient 0.3 v/cm.
Current 50-100 ma.
Charge transfer 1.33 coul.
Electrolyte $LiClO_4$

SAMPLE NO.	COMPARTMENT	ELAPSED TIME (HRS.)	RESIDUE VOLUME (ML)	SPECIFIC ACTIVITY (PICOCI/ML)
1196 std.	-	0	250.0	0. ± 0.
1196 std.	CT	0	200.0	0. ± 0.
1195 std.	+	0	250.0	917.4±15.6
1201A	-	24	248.5	59.7± 1.4
	CT	24	198.1	302.9± 3.9
	+	24	248.9	680.1± 9.0
1201B	-	48	244.9	126.6± 2.2
	CT	48	194.1	333.7± 4.7
	+	48	245.8	520.4± 7.1
1201C	-	96[1]	239.9	200.2± 3.5
	CT	96	188.2	336.4± 3.9
	+	96	241.5	414.3± 3.8
1201D	-	192	229.8	267.1± 4.5
	CT	192	176.5	313.3± 5.3
	+	192	233.0	336.8± 5.7
1201E	-	288	221.6	263.8± 3.4
	CT	288	166.7	295.4± 3.6
	+	288	226.6	314.5± 3.2
1201F	-	336	214.6	266.9± 2.2
	CT	336	157.8	289.6± 3.6
	+	336	220.3	291.7± 3.0
1201G	-	408	208.0	272.8± 3.4
	CT	408	149.0	292.9± 3.6
	+	408	215.0	297.3± 3.4

[1]Current up to 100 ma.
Voltage gradient no change.

TABLE IV (cont'd)

Chemical analysis of the water after experiment			
	- COMPARTMENT	C COMPARTMENT	+ COMPARTMENT
Na^{+}(meq)	0.6	-	0.2
K^{+} (meq)	0.1	-	0.0
Mg^{++}(meq)	0.0	-	0.3
Ca^{++}(meq)	0.2	-	2.8
PH	12.3	-	0.3
Total cations	0.9	-	3.3

TABLE V DATA FROM EXPERIMENT

USING KAOLINITE API NO.4

Weight of clay 100 gms. Current 10.0 ma.
Mesh size 53-74 microns
Voltage gradient 2 v/cm. Charge transfer 0.46 coul.

SAMPLE NO.	COMPARTMENT	ELAPSED TIME (HRS.)	RESIDUE VOLUME (ML)	SPECIFIC ACTIVITY (PICOCI/ML)	PH	CONCENTRATION (MEQ.) Na^+	K^+	Mg^{++}
1196 std.	-	0	250.0	0. ± 0.	6.2			
1196 std.	CT	0	210.0	0. ± 0.	6.2			
1195 std.	+	0	250.0	917.4±15.6	6.2			
1257A	-	16.5	250.0	65.5± 1.5	12.2	0.6	1.5	0.0
	CT	16.5	210.0	190.5± 4.2	6.0	I.S.[1]	0.0	0.0
	+	16.5	250.0	672.8±13.3	2.3	0.3	0.0	0.0
1257A'	CT	16.5	208.0	207.8± 4.3				
1257B	-	124	241.4	307.1± 5.7	12.0	0.4	1.2	0.0
	CT	124	199.5	307.3± 5.7	5.0	0.0	0.0	0.0
	+	124	238.7	312.5± 5.8	2.3	0.3	0.0	0.0
1257B'	CT	124	197.5	317.3± 5.7				
1257C	-	694	213.2	260.2± 5.9	11.3	0.3	1.1	0.0
	CT	694	161.1	263.5± 6.1	5.5	0.0	0.0	0.0
	+	694	196.2	263.4± 6.1	3.1	0.0	0.0	0.0
1257C'	CT	694	159.1	263.4± 6.0				
1257D	-	1288	184.0	216.5± 4.8	10.9	0.2	0.8	0.0
	CT	1288	121.2	218.4± 5.3	4.8	0.0	0.1	0.0
	+	1288	152.1	213.4± 4.9	2.1	0.0	0.0	0.0
1257D'	CT	1288	119.2	216.5± 5.1				

All primed samples (1257A' CT, 1257B' CT etc.) were taken after the clay-water mixture was stirred and allowed to settle. The time difference between the sampling of 1257A CT and 1257A' CT was 15 minutes.

[1]Insufficient sample.

TABLE V (cont'd)

Chemical analysis of the water after experiment precipitation included

	- COMPARTMENT	C COMPARTMENT	+ COMPARTMENT
Na^+ (meq)	0.2	0.0	0.0
K^+ (meq)	1.0	0.1	0.0
Mg^{++} (meq)	1.0	0.0	0.0
Ca^{++} (meq)	8.2		0.0
Specific conductance (micromhos/cm)	795	156	3976
Total cations (meq)	10.4	0.1	0.0

TABLE VI DATA FROM EXPERIMENT

USING KAOLINITE API NO. 9

Weight of clay 100 gms. Current 1.0 ma.
Mesh size 53-74 microns Charge transfer 0.02 coul.
Voltage gradient 2.9 v/cm.

SAMPLE NO.	COMPARTMENT	ELAPSED TIME (HRS.)	RESIDUE VOLUME (ML)	SPECIFIC ACTIVITY (PICOCI/ML)	PH	CONCENTRATION (MEQ.) Na^+	K^+	Mg^{++}
1196 std.	-	0	250.0	0. ± 0.	6.2			
1196 std.	CT	0	200.0	0. ± 0.	6.2			
1195 std.	+	0	250.0	917.4±15.6	6.2			
1199A[1]	-	24		78.3± 1.4				
	CT	24		277.1± 4.0				
	+	24		634.1± 8.1				
1199B	-	72		247.3± 3.3				
1245A	-	99	245.5	269.2± 5.1	9.7	0.5	0.0	0.1
	CT	99	193.2	312.8± 5.9	7.2	0.0	0.0	0.0
	+	99	244.6	373.8± 7.4	3.3	0.0	0.0	0.0
1245A'	CT	99	191.2	314.8± 6.3				
1245B	-	182	239.8	304.5± 5.8	9.3	0.5	0.1	0.1
	CT	182	183.5	317.7± 6.4	7.5	0.0	0.0	0.0
	+	182	238.0	324.2± 6.4	3.3	0.0	0.0	0.0
1245C	-	228	233.7	313.0± 6.3	9.3	0.5	0.2	0.0
	CT	228	176.3	311.1± 6.2	7.5	0.0	0.0	0.0
	+	228	231.5	316.9± 6.2	3.3	0.0	0.0	0.0
1245D	-	342	224.6	300.7± 6.2	9.4	0.5	0.2	0.0
	CT	342	164.5	300.4± 5.7	5.3	0.0	0.0	0.0
	+	342	221.2	298.8± 5.9	3.3	0.0	0.0	0.0
1245E	-	510	213.0	284.7± 5.7	8.3	0.5	0.1	0.0
	CT	510	149.0	279.7± 5.3	5.6	0.1	0.0	0.0
	+	510	208.0	283.2± 5.6	3.3	0.0	0.0	0.0

[1]Taken from a run with NaCl as electrolyte.
Not included with total activity calculations.

TABLE VI (cont'd)

Chemical analysis of the water after experiment precipitation included

	- COMPARTMENT	C COMPARTMENT	+ COMPARTMENT
Na^+ (meq)	0.5	0.1	0.0
K^+ (meq)	0.0	0.0	0.0
Mg^{++} (meq)	0.4	0.0	0.0
Ca^{++} (meq)	1.1	0.0	0.1
Specific conductance (micromhos/cm)	278	102	363
Total cations (meq)	2.0	0.1	0.1

TABLE VII DATA FROM EXPERIMENT

USING ILLITE API NO. 35

Weight of clay 100 gms. Current 10-1 ma.[1]
Mesh size 53-74 microns Charge transfer 0.07 coul.
Voltage gradient 2 v/cm.

SAMPLE NO.	COMPARTMENT	ELAPSED TIME (HRS.)	RESIDUE VOLUME (ML)	SPECIFIC ACTIVITY (PICOCI/ML)	PH	CONCENTRATION (MEQ_+) Na^+	K^+	Mg^{++}
1196 std.	-	0	250.0	0. ± 0.	6.2			
1196 std.	CT	0	200.0	0. ± 0.	6.2			
1195 std.	+	0	250.0	917.4±15.6	6.2			
1271A	-	8	250.0	2.8± 0.3	11.6	1.8	0.7	0.0
	CT	8	200.0	133.4± 1.5	6.6	0.4	0.1	0.2
	+	8	250.0	795.7± 8.6	2.6	0.0	0.0	0.0
1271A'	CT	8	198.0	136.6± 1.6	6.6			
1271B	-	12	246.0	9.4± 0.3	11.6			
	CT	12	196.0	178.9± 2.5	7.6			
	+	12	246.0	755.7± 8.9	2.3			
1271C	-	24	233.6	38.7± 0.8	11.3	1.6	1.7	0.0
	CT	24	196.2	260.1± 3.4	6.3	0.0	0.0	0.1
	+	24	250.0	641.4± 7.1	2.1	0.0	0.0	0.0
1271D	-	48	221.3	80.7± 1.4	11.3	1.5	1.8	0.0
	CT	48	184.8	357.4± 3.8	6.4	0.0	0.0	0.0
	+	48	250.0	524.0± 5.9	2.1	0.0	0.0	0.0
1271E	-	63	213.1	120.7± 1.9	11.4			
	CT	63	177.2	388.1± 4.6	3.6			
	+	63	233.8	461.7± 4.9	2.1			
1271F	-	120	209.0	166.7± 1.9	11.6			
	CT	120	177.2	394.0± 4.5	6.6			
	+	120	233.8	424.8± 4.6	2.2			
1271G	-	252	209.0	240.3± 2.5	11.0	1.6	2.3	0.0
	CT	252	169.6	365.4± 3.6	6.5	0.0	0.0	0.1
	+	252	228.4	382.6± 3.8	2.3	0.0	0.0	0.0

[1]Within the first 192 hrs. current dropped from 10 ma to 3 ma.

TABLE VII (cont'd)

SAMPLE NO.	COMPART-MENT	ELAPSED TIME (HRS.)	RESIDUE VOLUME (ML)	SPECIFIC ACTIVITY (PICOCI/ML)	PH	CONCENTRATION (MEQ.) Na^+	K^+	Mg^{++}
1271H	-	420	196.7	266.7± 3.0	10.4	1.7	I.S.[1]	0.2
	CT	420	162.0	355.9± 4.3	6.5	0.0	I.S.	0.2
	+	420	217.6	363.3± 3.6	2.4	0.0	I.S.	0.1
1271H'	CT	420	160.0	356.2± 4.9	6.5			
1271I	-	516	180.3	277.1± 3.0	10.5			
	CT	516	158.2	342.6± 3.7	6.2			
	+	516	212.2	357.2± 4.5	2.3			
1271J	-	684	144.0	293.0± 3.5	10.6	1.8	2.3	0.2
	CT	684	166.0	338.8± 4.2	4.4	0.0	0.1	0.1
	+	684	223.0	344.3± 3.4	2.3	0.0	0.0	0.2

Chemical analysis of the water after experiment precipitation included

	- COMPARTMENT	C COMPARTMENT	+ COMPARTMENT
Na^+ (meq)	1.8	0.0	0.0
K^+ (meq)	2.3	0.1	0.0
Mg^{++} (meq)	0.9	0.1	0.2
Ca^{++} (meq)	27.4	1.1	0.7
Specific conductance (micromhos/cm)	3114	795	3892
Total cation (meq)	32.4	1.3	0.9

[1]Insufficient sample.

APPENDIX III: EFFECTIVE VOLUME AND BACKGROUND RATE CALCULATIONS, COMPUTER PROGRAM

The precision of all measurements was limited by the statistical accuracy of counting of the unknown samples, the variations in the effective volume, and the background rate.

The computations were done by a computer. The computer program as used is listed in Table VIII (Appx. III.) Comment cards are inserted before each unit of calculations.

Formulas

The basic relation used in calculating the effective volume and the activity of the unknown samples is:

$$T.U. = (481.0)\,(e^{N/212})\,\frac{(\text{net rate})\,(273.16+{}^{\circ}C)}{(E.V.)\qquad(P)} \qquad (5)$$

Equation (5) is a modification of a relation presented by Von Buttlar and Stahl [1962]. In equation (5),

481.0 = a constant combines dpm/mole H_2 with concentration of 1 T.U., the ideal gas constant, and the conversion from torr to atmosphere

$e^{N/212}$ = decay time correction

net rate = cpm of the sample corrected for background rate

E.V. = effective volume in liters

$^{\circ}C$ = the counter's temperature

P = hydrogen gas pressure in torr

By interchanging E.V. with T.U., equation (5) can be readily used to calculate the effective volume of the counter with a known value for T.U.

The system's background rate is determined by a single measurement with a statistically significant number of counts

$$BG \pm SIGBG = R \pm \sqrt{R/t} \text{ cpm} \qquad (6)$$

where $\pm SIGBG$[1] = background standard deviation $= \sqrt{R/t}$

R = background rate

t = total time (mins.)

To calculate the tritium concentration in a measured sample equation (5) is used. The sample is than said to be indirectly evaluated by calculation from directly measured quantities which are containing errors. The reliability of the calculated sample is found by applying the theory of propagation of errors (Overman and Clark, 1960). Thus, equation (5) takes the form of

$$T.U. \pm SIGT.U. = \frac{\left[\left(\frac{N \pm \sqrt{N}}{t}\right) - (BG \pm SIGBG)\right]}{(E.V. \pm SIGE.V.)} \cdot f(C,P,T) \qquad (7)$$

where $\pm SIGT.U.$ = tritium units standard deviation

$\frac{N \pm \sqrt{N}}{t}$ = count rate and standard deviation of the sample

$\pm SIGE.V.$ = effective volume standard deviation

$f(C,P,T)$ = physical quantities with negligible source of error.

---

[1]Notations used are identical to the ones used in the computer program.

The numerical solution of equation (7) is obtained by using the computer program listed below. Each sample to be evaluated was counted once with an accuracy of ±1% to ±2% depending on the activity. The background rate and the effective volume are variables (Fig. 5) and are changing with time. An average value from four consecutive measurements of standards (which represent a time span of two months) was assigned to those samples which were counted between the second and third sets of standards. The process of calculation is sequential and assures continuity.

Computer Program

The computer program was written for a complete calculation and error analysis for the background, effective volume, and the unknown samples. The program comprizes a sample output for one complete cycle of calculations. The results are given in both tritium units and pc/ml. The background mean value is in cpm. The mean effective volume is in liters.

TABLE VIII COMPUTER PROGRAM LIST

```
C       THIS ROUTINE WILL READ 4 CARDS TO FIGURE EV, SIGMA EV, BG, & SIGMA BG
C       FOR THE PERIOD. NEXT IT WILL READ DATA TO FIGURE TU'S IN THAT PERIOD
C       FOR AS MANY SAMPLES AS ARE DESIGNATED ON THE 5'TH CARD.
C       ONCE SAMPLES ARE DONE, A NEW CARD IS READ TO FIGURE A NEW EV AND BG.
C       DATA FOR TU'S ARE THEN READ AND FIGURED FOR SAMPLES IN THIS PERIOD AND
C       THE PROCESS CONTINUES.
C       IF THERE ARE NO TU'S TO BE FIGURED FOR A PERIOD, A BLANK CARD SHOULD BE
C       INSERTED WHERE DATA WOULD APPEAR,BEFORE AND AFTER DECAY.
C       THE ROUTINE WILL KNOW TO DECAY WHEN LAST EV-BG CARD IS READ IF IT
C       ENCOUNTERS A 99 IN AN A4 FIELD WHERE THE NEXT EV-BG CARD WOULD APPEAR.
C       IT WILL READ 2 SETS OF DATA AFTER THIS, COMPUTING EV & BG, AND TU FROM
C       3,&2 READINGS.
C
C
0001          INTEGER TIME(6),THYME(6),DATE(6),TYEM,DAYT1,DAYT2
0002          DIMENSION    C(6),KWNT(6),TEMP(6),P(6),RATE(6),RATDEV(6),DEVSQ(6),
             2WEYFAC(6),SDBG(6),CNTDEV(6),DUBDEV(6),TEMPRS(6),WDECAY(6),EV(6),SI
             3GEV(6),DIFF(6),DIFFSQ(6),DAIT(6),KUNT(6),RSD(6),DECAY(6),TU(6),ID(
             46),IDAY(6),CK(6)
0003          DATA MARG/Z4040F9F9/
0004        001 JILL=4
0005          JUBJUB=0
0006          RSUM=0.
0007          DOOM=0.
C
C       READ DATA & FIGURE BACKGROUND
C
0008          DO 100 I=1,JILL
0009            5 FORMAT(2A4,I6,I5,F5.1,F6.1,F9.2,1X,2A4,I6,I5,F6.2)
0010        100 READ(5,5,END=1100)DATE(I),ID(I),KWNT(I),TIME(I),TEMP(I),P(I),TU(I)
             2,DAIT(I),IDAY(I),KUNT(I),THYME(I),DECAY(I)
0011          IF(JUBJUB.EQ.1)GO TO 101
0012          IF(DATE(JILL).EQ.MARG)GO TO 1100
0013        101 DO 200 I=1,JILL
0014          C(I)=KWNT(I)
0015          RATE(I)=C(I)/TIME(I)
0016        200 RSUM=RSUM+RATE(I)
0017          DIV=JILL
0018          RSUM=RSUM/DIV
0019          SDSUM=0.
0020          WEYSUM=0.
0021          DO 300 I=1,JILL
0022          RATDEV(I)=RATE(I)-RSUM
0023          DEVSQ(I)=RATDEV(I)**2
0024          WEYFAC(I)=KWNT(I)/1000.
0025          SDBG(I)=WEYFAC(I)*DEVSQ(I)
0026          SDSUM=SDSUM+SDBG(I)
0027        300 WEYSUM=WEYSUM+WEYFAC(I)
0028          SIGBG=SQRT(SDSUM/WEYSUM)
```

```
C
C       PRINT BACKGROUND DATA
C
0029          PRINT 10
0030          PRINT 20,(DATE(I),ID(I),KWNT(I),TIME(I),RATE(I),RSUM,RATDEV(I),DEV
             2SQ(I),WEYFAC(I),SDBG(I),I=1,JILL)
0031          PRINT 30,RSUM,SIGBG
0032       10 FORMAT('1',6(/),10X,'  DATE      COUNTS   TIME    RATE       AVG
             2R-AVG    DEVSQ    N/1000   WDEVSQ')
0033       30 FORMAT(/,10X,'BACKGROUND= ',F8.4,' +OR-',F8.4,' CPM')
C
C       FIGURE EFFECTIVE VOLUME
0034       20 FORMAT(10X,75('*'),6(/,10X,2A4,2X,I7,3X,I5,1X,F8.4,1X,5(F8.4)))
C
0035          EVSUM=0.
0036          DO 400 I=1,JILL
0037          AK=KUNT(I)
0038          CNTDEV(I)=SQRT(AK)/THYME(I)
0039          CK(I)=KUNT(I)
0040          RATE(I)=CK(I)/THYME(I)
0041          RSD(I)=RATE(I)-RSUM
0042          DUBDEV(I)=SQRT((CNTDEV(I)**2)+SIGBG**2)
0043          TEMPRS(I)=(TEMP(I)+273.16)/P(I)
0044          WDECAY(I)=(481.000*TEMPRS(I))/((TU(I)*EXP(-DECAY(I)/212)))
0045          EV(I)=RSD(I)*WDECAY(I)
0046          SIGEV(I)=DUBDEV(I)*WDECAY(I)
0047      400 EVSUM=EVSUM+EV(I)
0048          EVFINI=0.
0049          EVSUM=EVSUM/DIV
0050          DO 500 I=1,JILL
0051          DIFF(I)=EV(I)-EVSUM
0052          DIFFSQ(I)=DIFF(I)**2
0053      500 EVFINI=EVFINI+DIFFSQ(I)
0054          EVFINI=SQRT(EVFINI/(JILL-1))
C
C       PRINT EFFECTIVE VOLUME DATA
C
0055          PRINT 40
0056          PRINT 50,(DAIT(I),IDAY(I),KUNT(I),THYME(I),RATE(I),CNTDEV(I),RSD(I
             2),DUBDEV(I),TEMPRS(I),WDECAY(I),EV(I),SIGEV(I),EVSUM,DIFF(I),DIFFS
             3Q(I),I=1,JILL)
0057          PRINT 60,EVSUM,EVFINI
0058       40 FORMAT(///,1X,'  DATE      COUNTS TIME    RATE      SD      R-BG     S
             2D&SDBG    A         B      EV( )SIGMA EV    AVG EV EV-AVGEV DIFFSQ')
0059       50 FORMAT(1X,112('*'),6(/,1X,2A4,I8,I5,3X,11(F8.4)))
0060       60 FORMAT(/,1X,'EFFECTIVE VOLUME=',F8.4,' +OR-',F8.4,' LITERS')
C
C       READ & COMPUTE TU'S FROM COMPUTED EV & BG
C
0061          READ(5,2000,END=1100)NUMB
0062       2000 FORMAT(I2)
0063          IF(NUMB.EQ.0)GO TO 80
0064          PRINT 2100
```

```
0065        2100 FORMAT(6(/),2X,
                2 'SAMPLE#   DATE   COUNT TIME     RATE       SD      R-BG  SD&'
                2 'SDBG  R-BG/EV( )R-BG/EV TU +OR- SGMATU PICI/ML +OR- SGPICI/ML'
                2 ,/,2X,118('*'))
0066             DO 2400 I=1,NUMB
0067             READ(5,2200,END=1100)MARK1,MARK2,KOWNT,TYEM,ANN,ATEMP,PRESS,DAYT1,
                2 DAYT2
0068        2200 FORMAT(A4,A2,I7,I5,F7.2,F5.2,F5.1,1X,2A4)
0069             AA=KOWNT
0070             TYM=TYEM
0071             RAIT=AA/TYM
0072             SDRATE=SQRT(AA)/(TYM)
0073             ALOWA=SQRT((SDRATE**2)+(SIGBG**2))
0074             A=RAIT-RSUM
0075             B=EVSUM
0076             BOX1=A/B
0077             SGBOX1=(1./B**2)*SQRT(((ALOWA*B)**2)+(EVFINI*A)**2)
0078             STU=BOX1*481.000*EXP(ANN/212.)*(273.16+ATEMP)/PRESS
0079             SIGTU=STU*SGBOX1/BOX1
0080             CI=STU*3.237E-03
0081             SIGCI=SIGTU*3.237E-03
0082        2400 PRINT 2500,MARK1,MARK2,DAYT1,DAYT2,
                2                    KOWNT,TYEM,RAIT,SDRATE,A,ALOWA,BOX1,SGBOX1,
                3 STU,SIGTU,CI,SIGCI
0083        2500 FORMAT(2X,A4,A2,2X,2A4,1X,I5,1X,I4,2X,
                &                              F8.4,2X,F6.4,1X,F8.4,1X,F6.4,2X,
                2 2F8.4,1X,F8.1,1X,F6.1,2(2X,F9.3))
                C
                C      SHIFT ARRAYS FOR NEW BG & EV COMPUTATION
                C
0084           80 RSUM=0.
0085              DO 600 I=2,JILL
0086              DATE(I-1)=DATE(I)
0087              KWNT(I-1)=KWNT(I)
0088              TIME(I-1)=TIME(I)
0089              TEMP(I-1)=TEMP(I)
0090              P(I-1)=P(I)
0091              TU(I-1)=TU(I)
0092              DAIT(I-1)=DAIT(I)
0093              KUNT(I-1)=KUNT(I)
0094              THYME(I-1)=THYME(I)
0095              IDAY(I-1)=IDAY(I)
0096              ID(I-1)=ID(I)
0097          600 DECAY(I-1)=DECAY(I)
                C
                C      CHECKS FOR END OF DATA
                C
0098              IF(JUBJUB.EQ.1)GO TO 1200
```

```
0099                GO TO 100
0100          1100  JILL=I
0101                JUBJUB=1
0102                DOOM=1.
0103          1200  IF(JILL.LT.3)STOP 2
0104                JILL=JILL-1
0105                GO TO 101
0106          1300  STOP
0107                END

   TOTAL MEMORY REQUIREMENTS 001158 BYTES

COMPILER HIGHEST SEVERITY CODE WAS  0
// EXEC LNKEDT
```

DATE	COUNTS	TIME	RATE	AVG	R-AVG	DEVSQ	N/1000	WDEVSQ
18/10/68	8007	3112	2.5729	2.3837	0.1892	0.0358	8.0070	0.2867
29/10/68	4635	1973	2.3492	2.3837	-0.0345	0.0012	4.6350	0.0055
16/11/68	5425	2166	2.5046	2.3837	0.1209	0.0146	5.4250	0.0793
29/11/68	12290	5830	2.1081	2.3837	-0.2756	0.0760	12.2900	0.9338

BACKGROUND= 2.3837 +OR- 0.2074 CPM

DATE	COUNTS	TIME	RATE	SD	R-BG	SD&SDBG	A	B	EV( )SIGMA EV	AVG EV	EV-AVGEV	DIFFSQ
17/10/68	37750	448	84.2634	0.4337	81.8797	0.4807	1.4309	0.0122	0.9960	0.0058	0.9984	-0.0024	0.0000
01/11/68	15523	173	89.7283	0.7202	87.3446	0.7494	1.4383	0.0114	0.9968	0.0086	0.9984	-0.0015	0.0000
18/11/68	50592	610	82.9377	0.3687	80.5540	0.4230	1.4208	0.0121	0.9777	0.0051	0.9984	-0.0207	0.0004
03/12/68	15009	174	86.2586	0.7041	83.8749	0.7340	1.4244	0.0122	1.0230	0.0090	0.9984	0.0246	0.0006

EFFECTIVE VOLUME= 0.9984 +OR- 0.0186 LITERS

SAMPLE#	DATE	COUNT	TIME	RATE	SD	R-BG	SD&SDBG	R-BG/EV( )R-BG/EV	TU	+OR-	SGMATU	PICI/ML	+OR-	SGPICI/ML
1245A+	04/11/68	22783	139	163.9065	1.0859	161.5228	1.1055	161.7860	3.2146	115479.9	2294.5	373.808		7.427
1245AC	04/11/68	91918	668	137.6018	0.4539	135.2181	0.4990	135.4384	2.5753	96635.2	1837.5	312.808		5.948
1245A'	05/11/68	19234	140	137.3857	0.9906	135.0020	1.0121	135.2220	2.7184	97242.0	1954.9	314.772		6.328
1245A-	05/11/68	79434	666	119.2703	0.4232	116.8866	0.4713	117.0770	2.2343	83149.6	1586.8	269.155		5.137
1245BC	06/11/68	19755	142	139.1197	0.9898	136.7360	1.0113	136.9588	2.7482	98133.4	1969.1	317.658		6.374
1245B-	06/11/68	89064	664	134.1325	0.4495	131.7488	0.4950	131.9635	2.5110	94060.4	1789.8	304.474		5.793
1245C+	08/11/68	29643	214	138.5187	0.8045	136.1350	0.8308	136.3568	2.6762	97906.2	1921.5	316.922		6.220
1245B+	09/11/68	*****	900	127.5533	0.3765	125.1696	0.4298	125.3736	2.3779	98775.9	1873.5	319.737		6.064
1245D-	13/11/68	15021	115	130.6174	1.0657	128.2337	1.0857	128.4426	2.6311	92892.7	1902.9	300.694		6.160
1245DC	13/11/68	77897	596	130.6997	0.4683	128.3159	0.5121	128.5250	2.4517	92811.9	1770.4	300.432		5.731
1245B+	14/11/68	25798	182	141.7472	0.8825	139.3635	0.9065	139.5906	2.7576	100159.7	1978.7	324.217		6.405
1245D+	14/11/68	29239	223	131.1166	0.7668	128.7329	0.7943	128.9426	2.5334	92297.2	1813.4	298.766		5.870

DATE	COUNTS	TIME	RATE	AVG	R-AVG	DEVSQ	N/1000	WDEVSQ
29/10/68	4635	1973	2.3492	2.2240	0.1252	0.0157	4.6350	0.0727
16/11/68	5425	2166	2.5046	2.2240	0.2806	0.0788	5.4250	0.4272
29/11/68	12290	5830	2.1081	2.2240	-0.1159	0.0134	12.2900	0.1652
14/12/68	4810	2487	1.9341	2.2240	-0.2899	0.0841	4.8100	0.4043

BACKGROUND= 2.2240 +OR- 0.1984 CPM

DATE	COUNTS	TIME	RATE	SD	R-BG	SD&SDBG	A	B	EV( )	SIGMA EV	AVG EV	EV-AVGEV	DIFFSQ
01/11/68	15523	173	89.7283	0.7202	87.5043	0.7470	1.4383	0.0114	0.9987	0.0085	1.0006	-0.0020	0.0000
18/11/68	50592	610	82.9377	0.3687	80.7137	0.4187	1.4208	0.0121	0.9796	0.0051	1.0006	-0.0210	0.0004
03/12/68	15009	174	86.2586	0.7041	84.0346	0.7315	1.4244	0.0122	1.0249	0.0089	1.0006	0.0243	0.0006
16/12/68	15178	181	83.8563	0.6807	81.6323	0.7090	1.4267	0.0122	0.9993	0.0087	1.0006	-0.0013	0.0000

EFFECTIVE VOLUME= 1.0006 +OR- 0.0186 LITERS

SAMPLE#	DATE	COUNT	TIME	RATE	SD	R-BG	SD&SDBG	R-BG/EV( )	R-BG/EV	TU +OR-	SGMATU	PICI/ML +OR-	SGPICI/ML
1245C-	18/11/68	19190	140	137.0714	0.9895	134.8474	1.0092	134.7630	2.6986	96703.4	1936.5	313.029	6.268
1245CC	21/11/68	22449	164	136.8841	0.9136	134.6601	0.9349	134.5758	2.6685	96111.4	1905.8	311.112	6.169
1245EC	21/11/68	80224	648	123.8025	0.4371	121.5785	0.4800	121.5023	2.3072	86417.4	1641.0	279.733	5.312
1245E+	22/11/68	22020	184	119.6739	0.8065	117.4499	0.8305	117.3764	2.3328	87484.4	1738.7	283.187	5.628
1245E-	27/11/68	17667	141	125.2979	0.9427	123.0739	0.9633	122.9968	2.4791	87944.2	1772.6	284.675	5.738

DATE	COUNTS	TIME	RATE	AVG	R-AVG	DEVSQ	N/1000	WDEVSQ
16/11/68	5425	2166	2.5046	2.0908	0.4138	0.1713	5.4250	0.9291
29/11/68	12290	5830	2.1081	2.0908	0.0173	0.0003	12.2900	0.0037
14/12/68	4810	2487	1.9341	2.0908	-0.1567	0.0246	4.8100	0.1181
02/01/69	10306	5674	1.8164	2.0908	-0.2744	0.0753	10.3060	0.7761

BACKGROUND= 2.0908 +OR- 0.2359 CPM

DATE	COUNTS	TIME	RATE	SD	R-BG	SD&SDBG	A	B	EV( )SIGMA EV	AVG EV	EV-AVGEV	DIFFSQ
18/11/68	50592	610	82.9377	0.3687	80.8469	0.4377	1.4208	0.0121	0.9812 0.0053	1.0009	-0.0197	0.0004
03/12/68	15009	174	86.2586	0.7041	84.1678	0.7426	1.4244	0.0122	1.0265 0.0091	1.0009	0.0256	0.0007
16/12/68	15178	181	83.8563	0.6807	81.7656	0.7204	1.4267	0.0122	1.0009 0.0088	1.0009	0.0000	0.0000
06/01/69	15190	182	83.4615	0.6772	81.3708	0.7171	1.4208	0.0122	0.9950 0.0088	1.0009	-0.0059	0.0000

EFFECTIVE VOLUME= 1.0009 +OR- 0.0190 LITERS

SAMPLE#	DATE	COUNT	TIME	RATE	SD	R-BG	SD&SDBG	R-BG/EV( )	R-BG/EV	TU +OR-	SGMATU	PICI/ML	+OR-	SGPICI/ML
1257A+	11/12/68	35202	120	293.3499	1.5635	291.2590	1.5812	290.9856	5.7323	207833.5	4094.2	672.757		13.253
1257A-	10/12/68	10227	335	30.5284	0.3019	28.4376	0.3831	28.4109	0.6603	20231.2	470.2	65.489		1.522
1257AC	09/12/68	10661	220	48.4591	0.4693	46.3683	0.5253	46.3248	1.0222	33263.0	734.0	107.672		2.376
1257A'	09/12/68	16019	168	95.3512	0.7534	93.2604	0.7894	93.1729	1.9327	65296.4	1354.4	211.365		4.384
1257A'	09/12/68	16019	168	95.3512	0.7534	93.2604	0.7894	93.1729	1.9327	64192.6	1331.5	207.791		4.310
1245EC	05/12/68	69987	601	116.4509	0.4402	114.3601	0.4994	114.2528	2.2204	88631.4	1722.4	286.900		5.576
1254F+	05/12/68	23761	176	135.0057	0.8758	132.9149	0.9070	132.7902	2.6729	95304.8	1918.4	308.501		6.210
1254FC	04/12/68	83683	630	132.8302	0.4592	130.7394	0.5162	130.6167	2.5267	92908.7	1797.2	300.745		5.818
1254F-	04/12/68	18174	141	128.8936	0.9561	126.8028	0.9848	126.6838	2.5929	91715.3	1877.2	296.882		6.076

DATE	COUNTS	TIME	RATE	AVG	R-AVG	DEVSQ	N/1000	WDEVSQ
29/11/68	12290	5830	2.1081	1.9338	0.1743	0.0304	12.2900	0.3733
14/12/68	4810	2487	1.9341	1.9338	0.0003	0.0000	4.8100	0.0000
02/01/69	10306	5674	1.8164	1.9338	-0.1174	0.0138	10.3060	0.1421
15/01/69	4305	2294	1.8766	1.9338	-0.0571	0.0033	4.3050	0.0141

BACKGROUND= 1.9338 +OR- 0.1292 CPM

DATE	COUNTS	TIME	RATE	SD	R-BG	SD&SDBG	A	B	EV( )SIGMA EV	AVG EV	EV-AVGEV	DIFFSQ
03/12/68	15009	174	86.2586	0.7041	84.3248	0.7158	1.4244	0.0122	1.0284 0.0087	1.0146	0.0138	0.0002
16/12/68	15178	181	83.8563	0.6807	81.9226	0.6928	1.4267	0.0122	1.0029 0.0085	1.0146	-0.0117	0.0001
06/01/69	15190	182	83.4615	0.6772	81.5278	0.6894	1.4208	0.0122	0.9970 0.0084	1.0146	-0.0176	0.0003
20/01/69	18104	212	85.3962	0.6347	83.4624	0.6477	1.4308	0.0123	1.0301 0.0080	1.0146	0.0155	0.0002

EFFECTIVE VOLUME= 1.0146 +OR- 0.0171 LITERS

SAMPLE#	DATE	COUNT	TIME	RATE	.SD	R-BG	SD&SDBG	R-BG/EV( )	R-BG/EV TU	+OR- SGMATU	PICI/ML	+OR- SGPICI/ML
1195	16/12/68	53083	142	373.8237	1.6225	371.8899	1.6277	366.5393	6.3953	273539.5 4772.6	885.447	15.449
1257B'	17/12/68	24539	169	145.2012	0.9269	143.2674	0.9359	141.2062	2.5571	98030.2 1775.2	317.324	5.746
1257BC	17/12/68	18984	141	134.6383	0.9772	132.7045	0.9857	130.7953	2.4133	94928.8 1751.5	307.284	5.670
1257B-	18/12/68	19441	144	135.0069	0.9683	133.0732	0.9769	131.1586	2.4154	94880.0 1747.3	307.126	5.656
1257B+	18/12/68	18875	135	139.8148	1.0177	137.8810	1.0258	135.8973	2.5081	96549.1 1781.9	312.529	5.768
1254G-	19/12/68	18256	135	135.2296	1.0008	133.2959	1.0092	131.3781	2.4317	93594.0 1732.3	302.964	5.608
1254GC	19/12/68	18892	141	133.9858	0.9748	132.0520	0.9833	130.1522	2.4024	92804.4 1713.0	300.408	5.545

DATE	COUNTS	TIME	RATE	AVG	R-AVG	DEVSQ	N/1000	WDEVSQ
14/12/68	4810	2487	1.9341	1.9231	0.0109	0.0001	4.8100	0.0006
02/01/69	10306	5674	1.8164	1.9231	-0.1068	0.0114	10.3060	0.1175
15/01/69	4305	2294	1.8766	1.9231	-0.0465	0.0022	4.3050	0.0093
31/01/69	9784	4737	2.0654	1.9231	0.1423	0.0203	9.7840	0.1982

BACKGROUND= 1.9231 +OR- 0.1056 CPM

DATE	COUNTS	TIME	RATE	SD	R-BG	SD&SDBG	A	B	EV( )SIGMA EV	AVG EV	EV-AVGEV	DIFFSQ
16/12/68	15178	181	83.8563	0.6807	81.9332	0.6888	1.4267	0.0122	1.0030	0.0084	1.0019	0.0011	0.0000
06/01/69	15190	182	83.4615	0.6772	81.5384	0.6854	1.4208	0.0122	0.9971	0.0084	1.0019	-0.0048	0.0000
20/01/69	18104	212	85.3962	0.6347	83.4731	0.6434	1.4308	0.0123	1.0302	0.0079	1.0019	0.0283	0.0008
02/02/69	42955	620	69.2823	0.3343	67.3591	0.3506	1.6789	0.0145	0.9773	0.0051	1.0019	-0.0246	0.0006

EFFECTIVE VOLUME= 1.0019 +OR- 0.0218 LITERS

SAMPLE#	DATE	COUNT	TIME	RATE	SD	R-BG	SD&SDBG	R-BG/EV( )	R-BG/EV TU	+OR-	SGMATU	PICI/ML	+OR-	SGPICI/ML
1195	05/01/69	47536	120	396.1333	1.8169	394.2100	1.8200	393.4546	8.7658	277428.0	6180.9	898.034		20.007
1195	05/01/69	*****	315	393.1238	1.1171	391.2004	1.1221	390.4507	8.5835	279636.9	6147.4	905.185		19.899
1257C'	07/01/69	20005	172	116.3081	0.8223	114.3850	0.8291	114.1658	2.6223	81392.7	1869.5	263.468		6.052
1257C+	09/01/69	20206	175	115.4628	0.8123	113.5397	0.8191	116.7674	2.6551	81361.1	1850.0	263.366		5.989
1257C-	09/01/69	25402	223	113.9103	0.7147	111.9872	0.7225	111.7726	2.5406	80390.7	1827.3	260.225		5.915

This thesis is accepted on behalf of the faculty of the Institute by the following committee:

Charles B. Holmes

C. E. Jacob

Frank Wolfgang Gross

L. R. Hathaway

Date: May 27, 69