DP - 470

Stable Isotope Separation

AEC Research and Development Report

RECOVERY OF DEGRADED HEAVY WATER AT THE SAVANNAH RIVER PLANT

Separations Technology Section
Works Technical Department
Savannah River Plant

July 1960

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Works Technical Department
Savannah River Plant

ABSTRACT

Information is presented on purification and reconcentration of heavy water at the Savannah River Plant. Process and equipment descriptions, typical operating costs, procedures for control of health hazards, standard analytical methods, and specifications for receipt of degraded heavy water for recovery at the Savannah River Plant are included.

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RECOVERY OF DEGRADED HEAVY WATER AT THE SAVANNAH RIVER PLANT

INTRODUCTION

Use of heavy water as a moderator for nuclear reactors generally results in degradation of the isotopic and chemical purity of the heavy water over a period of time. The isotopic purity of the heavy water in the reactor declines through inleakage of light water; heavy water drained or leaking from the system will usually be degraded both by light water and by chemical impurities.

Facilities installed at the Savannah River Plant (SRP) for purification of degraded heavy water provide for removal of light water by fractional distillation and for removal of chemical impurities by total distillation and by ion exchange. These facilities are typical of recovery equipment that might be installed in association with nuclear power reactors, but they do not represent the only design of equipment for recovery of heavy water. In some cases equipment that was designed for another function was adapted for heavy water recovery. More economic operation might have been obtained if the equipment had been designed originally for the specific function now being served.

Although these recovery facilities must render primary service to the reactors at SRP, heavy water degraded at other locations can be processed in selected portions of this equipment provided the material meets certain specifications. Arrangements for processing degraded heavy water are handled by direct negotiation with the Savannah River Operations Office of the Atomic Energy Commission, Savannah River Plant, Aiken, S. C.

SUMMARY

This report presents the following information on the recovery and purification of heavy water at the Savannah River Plant.

Descriptions of the processes and equipment used at SRP for reconcentration and purification of degraded heavy water.

Typical investment and operating costs for this recovery equipment.

Control of health hazards associated with tritium oxide in degraded heavy water.

Specifications and limitations for recovery at SRP of heavy water degraded at other locations.

Standard analytical methods to ensure that these specifications are met.

Methods of minimizing the degradation of heavy water are not covered by this report. Such preventive measures are inherently related to the design of a particular reactor and, as such, are beyond the scope of this report. The degradation rates are included merely for perspective, since these rates are specific only for reactors of a design similar to those in use at the Savannah River Plant.

DISCUSSION

A. RECONCENTRATION

Light water is eliminated from degraded heavy water at the Savannah River Plant by fractional distillation under vacuum. The tritium oxide generated in the moderator by nuclear reaction is not effectively separated from deuterium oxide by distillation, and no attempt is made to do so. Thus, tritium oxide follows the deuterium oxide throughout the recovery operations at essentially the ratio generated in the reactors. As a result, protection against health hazards associated with tritium was carefully designed into the facilities and the operating procedures. The control of health hazards is discussed in the section on Health Hazards Control.

The distillation facilities take advantage of the favorable equilibrium conditions for separating light water from heavy water that exist at pressures in the range of 60 to 300 mm Hg. Even so, the expenditure of energy required to effect the separation is quite large when compared with that required for the more common separation of chemically different compounds. Thus, it behooves the designer of facilities for heavy water distillation to minimize gas phase pressure drop wherever possible in order to avoid the large decrease in the separation factor that an increase in pressure produces. Further aspects of design and process theory are discussed briefly in Section A,3.

Separate distillation units are provided to perform two distinctly different functions. Light water is eliminated directly from the moderator circulating in the SRP reactors by distillation units installed at each of the five reactor sites. Distillate withdrawn from the top of these reactor-integrated units is then separated into a reusable product stream and a lean discard stream by processing through a distillation unit located in the heavy water manufacturing area. This separate Rework Unit also processes the leaks, spills, and drains collected in the reactor areas and degraded heavy water received from off-Plant customers.

1. PROCESS DESCRIPTION OF REACTOR-INTEGRATED EQUIPMENT(3)

Moderator is withdrawn from the reactor at a rate of about 5 to 7 gpm and fed through a vaporizer to the base of the first of two fractionating towers. Liquid flowing from the bottom plate of the first tower, countercurrent to the vapor feed, is returned, after cooling, to the reactor through an ion exchange system. Each tower is operated at a top pressure of 100 mm Hg and at a boilup rate of 3000 to 4000 pounds per hour. The pressure drop through each tower is about 200 mm Hg.

The schematic flow diagram in Figure 1 illustrates how the second tower is coupled to the first tower. The two towers constitute one large tower that has been divided in half for structural simplicity. Vapor from the first tower is condensed and fed as a liquid to the base of the second tower; this avoids a large difference in pressure from the base of the first tower to the top of the second, which would exist if the towers were coupled by flow of vapor. Thus, the top of each tower is maintained at a controlled vacuum, a high pressure at the base of the first tower is avoided, and a more favorable separation factor prevails throughout the first tower.

Distillate, at a concentration of about 90 mol % D_2O, is withdrawn from the top of the second tower at a rate of about 1-1/2 pounds per hour. This material is shipped to the heavy water manufacturing area for further processing in the separate Rework Unit.

The general method of calculation described in Section A,3 was used to define the operating characteristics of the reactor-integrated units. The characteristics are illustrated graphically in Figure 2, where the overhead distillate concentration in mol % H_2O is expressed as a function of the reactor moderator concentration in mol % H_2O at several distillate rates represented by the solid lines. The dashed lines correspond to conditions of constant rate of H_2O elimination from the reactor or inleakage into the reactor at steady state.

A detailed description of reactor-integrated equipment is presented in Appendix II, and additional process and equipment details are given in Reference 3.

2. PROCESS DESCRIPTION OF REWORK UNIT

The original design for SRP operation called for recovery of the distillate from the reactor-integrated units by direct injection at a suitable point in the heavy water manufacturing process. This method of operation was discontinued to avoid introducing tritium into the virgin product issuing from the manufacturing facility. To prevent such cross-contamination, three vacuum distillation towers were isolated from the manufacturing area and repiped to provide a separate recovery facility.

These three towers constitute one large tower from a process standpoint. The three towers are coupled with liquid streams here again, to avoid an unfavorable separation factor at the rich end as discussed in Section A,1.

A schematic flow diagram of the Rework Unit is shown in Figure 3.

Each tower is operated at a boilup of about 3000 pph. The pressure at the top of each tower is controlled at about 80 mm Hg. The pressure drop through each tower is about 200 mm Hg.

Four storage tanks are piped to the unit to permit flexible use as feed tanks, distillate-receiving tanks, or bottoms-receiving tanks. Two of the storage tanks have a capacity of 1600 gallons, one has a capacity of 3500 gallons, and one has a capacity of 9000 gallons. Each tower can be fed at four points, including direct feed to the top. Distillate can be withdrawn from the top of the lean tower, and product from the base of the rich tower, into drums or into any one of the four storage tanks.

In general, a separate recovery facility must operate over a wide range of concentrations, producing at one end of the process a stream rich in D_2O that may be returned directly to the reactors and discharging at the other end a stream low enough in D_2O to be discarded economically as waste. The Rework Unit at SRP produces a product stream at 99.5 mol % D_2O and a discard stream at 2.5 mol % D_2O.

Even at total reflux, the three towers of the Rework Unit cannot span the wide concentration range from 2.5 to 99.5 mol % D_2O in once-through operation. In order to span this range, the Rework Unit is operated alternately on a "product campaign", covering the concentration range from 75 to 99.5 mol % D_2O, and on a "waste campaign", covering the concentration range from 2.5 to 88 mol % D_2O. In addition to the feed accumulated in the reactor areas, each campaign must process a recycled stream from the other campaign, as illustrated in Figure 4. Thus, each pound of degraded heavy water introduced as initial feed to the Rework Unit generates a definite quantity of recycled feed that must be processed in subsequent product and waste campaigns.

In theory, the initial feed will generate an infinite number of separate recycle streams that will gradually diminish in size from one campaign to the next. Such a system is mathematically described by an infinite converging series with a finite value for the total weight of recycle feed generated for each of the two series of campaigns. In practice, this total weight of recycle feed must be processed during the period of time in which the initial feed is accumulated and fed; otherwise, the inventory of degraded moderator in process will not remain constant.

Figure 5 presents the amount of recycle feed for the product and the waste campaigns generated by one pound of initial feed as a function of the initial feed concentration. The data presented are based on the terminal campaign concentrations set forth above.

The optimum discard concentration as well as the optimum intermediate campaign concentrations will vary as a function of the load imposed on the Rework Unit. Therefore, the operating characteristics of the unit are best described by the general performance of the three towers at various feed concentrations for several terminal conditions. These characteristics were calculated with the general method outlined in Section A,3 and are presented in the seven graphs of Figure 6. Each curve in each of the seven graphs is drawn through four calculated data points at feed rates corresponding to 0, 75,000, 150,000, and 300,000 pounds of pure D_2O per year.

A detailed description of Rework Unit equipment is presented in Appendix III.

3. REVIEW OF THEORY AND CALCULATIONS

No attempt will be made here to give an exhaustive treatment of the theory of heavy water distillation. This is covered adequately in References 4 and 5. A brief review, however, may be relevant to a better understanding of this report. A few of the pertinent physical properties of heavy water are presented in Appendix I.

Reference 4 states, "any water which contains both hydrogen and deuterium contains three compounds, H_2O, HDO, and D_2O, existing together in equilibrium concentration. The equilibrium is established very rapidly; so rapidly that for practical purposes all such mixtures can be considered at equilibrium. At low concentrations of deuterium there are present H_2O and HDO, but very little D_2O; and similarly, at high concentrations of deuterium there are present D_2O and HDO, but very little H_2O. Only near the middle of the range are both H_2O and D_2O present in appreciable amounts. The effective separation factor for distillation, therefore, is the relative volatility of H_2O and HDO in the low range, and the relative volatility of HDO and D_2O in the high range. For practical purposes these are identical.

"In design calculations one may take the numerical value for the relative volatility of H_2O and HDO, and apply it over the entire range of concentration, on the basis of a two-component system. The assumption of a two-component system results in a slight overdesign near the midpoint of the concentration range where three components (H_2O, HDO, and D_2O) are actually present in appreciable amounts. The difference is not of practical significance.

"In setting up calculations for the two-component system, it is usual to express the entire deuterium content as mol % D_2O and the entire hydrogen content as mol % H_2O, and all figures herein quoted are on that basis. This is simply a matter of convenience; the relative volatility data take proper account of the fact that HDO is actually a major component of the system.

"Raoult's law, which states that the vapor pressure of each component of a solution is proportional to the mol fraction of that component present in the solution, is applicable to the water system. Under conditions of equilibrium, therefore, the vapor composition is related to the liquid composition by the following formula.

$$\alpha = \frac{y(1-x)}{x(1-y)}$$

where

α = relative volatility*

x = mol fraction of more volatile component in the liquid

y = mol fraction of more volatile component in the vapor

"The relative volatility of the water isotopes varies significantly with temperature, and consequently varies with the pressure prevailing in the distillation equipment."

With equilibrium data established as described above and with operating lines established by material balance, calculations can then be made in the usual plate-by-plate method of stepwise calculation. A different α is calculated for each plate in accordance with the linear pressure gradient down the tower. Calculation of the operating characteristics of existing units at SRP has been facilitated by use of an IBM 650 card-programmed computer.

In the case of the Rework Unit, with midpoint feed, the calculation was made by trial and error. Computer runs were made at several assumed distillate concentrations for the same feed rate, feed concentration, and base concentration. Under these conditions stepwise calculations were started at the rich end of the system. A final answer was obtained when the assumed distillate concentration matched the calculated distillate concentration on the top theoretical plate of the unit. This was simplified by plotting the results from a limited number of runs to determine the "match" concentration.

In the case of the reactor-integrated units, with feed addition and product drawoff at the base of the tower, the calculation does not need to be by trial and error if the stepwise procedure is initiated for conditions at the top of the lean tower.

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*Note particularly that this is the relative volatility of H_2O to HDO even though concentrations are expressed on the basis outlined above. The errors introduced by this simplification are described in mathematical terms on pp. 413-415 of Reference 5.

Operating tests indicate that the Rework Unit contains about 50 theoretical plates per tower and that the reactor-integrated units contain about 56 theoretical plates per tower. Thus, a plate efficiency of 70% can be assumed for design calculations for bubble-cap plates installed and operated as at SRP. For sieve plates installed and operated as at SRP, a plate efficiency of about 60 to 65% can be assumed.

4. CHARGE FOR RECOVERING HEAVY WATER

The charge for reconcentrating a specific quantity of heavy water in the Rework Unit at SRP is a function of the concentration of the material. In addition, a charge must be made for purifying heavy water if the total solids content is greater than 100 ppm.

The approximate charge schedule shown in the following table illustrates the general relationship between charge and concentration. It is included here for use only in making order-of-magnitude studies of power reactor economics and should not be construed as the actual charge that will be made for processing degraded heavy water. Actual charges should be obtained from the Atomic Energy Commission, Savannah River Operations Office, Aiken, S.C. The charges presented in the following table are based on returning one pound of D_2O to the customer for every pound of D_2O received at SRP.

Approximate Charge for Reconcentrating Degraded Heavy Water

Degraded Concentration, wt % D_2O	Reconcentration Charge, dollars per pound D_2O received
10	15.00
20	10.00
30	7.50
40	6.00
50	5.00
60	4.20
70	3.50
80	2.80
90	2.10
95	1.60
99	0.70

B. PURIFICATION

Degraded heavy water normally contains enough radioactive impurities to cause a handling problem. Such impurities must be removed before the heavy water can be fed to the Rework Unit for reconcentration. The method of purification that is used at SRP depends primarily upon the level of radioactivity from the impurities.

Degraded heavy water that accumulates from SRP sources and that exceeds the radioactivity specification for feed to the Rework Unit is purified in the reactor areas in facilities that are not available for use with off-Plant heavy water. The pertinent specifications, as given in Section E, are 10^{-4} microcurie of beta-gamma activity per ml and 5×10^{-6} microcurie of alpha activity per ml. Both measurements are made on the activity of the dry residue left by evaporation, and thus do not include tritium activity. In practice to date, the beta-gamma specification has always been exceeded before the alpha specification.

These purification facilities for SRP moderator consist of an ion exchange column and a remotely operated evaporator. Neither facility can be used to process degraded material received from off-Plant customers, because of limited capacity and the possibility of cross-contaminating the SRP reactors with trace quantities of undesirable, unexpected elements.

Degraded heavy water that meets the previously cited specifications can be processed in a natural recirculation evaporator located in the heavy water manufacturing area. This facility is used to purify heavy water received from off-Plant sources.

1. HIGH ACTIVITY HEAVY WATER (SRP MODERATOR ONLY)

β-γ activity $>10^{-4}$ μc/ml or α activity $>5 \times 10^{-6}$ μc/ml

a. Ion Exchange

Degraded heavy water with a content of beta-gamma activity between 1×10^{-4} and 4×10^{-4} microcurie per ml is purified in an ion exchange column. This column contains 150 pounds of mixed resin, equal weights IR-120 cation resin* and IRA-400 anion resin*. Each charge of resin is capable of reducing the dissolved solids content of 35,000 pounds of degraded heavy water from 100 ppm to less than 10 ppm. About 85 pounds of degraded heavy water is held in the hydrated resin and is not recovered when the depleted resin is replaced. No attempt is made to regenerate the depleted resin because of the radiation hazard associated with regeneration.

A schematic flow diagram of the ion exchange column and associated equipment is shown in Figure 7.

Typical operating costs for the ion exchange column are presented on the following page.

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*Rohm and Haas Company, Philadelphia, Pa.

Operating Cost of Ion Exchange Column

Basis: Annual processing rate of 50,000 pounds of degraded heavy water at an average content of ionic impurities of 200 ppm and a D_2O concentration of 99.5 mol %.

Item	Dollars per Year
Operating labor	$1500
Maintenance and power	2200
Material*	5700
Depreciation	200
Total	$9600

---

*For resin and unrecovered D_2O in discharged resin. The resin cost is $0.57 per pound of cation resin and $1.66 per pound of anion resin. The D_2O lost with the discharged resin is valued at $24 per pound.

b. Remotely Operated Evaporator

Degraded heavy water having a beta-gamma activity higher than 4×10^{-4} microcurie per ml by planchet is processed in a remotely operated tank evaporator. Heavy water is charged to a stainless steel tank and evaporator by means of steam coils in the tank. Vapor from the tank is passed through a glass fiber de-entrainment section and into a condenser.

2. LOW ACTIVITY HEAVY WATER (SRP AND OFF-PLANT MODERATOR)

β-γ activity $<10^{-4}$ $\mu c/ml$ and α activity $<5 \times 10^{-6}$ $\mu c/ml$

Degraded heavy water with acceptably low levels of radioactivity can be processed in the natural recirculation evaporator described below. This evaporator is located in the heavy water manufacturing area.

The de-entrainment column is 6 inches in diameter and contains three de-entraining trays on a 12-inch tray spacing. These trays, each containing one bubble cap, are normally operated without liquid on the trays. The vapor rate in the column is maintained at about 200 pph during normal operation. The purification factor, defined by the ratio of solids in the calandria to the solids in the condensate, has been a maximum of 130,000 (at end of run). The maximum allowable conductivity of the condensate is set at 20 micromhos per ml.

The components of the evaporator, de-entrainment column, condenser, and associated piping are made of AISI type 316 stainless steel to permit decontamination by refluxing nitric acid, if necessary.

The feed and product pumps are Eastern, single-stage, centrifugal pumps, Model D-11, also made of AISI type 316 stainless steel.

A schematic flow diagram of the evaporator facility is shown in Figure 8.

Typical operating costs of this evaporation facility are given in the following table.

Operating Cost of Evaporator

Basis: Annual processing rate* of 50,000 pounds of degraded heavy water at an average contamination of 200 ppm dissolved solids and a D_2O concentration of 99.5 mol %.

Item	Total Cost
Operating labor	$ 100
Maintenance and power	100
Material (D_2O lost during leaching of evaporator residue, valued at $24.00 per pound)	800
Depreciation	1000
Total	$2000

---

*Maximum processing rate - 1,750,000 pounds per year. The cost per pound decreases appreciably as the rate increases because of the fixed depreciation cost.

C. HEALTH HAZARDS CONTROL

Tritium constitutes a radiation hazard to operating personnel only when it is physically absorbed by the body. When the body is exposed to tritium oxide in air, approximately one-half of the absorption occurs directly in the respiratory tract and the remainder occurs by absorption through the skin.

Protection of operating personnel from tritium hazards is provided in the Rework Unit at SRP by separate ventilation of indoor equipment, continuous monitoring, protective clothing, and routine urinalysis.

The process pumps and process flow control equipment located indoors are separated from similar equipment for new heavy water production by partitions and separate ventilation. The outdoor drum unloading station is isolated by chains with warning signs. Both areas are provided with curbing to confine any leaks or spills that may occur.

The isolated pump room is continuously monitored with a Kanne system* for tritium detection.

Both an Air Activity Monitor (Model SS-2)* and a Vibrating Reed Electrometer** are used to measure the concentration of tritium in air in order to set time limits for personnel exposure.

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* Standard Engineering and Machine Company, Wilmington 8, Del.
**Applied Physics Corp., Pasadena, Calif.

Protective clothing is required in both areas and consists of skull cap, gloves, laboratory coat, and rubber overshoes for simple entry into the area. Maintenance work requires more elaborate clothing as specified by Special Work Permits. Urine samples from each person working in the area are obtained each week and analyzed for tritium.

Similar measures are used for protection of personnel operating the reactor-integrated distillation equipment. In this area, hard radiation from the unshielded equipment must also be taken into account in setting up protective measures.

Sources of hard radiation in degraded heavy water generally are associated with suspended solids, which are filtered from the feed before injection into the distillation equipment. Thus, the distillation equipment at SRP is operated safely without shielding.

Several ground rules are used at SRP to protect personnel from the hazards of tritium exposure. The maximum allowable body burden is 1 millicurie, which corresponds to 20 microcuries per liter of urine sample. On the basis of a biological half life of 10 days, an uptake of 1 millicurie will expose the body to 140 mrem during the period of discharge. The maximum body burden used at SRP is lower than that recommended by the National Committee on Radiation Protection(6) to allow for possible exposure to other forms of radiation.

In actual practice, the tritium uptake of each individual is followed carefully because of the significant variations in biological half life within a group of people. The tritium uptake of each individual is predicted during the week on the basis of the approximate relationship of uptake to exposure given by the following equation,

$$U = 2.5\text{x}10^{6}\ T$$

where U = uptake, microcuries per hour
T = tritium concentration in air, microcuries per cc

At the end of each week, body burden is adjusted to the value obtained by urinalysis as the basis for beginning the new week.

Time limits for working in an area are imposed when the air concentration reaches $5\text{x}10^{-5}$ microcurie per cc. Special respiratory protection is required when the air concentration reaches $1\text{x}10^{-3}$ microcurie per cc. Under these conditions, plastic suits, supplied with breathing air, give complete protection against tritium oxide. Self-contained breathing equipment, alone, doubles the allowable working time but does not give protection against skin absorption.

D. TYPICAL DEGRADATION RATES

The rate of degradation of heavy water moderator in the SRP production reactors has made it necessary to rework annually about 0.1 pound of

D_2O, at a concentration of 84 wt %, per pound of system inventory. Of this total, 0.038 pound of D_2O at 91 wt % was generated as overheads from the reactor-integrated stills and 0.062 pound at 71 wt % was collected from leaks, spills, and drains.

E. SPECIFICATIONS AND LIMITATIONS FOR RECOVERY OF HEAVY WATER AT SRP

1. SPECIFICATIONS FOR RECEIPT OF HEAVY WATER

Degraded heavy water shipped to SRP for recovery must meet the specifications given below. Methods of analysis to be used as standards in verifying that these specifications are met are presented in Appendix VI.

The limited specifications outlined cannot be expected to completely characterize the quality of all shipments of degraded heavy water received at SRP from other locations. Therefore, it is the responsibility of the shipper to advise SRP of any unusual chemical contamination that could cause injury to operating personnel or damage to process equipment. Such information should be transmitted both by letter and by suitable drum labeling.

Specifications for Receipt of Heavy Water at SRP

	Minimum
D_2O concentration[a]	10 wt %
	Maximum
Specific conductivity	4000 micromhos
Turbidity, equivalent SiO_2	1000 ppm
Total solids	5000 ppm
Mercury	0.01 ppm
Chloride	1 ppm
$KMnO_4$ demand	1×10^{-5} g/ml
Oil	Less than continuous film in drum
Gross beta-gamma activity[b]	1×10^{-4} microcurie/ml
Gross alpha activity	5×10^{-6} microcurie/ml
Drum radiation	1 mr/hr[c] at contact with drum

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[a] Reconcentration of heavy water from a concentration of less than 10 wt % D_2O must be handled as a special case. Material cannot be recovered from a concentration of less than 2.5 wt % D_2O unless the total of all types of radioactive contamination is less than 7 microcuries per liter on a 100% D_2O basis.

[b] Excluding tritium activity

[c] 4000 counts per minute by Thyac

2. TRITIUM CONTROL

Tritium is unavoidably generated in the heavy water used to moderate power reactors so some tritium content is to be expected in heavy water received for upgrading in facilities at SRP.

In general, SRP will return to the customer heavy water that contains an amount of tritium equal to, or less than, that received at SRP on a 100% D_2O basis.

3. SPECIFICATIONS FOR SRP HEAVY WATER

SRP will return to the customer heavy water meeting specifications that currently are as follows:

D_2O content	99.75 mol % minimum
Specific conductivity	15 micromhos maximum
$KMnO_4$ demand	1×10^{-5} g/ml D_2O maximum
Color	APHA Standard #5 maximum
Turbidity	Equivalent to 5 ppm SiO_2 maximum

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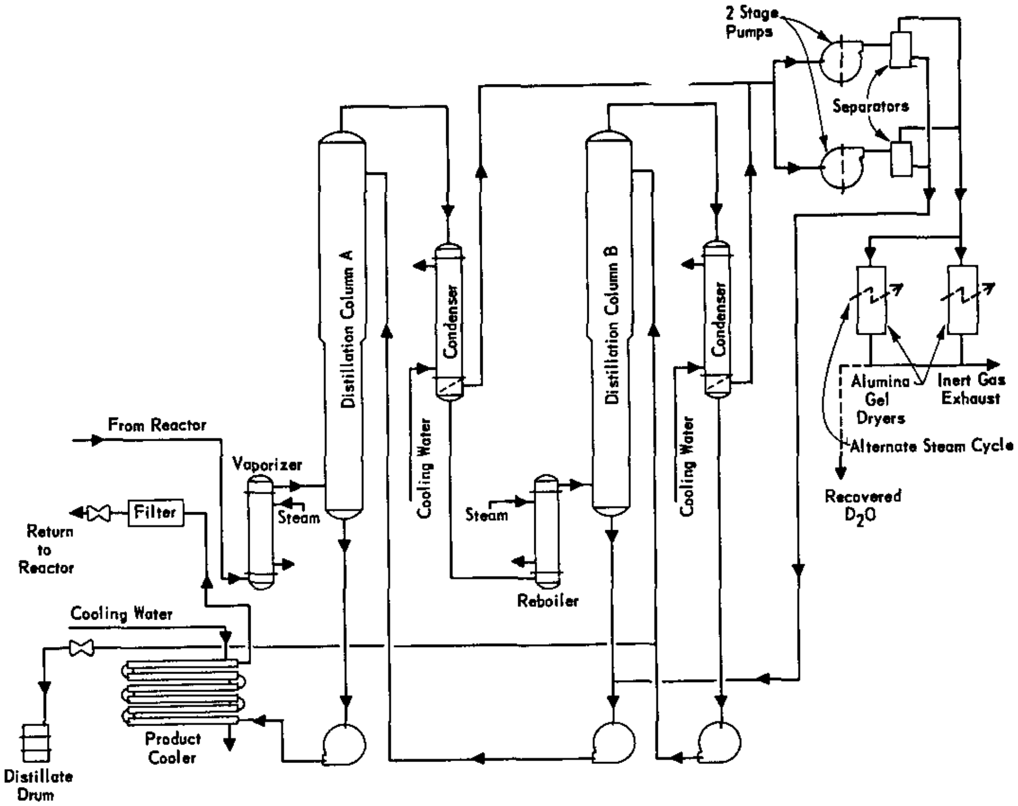


FIG. 1 SCHEMATIC FLOW DIAGRAM – REACTOR-INTEGRATED UNIT

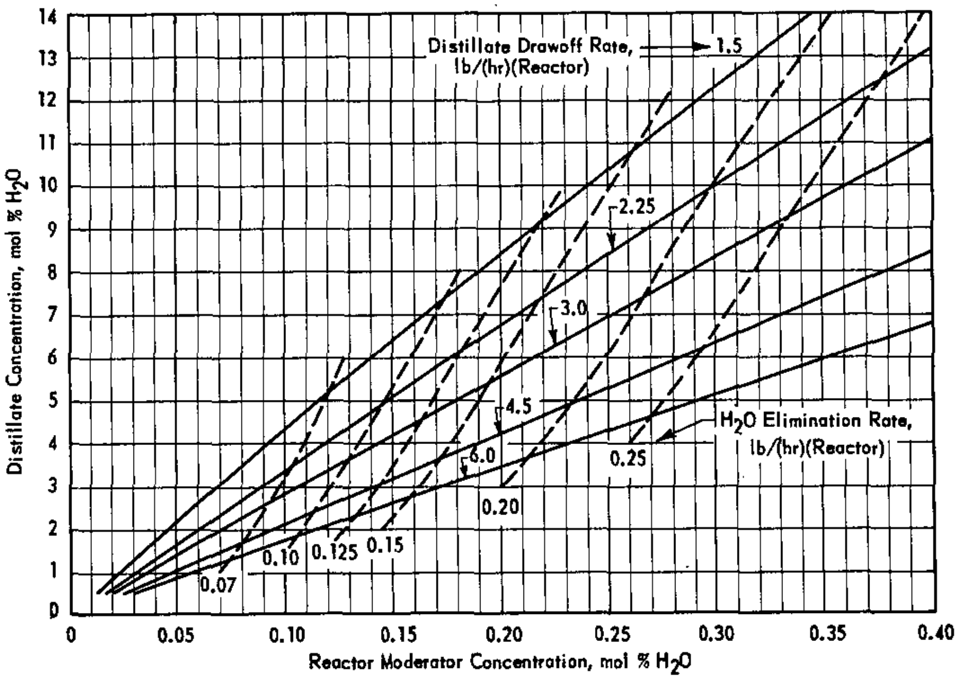


FIG. 2 OPERATING CHARACTERISTICS OF THE REACTOR-INTEGRATED SRP DISTILLATION UNITS

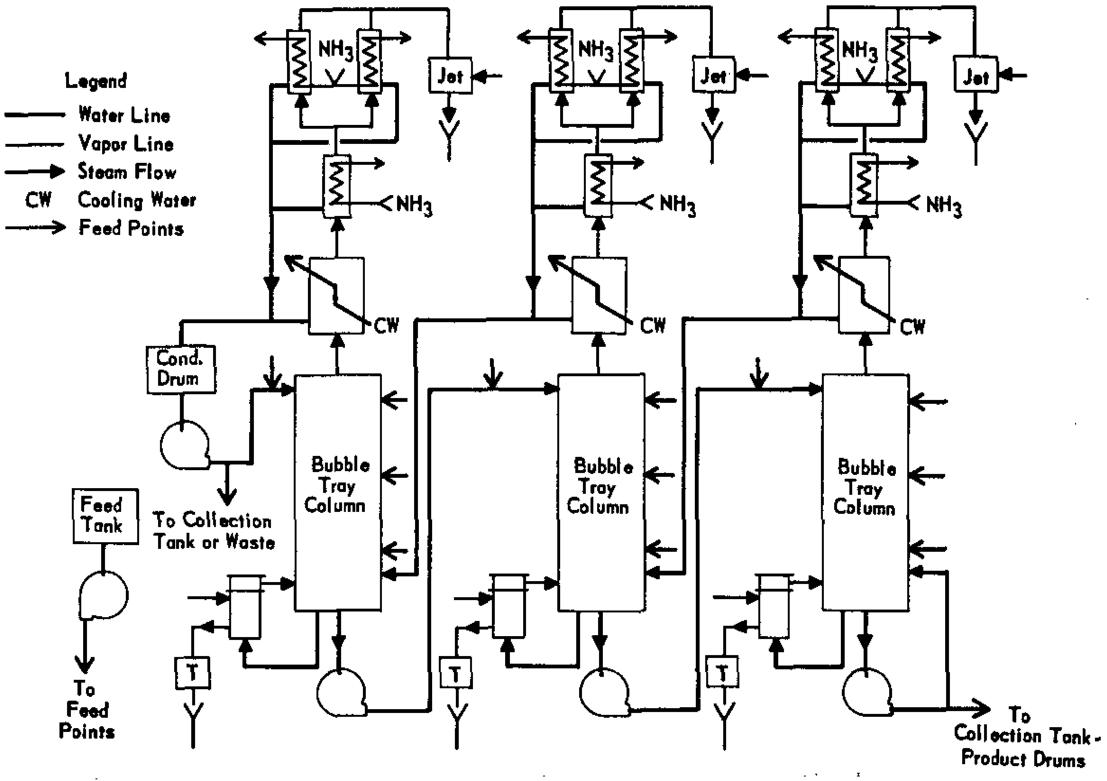


FIG. 3 SCHEMATIC FLOW DIAGRAM-REWORK UNIT

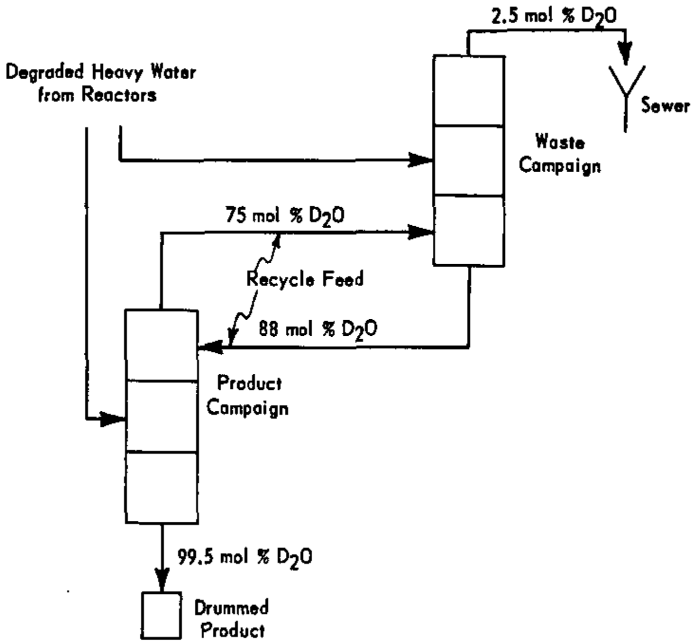


FIG. 4 REWORK UNIT CAMPAIGNS

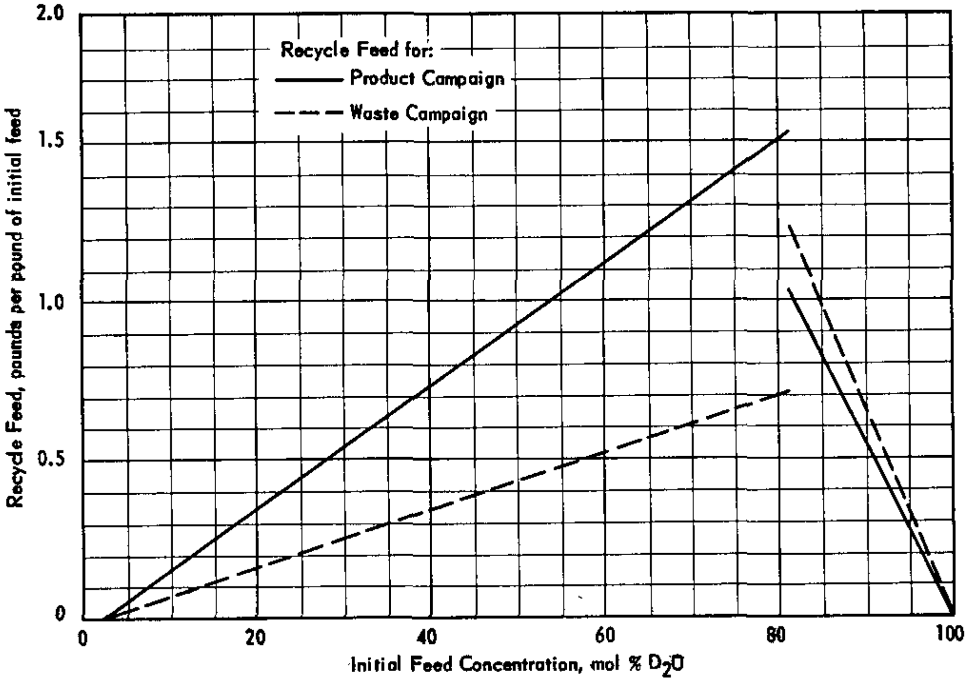


FIG. 5 RECYCLE FEED GENERATED BY INITIAL FEED

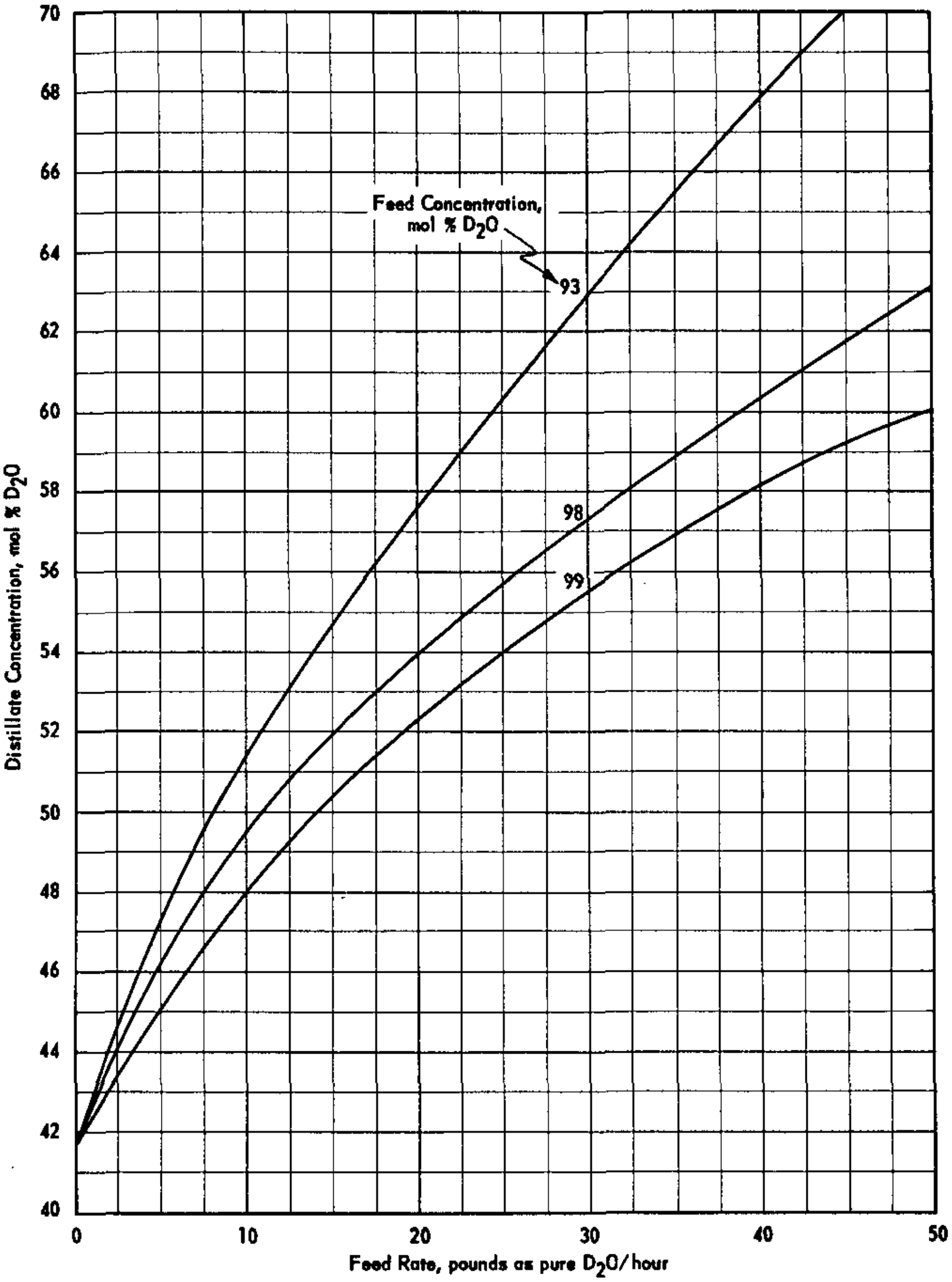


FIG. 6a REWORK UNIT OPERATING CHARACTERISTICS
Base Concentration - 99.8 mol % D_2O

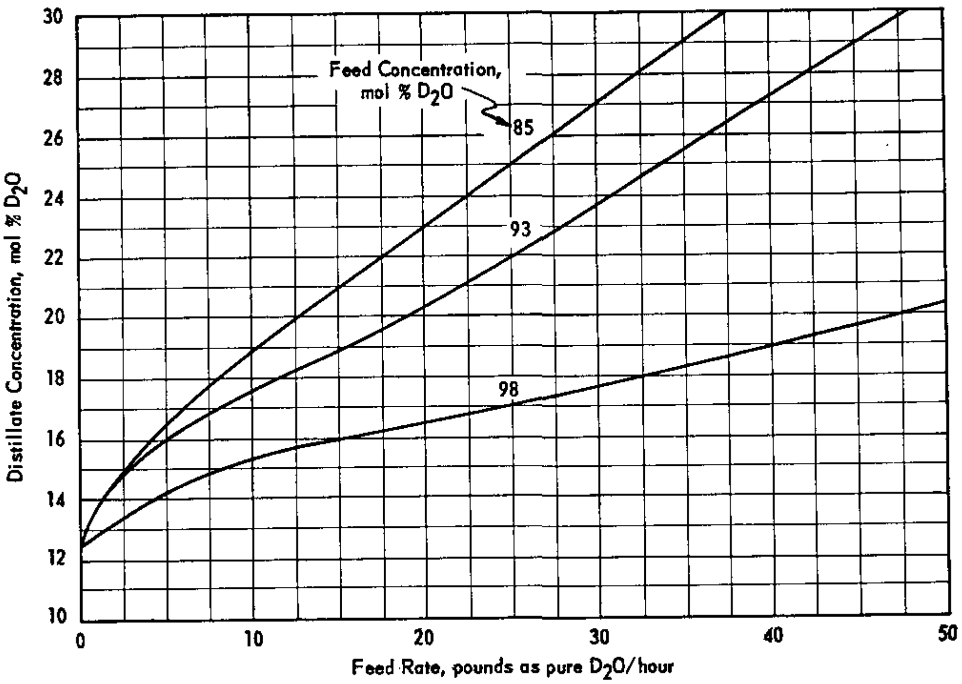


FIG. 6b REWORK UNIT OPERATING CHARACTERISTICS
Base Concentration - 99 mol % D_2O

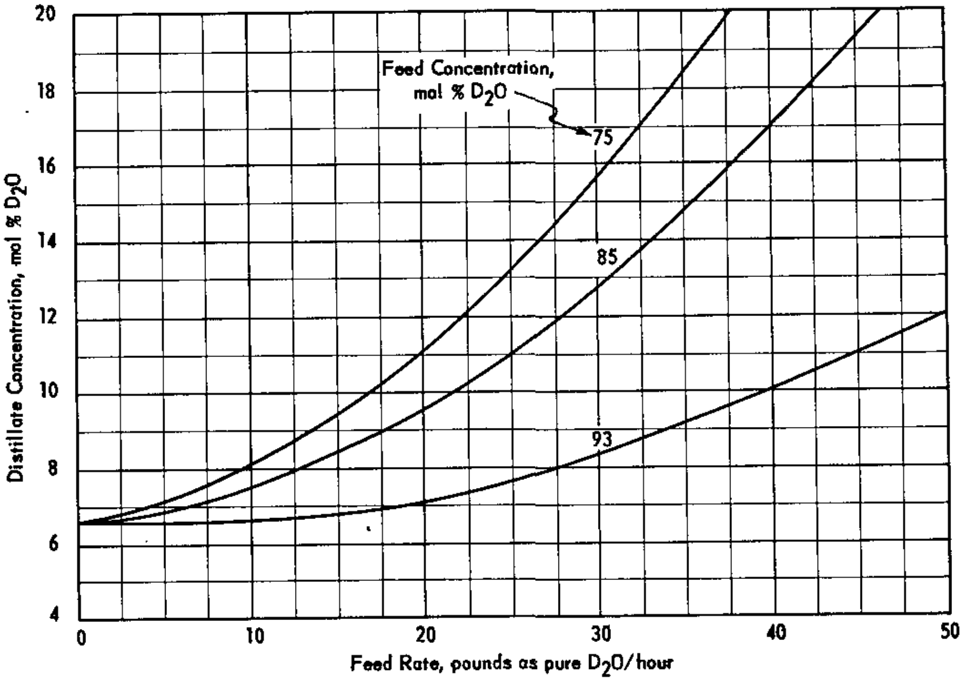


FIG. 6c REWORK UNIT OPERATING CHARACTERISTICS
Base Concentration - 98 mol % D_2O

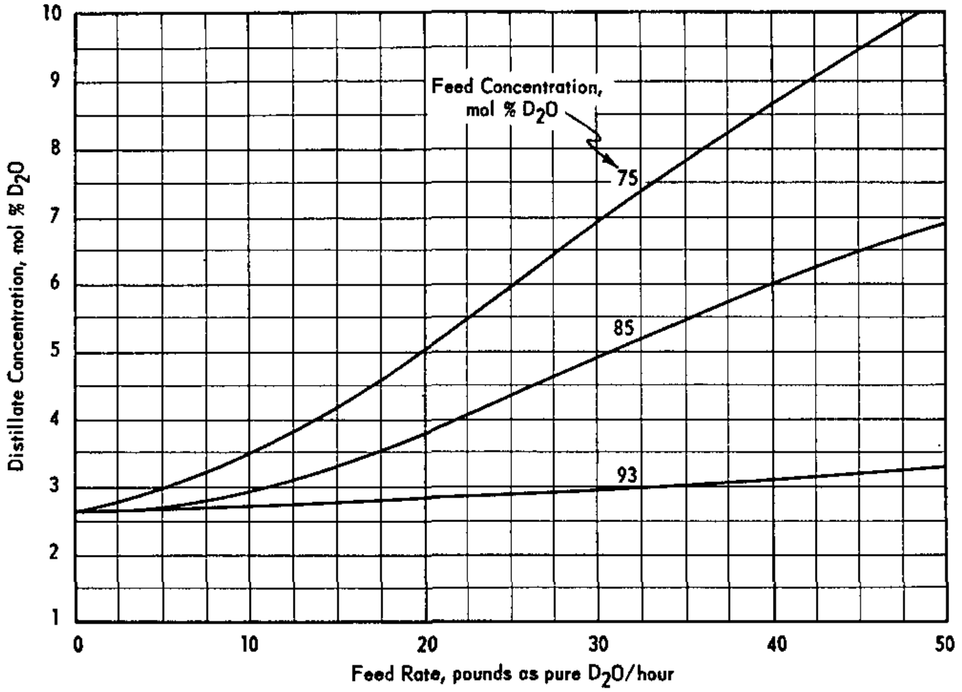


FIG. 6d REWORK UNIT OPERATING CHARACTERISTICS
Base Concentration - 95 mol % D_2O

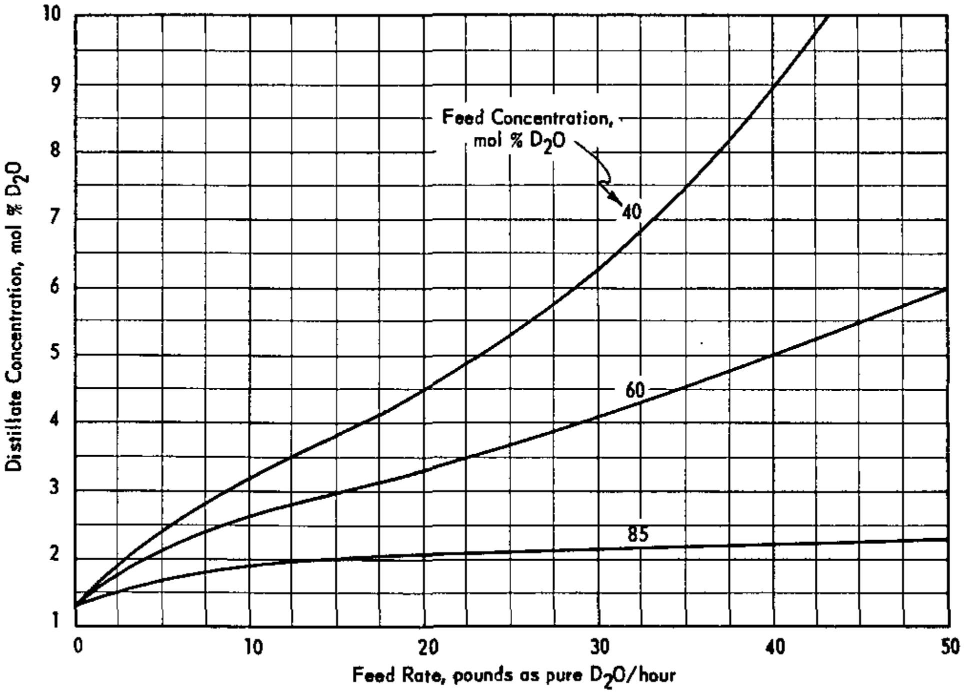


FIG. 6e REWORK UNIT OPERATING CHARACTERISTICS
Base Concentration - 90 mol % D_2O

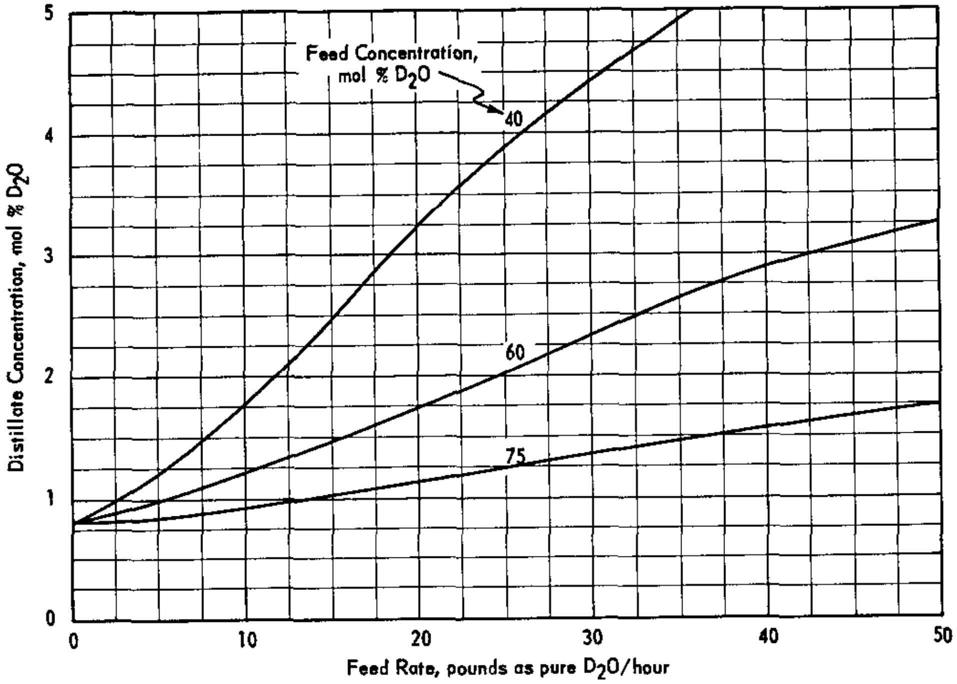


FIG. 6f REWORK UNIT OPERATING CHARACTERISTICS
Base Concentration - 85 mol % D_2O

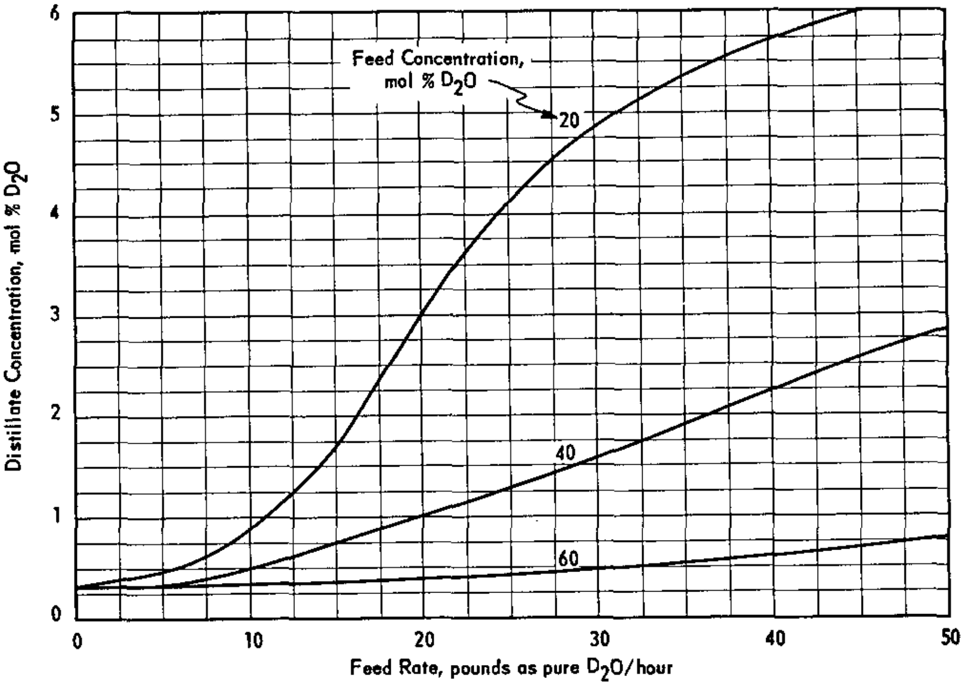


FIG. 6g REWORK UNIT OPERATING CHARACTERISTICS
Base Concentration - 70 mol % D_2O

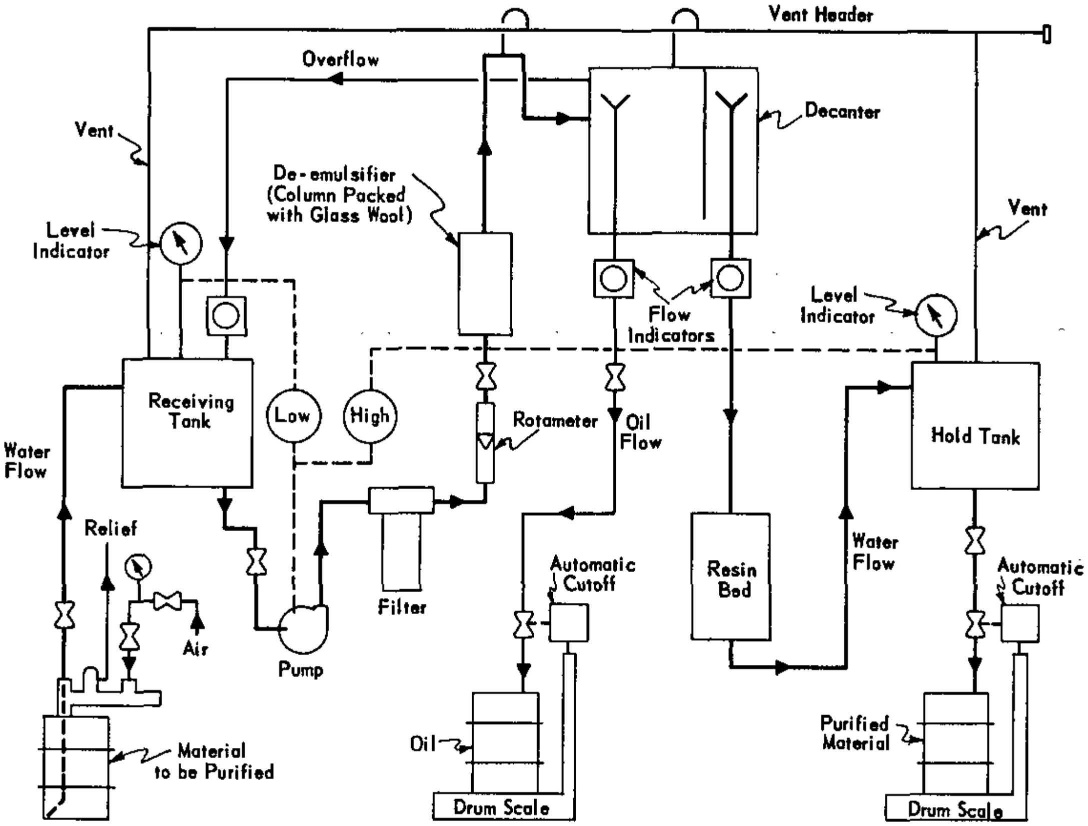
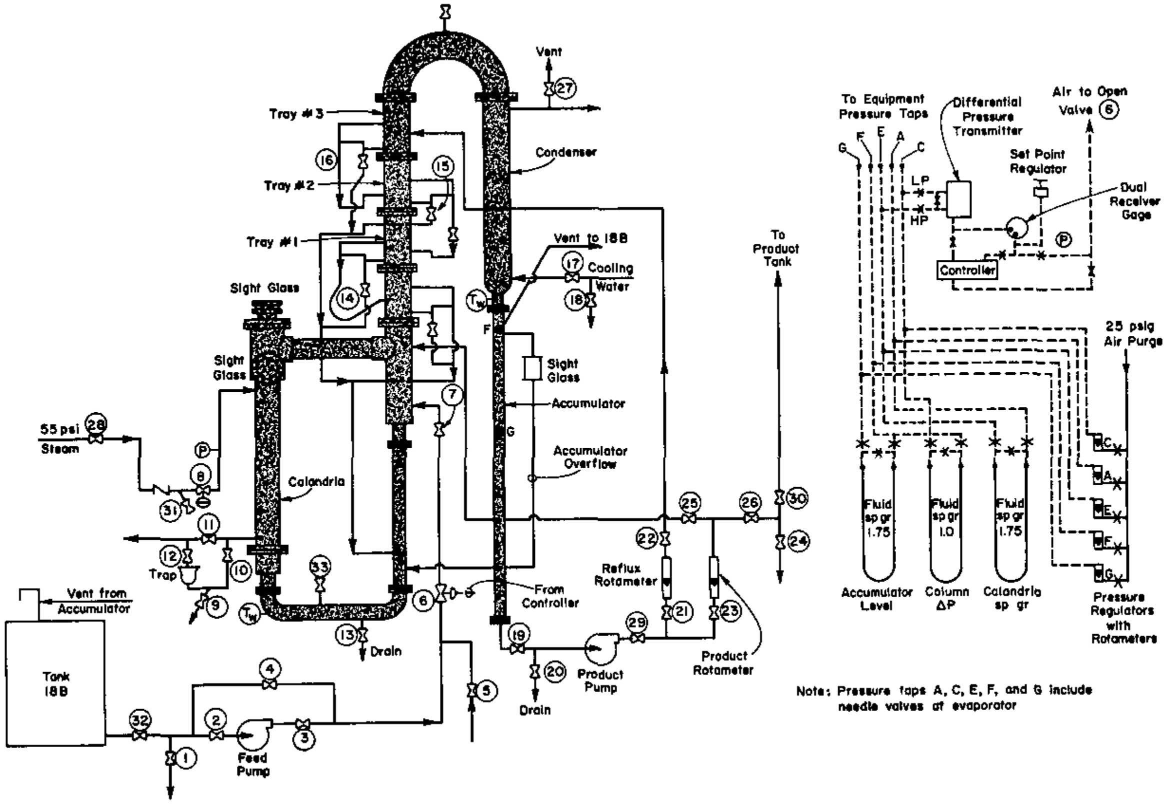


FIG. 7 PURIFICATION BY ION EXCHANGE



Note: Pressure taps A, C, E, F, and G include needle valves at evaporator

Valve List

1. Feed Drain
2. Feed Pump Suction
3. Feed Pump Discharge
4. Feed Pump Bypass
5. Drum Feed
6. Feed Control
7. Feed Block
8. Steam Pressure Release
9. Steam Trap Blowdown
10. Steam Trap Inlet
11. Steam Trap Bypass
12. Steam Trap Outlet
13. Calandria Drain
14. Tray No. 1 Drain
15. Tray No. 2 Drain
16. Tray No. 3 Drain
17. CW Inlet
18. CW Drain
19. Product Pump Suction
20. Product Pump Drain
21. Reflux Rotameter Block
22. Reflux
23. Product Rotameter Block
24. Product Drumming
25. Product Recirculation
26. Product Control
27. Condenser Vent
28. Steam Block
29. Product Pump Discharge Block
30. Tank Drawoff
31. Steam Line Blowdown
32. 18-B Outlet Block
33. REB Sample

FIG. 8. PIPING AND INSTRUMENT DIAGRAM
REWORK UNIT EVAPORATOR

APPENDIX I

PHYSICAL PROPERTIES OF HEAVY WATER

References

1. Kirshenbaum, I. Physical Properties and Analysis of Heavy Water. National Nuclear Energy Series, NNES III-4A, New York: McGraw-Hill, 438 pp. (1951).

2. FIAT Review of German Science Physical Chemistry (1939-46) pp.22-23.

A few of the pertinent physical properties of D_2O and mixtures of D_2O with H_2O are presented below. For additional detail consult References 1 and 2.

Pure $D_2O^{(1)}$

Freezing point	3.81°C
Boiling point	101.42°C
Density at 25°C	1.10451 g/ml

Mixtures of D_2O and H_2O

Density of a mixture of D_2O and H_2O is given$^{(1)}$ by the equation,

$$d = \frac{0.997058 + 0.111387x}{1 - 0.002778x} \tag{1}$$

where

d = density of mixture at 25°C

x = mol fraction D_2O in mixture

Relative volatility of H_2O with respect to HDO is given$^{(2)}$ by the expression,

$$\alpha = 1.1596\ e^{-\left[\frac{65.43}{T}\right]} \tag{2}$$

The relative volatility of HDO with respect to D_2O has essentially the same numerical value as that for H_2O/HDO.

Under the operating conditions existing in a vacuum distillation system, the relative volatility ranges from 1.038 to 1.056. The corresponding temperature at saturated conditions ranges from 81 to 50°C as a result of the pressure drop through the distillation tower.

The distribution of the isotopes in a mixture is dictated by the equilibrium for the reaction,

$$H_2O + D_2O = 2HDO \qquad (3)$$

The equilibrium constant for the reaction in terms of mol fraction concentrations is:

$$K = \frac{(HDO)^2}{(H_2O)(D_2O)} \qquad (4)$$

The equilibrium constant K as a function of temperature is given⁽¹⁾ below for the vapor phase reaction:

Temperature, °C	K
0	3.76
25	3.80
50	3.83
75	3.85
100	3.87
125	3.89

APPENDIX II

SRP REACTOR-INTEGRATED EQUIPMENT

Distillation Columns

Two distillation columns, operated in series, are provided for each reactor system. Both columns are identical in design.

Towers

Diameter, lower section (bottom 27 ft)	3 ft 5 in.
upper section (top 30 ft)	3 ft 11 in.
Height, bottom tray to top tray	58 ft 7 in.
over-all	82 ft 6 in.
Design Pressure	full vacuum to 30 psig

Trays

Number, lower section	44 trays
upper section	46 trays

Spacing, trays 1 to 35	7 in.
trays 35 to 44	8 in.
trays 45 to 81	7 in.
trays 81 to 90	8 in.

Design, sieve trays with 1/8-in. diameter holes on a 3/8-in. triangular pitch

Calandrias (Vaporizer and Reboiler)

Each column is serviced by a single tube-and-shell type calandria. The calandrias are identical in design.

Shell

Service	Steam
ID	20 in.
Number of passes	1
Design pressure	50 psig

Tubes

Service	Water (process)
Size	1 in. - 14 BWG
Number	120
Length	48 in. (31-1/8 in. between inner tube sheets)

Layout	1-3/8-in. triangular pitch
Number of passes	1
Effective heat exchange surface	68 sq ft
Design pressure	Full vacuum

(Double tube sheets are used at each end of tube bundle. The outer sheets are welded to the tubes; the tubes are rolled into the inner sheet.)

Condensers

Each column is serviced by a single tube-and-shell type condenser having the same basic design as the calandrias.

Shell

Service	Cooling water
ID	30 in.
Number of passes	1
Design pressure	75 psig

Tubes

Service	Water vapor and air (process)
Size	1 in. - 14 BWG
Number	376
Length	8 ft (7 ft 2-1/8 in. between tube sheets)
Layout	1-3/8-in. triangular pitch
Number of passes	1
Effective heat exchange surface	590 sq ft
Design pressure	Full vacuum to 20 psig

(Tube sheets are constructed similar to those in calandrias.)

Bottoms Cooler

A tube-and-shell heat exchanger cools product withdrawn from the base of the distillation unit.

Shell

Service	Cooling water
Size	6 in., schedule 40 pipe
Number of passes	1
Design pressure	100 psig

Tubes

Service	Process water
Size	1/2 in. - 18 BWG
Number	40
Length	16 ft (14 ft 10-1/2 in. between tube sheets)
Layout	3/4-in., triangular pitch
Number of passes	2
Effective heat exchange surface	43 sq ft
Design pressure	Full vacuum

Vacuum Pump System

The vacuum in both columns is maintained by a single vacuum pump system. Major components are duplicated within the one system.

Vacuum Pumps (2)

Type	Nash Engineering Co., Type TS-8-L2, two-stage unit, mechanical shaft seals (Durametallic Co.)
Capacity	55 cfm (measured at suction-side vacuum)
Motor	5 hp, 1750 rpm

Vacuum Pump Separators (2)

Type	Centrifugal separator

Vacuum Pump Coolers (2)

Type	Double-pipe heat exchanger
Sections, number	9
inner pipe	5 ft of 1-1/4-in. schedule 80 with process water flow
outer pipe	5 ft of 2-in. schedule 40 with cooling water in annulus
Effective heat exchange surface	15 sq ft
Design pressure	Full vacuum to 100 psig

Vent Drying System

The gas removed from the two columns by the vacuum pump system contains a small amount of process vapor. Before this gas is exhausted to the atmosphere, the moisture is removed in alumina gel dryers.

Type	Pittsburgh "Lectrodryer" Type BWC, size 150-SP consisting of two alumina gel units in alternating use. Reduces dew point of exhausted gas to -35°C. Regenerated by heat via steam coils.

Pumps and Motors

The three pumps and motors for transfer of primary flows are of the same design. Specifications are shown below.

70 gpm, 113 ft head, centrifugal pump, 3 hp, 3450 rpm, Ingersoll Rand 1 CRV motor

Instrumentation

Flow

Primary feed	Orifice-type flow recorder
Bottoms flow	Orifice-type flow recorder
Steam flow	Orifice-type flow recorder
Reflux return	Rotameter
Overheads drawoff	Rotameter

Level

Condenser level	Float-type controller
Vacuum pump separator	Float-type controller

Pressure and Pressure Drop

Column pressure	Controller in gas line between column and condenser (shuts system down at excessive pressure)
Column differential pressure	Recorder
Pressure in entire system	Recorder-controller in common suction line to both vacuum pumps (controls absolute pressure of system

Temperature

Column condenser	Recorder-controllers on each column condenser to control the temperature of the effluent process water by throttling cooling water flow
Bottoms cooler	Recorder-controller similar to above

Power Failure. Instrumentation is provided so that an electrical power failure will close automatic solenoid valves at the suction of the vacuum pumps and prevent immediate loss of vacuum. Such a power failure will also close the steam admission valves to the reboiler, which in turn will operate the isolation switch and close the distillation system feed and return valves.

Radiation. A radiation recording instrument is provided in the feed line to A-column from the purification system, to prevent the unshielded distillation equipment from becoming excessively radioactive. If radiation becomes excessive, the distillation system feed and return valves (isolation valves) are automatically closed.

Conductivity. A conductivity recording instrument is provided in the feed line to prevent dissolved contaminants, which might cause corrosion, from entering the distillation system. If conductivity becomes excessive, the distillation system feed and return valves (isolation valves) are automatically closed.

Specific Gravity. A continuous specific gravity instrument, "Densitrol", measures the isotopic purity of the moderator being returned to the coolant return tank from distillation. An isotopic purity lower than that of the influent feed moderator indicates a leak of light water from a reboiler, condenser, or cooler, and automatically closes the isolation valves (distillation feed and return valves).

Materials of Construction

Mild steel was used originally throughout the distillation systems. Stainless steel tubes and tube sheets were installed in the condensers and calandrias after several of the original mild steel units failed due to corrosion.

Stainless steel or other corrosion-resistant material was not considered justified, since only moderator that has previously been purified is added to the distillation equipment during normal distillation. The distillation feed stream is taken as a sidestream from the effluent issuing from the resin purification system through which reactor moderator is continually recirculated. Thus, it has been deionized and filtered through a 10-micron filter.

APPENDIX III

SRP REWORK UNIT EQUIPMENT

Distillation Columns

All three distillation columns in the separate reworking facility are identical in design.

Towers

Diameter	4 ft 0 in.
Height	78 ft (tangent to tangent)
Shell thickness	1/2 in. (ground to about 22 ft level)
	3/8 in. (remainder of column)
Design pressure	Full vacuum
Operating pressure	60 to 100 mm Hg at top of column

Trays

Number	72
Caps per tray	36
Layout (center to center)	12
Cap size, ID	4 in.
Tray, spacing	12 in.

Materials of Construction

Shell and heads	A285 Grade C Firebox Quality Steel
Trays and caps	A283 Grade C Steel
Flanges and nozzles	A181 Grade I Steel

Vendor

Vulcan Copper and Supply Co.

Calandrias

Each column is serviced by a single tube-and-shell type calandria. These three calandrias are identical in design.

Shell

Service	Steam
ID	16 in.
Number of passes	1
Design pressure	75 psig
Operating pressure	About 40 psig

Tubes

Service	Water (process)
Size	1 in. - 14 BWG
Number	60
Length	8 ft
Number of passes	1
Effective heat exchange surface	110 sq ft
Design pressure	Full vacuum
Operating pressure	About 320 mm Hg

(Tubes are welded into double tube sheets at each end of tube bundle.)

Material of Construction

Shell	Carbon steel
Tubes	Carbon steel

Vendor

Dowington Iron Works

Condensers

Each column is serviced by a single tube-and-shell type condenser. These three condensers are identical in design and are of the falling film type.

Shell

Service	Water vapor and air (process)
ID	3 ft 0 in.
Number of passes	1
Design pressure	Full vacuum
Operating pressure	About 60 to 100 mm Hg

Tubes

Service	Cooling water
Size	2 in. - 12 BWG
Number	151
Length	16 ft
Number of passes	1
Effective heat exchange surface	1210 sq ft
Design pressure	Atmospheric
Operating pressure	Atmospheric

Material of Construction

Shell	Carbon steel
Tubes	Carbon steel

Vendor

Southwestern Engineering Co.

Coolers

A single cooler condenses vapors leaving the condenser on each column. The three coolers are identical in design.

Shell

Service	Water vapor and air (process)
ID	6 in.
Number of passes	1
Design pressure	Full vacuum
Operating pressure	60 to 100 mm Hg

Tubes

Service	Ammonia refrigerant
Size	1/2 in. - 18 BWG
Number	2 (coil type)
Number of passes	2
Design pressure	200 psig
Operating pressure	54 to 59 psig

Material of Construction

Shell	Carbon steel
Tubes	Carbon steel

Vendor

Dowington Iron Works

Freezers

Two freezers, used alternately, provide the final condensation of any water vapor leaving the cooler on each column. The six freezers are double-pipe heat exchangers, identical in design.

Shell

Service	Ammonia refrigerant
ID	6 in.
Length	20 ft
Number of passes	1
Design pressure	200 psig
Operating pressure	5 to 10 psig

Inner Pipe

Service	Water vapor and air (process)
Size	3 in. - schedule 40
Number	1
Number of passes	1
Design pressure	Full vacuum
Operating pressure	60 to 100 mm Hg

Material of Construction

Shell	Carbon steel
Tube	Carbon steel

Vendor

Whitlock Mfg. Co.

Steam Ejectors

Inerts leaving the freezers on each column are ejected to the atmosphere through steam jet ejectors. All three ejectors are identical in design.

Ejector

Type	200 N
Stages	Two stages, noncondensing
Rating	10 pounds of air per hour at 88 mm Hg
Operating steam pressure	100 psig
Maximum back pressure	1 psig

Materials of Construction

Steam nozzle	Type 304 stainless steel
Air chamber	Cast iron
Diffuser	Cast iron
Steam chest	Carbon steel

Vendor

Croll Reynolds Engineering Co.

Pumps and Motors

All process pumps and motors for the separate reworking facility are of the same design.

Pumps

Type 1-1/2 x 1-1/4-in., Type SS-DHB, single-stage centrifugal pump; single "Durametallic" mechanical seal, carbon on "Stellite".

Motors

Allis Chalmers type AP2, 5 hp, 3500 rpm, 440 volt, 3 phase, 60 cycle, totally enclosed.

Instrumentation

The instrumentation associated with a typical distillation column and its auxiliary equipment is outlined below:

1. Liquid Flow From Bottom of Column - Recorder and Controller

	Vendor
Concentric orifice	Taylor
Differential pressure transmitter	Brown
Indicating pneumatic receiver	Moore
Recording control station	Taylor
Pneumatic controller	Moore
Control valve	Hammel-Dahl

2. Overheads Condensate Flow - Recorder

Concentric orifice	Taylor
Differential pressure transmitter	Brown
Indicating pneumatic receiver	Moore
Pneumatic recorder	Taylor

3. Liquid Level in Bottom of Column - Recorder

External displacement type level transmitter	Mason-Neilan
Pneumatic recorder	Taylor
Reflex gage glass	Jerguson

4. Column Pressure - Recorder and Controller

Indicating absolute pressure transmitter	Foxboro
Recording control station	Taylor
Pneumatic controller	Moore
Control valve	Hammel-Dahl

5. Column Differential Pressure - Indicator

	Vendor
Differential pressure transmitter	Brown
Indicating pneumatic receiver	Moore

6. Steam Flow to Calandria - Recorder and Controller

Concentric orifice	Taylor
Differential pressure transmitter	Brown
Indicating pneumatic receiver	Moore
Recording control station	Taylor
Pneumatic controller	Moore
Control valve	Hammel-Dahl

7. Condenser Temperature Indicators

Cooling water inlet and process vapor inlet thermowells	Trinity
Condensate outlet bimetallic dial thermometers	Moeller

Corrosion Experience

Corrosion of equipment, after the first five years of operation, was insignificant. The inspection was quite limited, however, because a more thorough inspection would have required destruction or cutting of the equipment. Visual examination and instrument measurements ("Audigage") showed no corrosive attack on the internal walls of the distillation tower. Some pitting was observed on the outside of tubes in the calandrias. This pitting was generally 5 mils deep and 10 mils in diameter. The outside of the calandria tubes are exposed to steam that contains negligible CO_2 concentrations. The inside of tubes in condensers showed some metal loss of about 1/64 in. deep under a 1/32 in. scale. Untreated raw water from the Savannah River is passed through these tubes as a coolant.

APPENDIX IV

TYPICAL OPERATING COSTS FOR SRP REWORK UNIT*

Direct Operation	Operating Cost, dollars/year	
Labor	18,500	
Supplies	2,000	
Supervision	19,900	
Miscellaneous	500	
Total		40,900
Maintenance		
Labor	15,200	
Material	3,300	
Direct overhead	6,300	
Total		24,800
Power		
Electricity	600	
Steam	40,000	
Cooling water	2,000	
Total		42,600
Technical		
Process Assistance	22,000	
Control Laboratory	28,000	
Health Physics	14,500	
Total		64,500
Total Direct Cost		172,800

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*Because of the accounting system used, operating costs for the reactor-integrated distillation facilities are not readily separable from the operating costs for the reactor as a whole. As a result, figures for the reactor facility were not available for inclusion in this report.

APPENDIX V

INVESTMENT IN SRP DISTILLATION FACILITIES

The figures given below correspond to cost conditions existing at the time of construction in 1952.

	Investment, dollars
1. Rework Unit	
Equipment (Towers, pumps, heat exchangers, tanks, etc; installed and insulated.)	219,000
Piping and instrumentation	194,000
Building and structure	42,000
Total	455,000
2. Reactor-Integrated Facilities	
Equipment (Towers, pumps, heat exchangers, tanks, etc; installed and insulated.)	203,000 per reactor system
Piping and instrumentation	180,000*
Building and structure	39,000*
Total	422,000 per reactor system

---

*The cost for these items cannot be obtained directly because of the method of equipment accounting employed. The cost for these comparable items is known for the Rework Unit and is shown above. The ratio of the equipment cost in the reactor-integrated facility to that in the Rework Unit was used to approximate the investment in these items.

APPENDIX VI

STANDARD ANALYTICAL METHODS

HEAVY WATER: CONCENTRATION D_2O
Gravimetric Method - Pycnometer

References

Kirshenbaum, I. *Physical Properties and Analysis of Heavy Water.* National Nuclear Energy Series, NNES III-4A, New York: McGraw-Hill (1951) pp. 2 and 16.

Principle and Limitations

Since the densities of ordinary water and heavy water differ, a sample consisting of only these substances can be accurately analyzed by measuring its density. By suitable calculations density may be converted to mol % deuterium expressed as deuterium oxide.

It is necessary to purify the sample by means of an alkaline permanganate distillation to remove organic and other impurities that would introduce an error in the result.

A pycnometer is used for the determination of the density. The effects of buoyancy, humidity, etc. are eliminated by the use of a filled and sealed pycnometer as a counterweight. Calibration of the counterweight pycnometer and the sample pycnometer must include the correction for buoyancy so that the density obtained will be based on the true weight of the sample. An error of 0.0001 in the density introduces an error of approximately 0.1 mol % in the result.

This method does not correct for the O^{18} content of the sample. The range of the method is 10 to 99 mol % D_2O.

Equipment

Carborundum
1 Distilling flask, "Pyrex", round bottom with 24/40 ₸ ground-glass joint at neck, 300 ml (See Note 1)
Glass wool
1 Bent condenser, water-cooled with 24/40 ₸ ground-glass joint at neck, and 14/35 ₸ ground-glass joint at end (See Note 1)
2 Scoopulas
1 Drying tube containing silica gel
1 Receiving flask with 14/35 ₸ ground-glass joint at neck and 7/25 ₸ ground-glass side connection, with caps
2 Hypodermic syringes, 50 ml, with needles, large bore

1 Electric heater
1 Bunsen burner
1 Reischauer pycnometer, 25 ml
1 Reischauer pycnometer, counterweight, 25 ml
1 Constant temperature bath
1 Rubber bulb
1 Hypodermic needle, small bore

Reagents and Chemicals

Potassium permanganate, CP, $KMnO_4$
Sodium peroxide, CP, Na_2O_2

Procedure

1. Add a few pieces of carborundum to a clean, dry, 300 ml, round-bottom distilling flask. (See Note 2)

2. Using a scoopula, add about 50 mg each of potassium permanganate and sodium peroxide.

3. Insert a fine layer of glass wool into the upper end of the condenser.

4. Attach the silica gel drying tube to the side connection of the condenser, then connect the receiving flask to the lower end of the condenser.

5. Cap the side arm of the receiving flask.

6. Insert the condenser into the distilling flask and clamp the apparatus in position for distillation.

7. Shake the sample thoroughly. With a clean, dry, 50 ml syringe withdraw about 35 ml of sample. Replace the bottle cap immediately.

8. Introduce the sample into the distilling flask and connect the flask to the condenser immediately.

9. Connect the cooling water to the condenser. Use an electric heater to distill the sample at a rate of about 20 drops per minute. (See Note 3)

10. Allow the distillation to proceed to dryness.

11. Using a Bunsen burner, lightly flame first the distilling flask and then the neck of the condenser to ensure complete distillation.

12. Allow the neck of the condenser to cool. Again flame the flask lightly. Drive over any moisture that collects in the neck of the condenser.

13. Repeat Steps 11 and 12 until no moisture is evident.

14. Check the receiving flask to see that the sample is free of turbidity and pink color. If not, redistill the sample.

15. When the distillation is complete, remove the receiving flask from the condenser and immediately place the large cap in position to seal it.

16. Remove the small cap from the side arm of the receiving flask, insert the large bore hypodermic needle of a clean, dry, 50 ml syringe and fill the syringe.

17. Insert the hypodermic needle into a dry 25 ml Reischauer pycnometer that has been previously weighed and calibrated. Fill the pycnometer slowly to above the graduation mark, being careful to see that no bubbles form on the bottom and sides of the pycnometer. Cap the pycnometer and record the weight and volume of the pycnometer.

18. Place the pycnometer in a constant temperature bath that is adjusted to 25.00 ±0.02°C. Allow it to remain in the bath from 15 to 20 minutes.

19. Using a rubber bulb and a small bore hypodermic needle with the pointed end ground off, remove the excess liquid in the pycnometer until the bottom of the meniscus is level with the graduation mark.

20. Place the pycnometer in the bath again for 5 minutes to be certain that the temperature of the sample is the same as that of the bath.

21. Remove the pycnometer from the bath and check to see that the meniscus is still level with the graduation mark. If it is not, repeat Steps 19 and 20.

22. Carefully dry the outside of the pycnometer with a lint-free cloth.

23. With a hypodermic needle attached to a vacuum line, carefully remove any excess sample adhering to the inside wall above the graduation mark.

24. Replace the stopper and allow the pycnometer to stand until it comes to room temperature.

25. Weigh the pycnometer on an analytical balance using a counterweight pycnometer of known weight. Record, to the nearest 0.0001 g, the weights used to bring the balance to equilibrium.

26. Pour the sample remaining in the receiving flask into the waste heavy water container.

27. Wash the distilling flask thoroughly with oxalic acid, rinse with distilled water, and dry in the oven reserved for glassware used for heavy water analyses.

28. The receiving flask may be put directly into the drying oven and needs no further cleaning unless it has been soiled with permanganate, etc.

29. Place the condenser in the holder provided and pass air through it until it is dry.

30. The pycnometer is left filled with the purified sample until it is to be used again, at which time it is emptied, by means of a syringe, into the waste heavy water container. The pycnometer is dried with acetone and a vacuum.

Calculations

1. $A = B - C$
2. $d = \frac{A}{E}$
3. $\Delta d = d - d_1$
4. $\text{Mol \% } D_2O = \frac{927.35 \times \Delta d}{1 - (0.039 \times \Delta d)}$ (See Note 4)

where

A = true weight of the sample, g
B = total weight of counterweight pycnometer and brass weights, g
C = true weight of the sample pycnometer, g
d = density of the sample at 25.00°C, g/ml
E = volume of the sample pycnometer, ml
Δd = the difference between the density of the sample and the density of protium oxide
d_1 = the density of protium oxide, g/ml assuming that protium oxide is lighter in density than normal water by 1.6×10^{-5} g/ml = 0.997058 (See Note 5)

Notes

1. The distillation equipment, shown in Figure VI-1 can be obtained from Eck and Krebs, Inc., 27-09 40th Ave., Long Island City 1, N. Y.

2. The carborundum is added to prevent bumping.

3. If the wine-red permanganate color does not persist during the distillation it will be necessary to add more potassium permanganate to the sample. Distillation should be discontinued, the apparatus allowed to cool to room temperature, and a small amount of permanganate added to the flask.

4. The formula and constants are derived in Kirshenbaum, I. Physical Properties and Analysis of Heavy Water. National Nuclear Energy Series, NNES III-4A, New York: McGraw-Hill (1951) p. 14.

5. Protium oxide is normal water from which deuterium oxide has been removed.

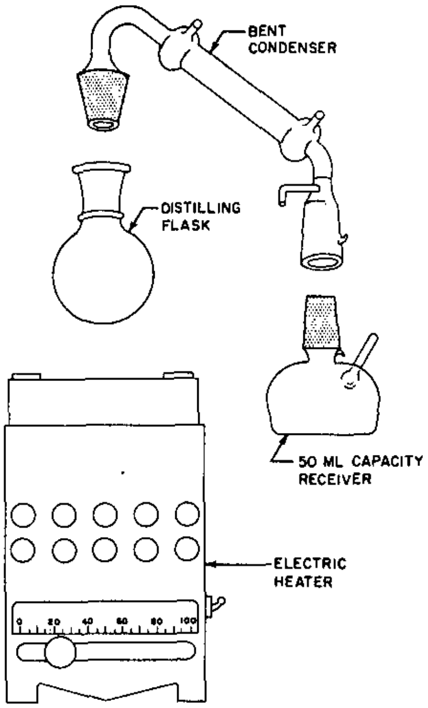

FIG. VI-1 DISTILLATION ASSEMBLY

HEAVY WATER: SPECIFIC CONDUCTIVITY

Principle and Limitations

The ionizable solids in water have the ability to conduct an electric current through a solution. This property of electrical conductance is used as a measure of the quantity of ionizable solids in solution. Conductivity is measured in micromhos by means of a conductivity cell and conductivity bridge.

The procedure is limited by the range of the conductivity bridge.

Equipment

1	Graduated cylinder, 250 ml
1	Conductivity bridge, Leeds and Northrup No. 4866 or equivalent
1	Conductivity cell, cell constant of approximately 0.1

Procedure

1. Transfer approximately 200 ml of sample to a clean, dry 250 ml graduated cylinder. Dilute as necessary to avoid exceeding the range of conductivity bridge.

2. Using a Leeds and Northrup No. 4866 Conductivity Bridge or equivalent, measure the conductivity of the sample and record as micromhos/cm, corrected for dilution, if any.

   Note: Refer to the manufacturer's direction booklet to obtain details on the exact operation of the conductivity bridge. To determine the cell constant, one of the standard reference solutions of known conductivity may be prepared as listed in Lange, N. A. Handbook of Chemistry. 8th Ed. Sandusky, Ohio: Handbook Publishers (1952) p. 1241.

HEAVY WATER: TURBIDITY
Turbidimetric Method

Principle and Limitations

Turbidity is measured by passing a beam of light through the sample. The particles that cause the solution to be turbid absorb and disperse the light. The amount of light absorbed by the solution is proportional to its turbidity.

Although it is known that the particle size has a pronounced effect on the absorption and dispersion of light, the photoelectric method is as good or better than other methods.

Turbidity is generally expressed as ppm silica. The concentration range is 2 to 70 ppm. As would be expected, the more concentrated solutions have a tendency to settle out during a determination. A highly turbid solution may be analyzed by diluting until its turbidity is within the concentration range of this method.

Equipment

5	Volumetric flasks, 250 ml
1	Transfer pipet, 5 ml
1	Transfer pipet, 20 ml
1	Transfer pipet, 10 ml
1	Transfer pipet, 25 ml
1	Transfer pipet, 50 ml
2	Absorption cells, 50 mm light path
or 2	Absorption cells, 40 mm light path
1	Spectrophotometer, Beckman Model B
or 1	Spectrophotometer, Coleman Model 14

Reagents and Chemicals

Silica turbidity standard, "Hellige", 200 ppm silica or equivalent

Procedure

A. Preparation of Standard Curve (See Note 2)

1. Using the "Hellige" silica turbidity standard, (See Note 1) prepare a series of standard turbidity solutions containing 4, 16, 24, 48, and 72 ppm silica as follows:

   a. Pipet into 250 ml volumetric flasks 5, 20, 30, 60, and 90 ml aliquots of the silica turbidity standard, 200 ppm silica.

b. Dilute the solution in each flask to the calibration mark with distilled water. Stopper the flasks and invert each one several times to mix the solution thoroughly.

2. Shake each standard thoroughly and fill the appropriate cell. (See Note 3). Shake the cell for about 10 seconds after filling it. (See Note 4).

3. Measure the absorbancy of the various standards as compared to distilled water, using a spectrophotometer (See Note 5) at a wave length of 490 mμ. This is the observed standard absorbancy.

4. Using the same cell arrangement, obtain the cell correction absorbancy with water in both cells.

5. Subtract the cell correction absorbancy from the observed standard absorbancy to obtain the true standard absorbancy.

6. Plot the true standard absorbancy as the ordinate versus the known concentration as the abscissa using standard graph paper.

B. Determination of Sample

In the analysis of a single sample, run duplicate determinations.

1. Shake the material to be analyzed thoroughly to ensure a representative sample.

2. Rinse and fill an appropriate cell with the sample to be analyzed. Shake the cell thoroughly for approximately 10 seconds. (See Notes 3 and 4). Place the cell in the spectrophotometer (See Note 5), and measure the absorbancy as rapidly as possible against distilled water at 490 mμ. Record the result as the observed sample absorbancy. (See Note 6).

3. Using the same cell arrangement, determine the cell correction absorbancy when all cells contain distilled water. Record the result as the cell correction absorbancy.

4. Subtract the cell correction absorbancy from the observed sample absorbancy to obtain the true sample absorbancy.

5. Determine the turbidity as ppm silica from the standard curve.

Notes

1. In the absence of the "Hellige" silica turbidity standard, fuller's earth may be used to prepare the standards.

2. The standard curve should be based on at least two sets of data.

3. With the Beckman spectrophotometer use cells having a 50 mm light path and a sensitivity setting of 2. For a Coleman spectrophotometer use cells having a 40 mm light path.

4. When shaking the sample in the absorption cells, do not touch the optical faces with the fingers. Any smudges or finger prints on these faces will render the results worthless.

5. Refer to the manufacturer's instruction booklet, for details of operation of the Beckman Model B spectrophotometer or the Coleman Model 14 spectrophotometer.

6. If the absorbancy changes due to the settling out of particles, dilute the sample and redetermine the absorbancy. (Correct the measured turbidity for the dilution).

HEAVY WATER: TOTAL SOLIDS

Gravimetric Method

References

American Public Health Association, American Water Works Association, and Federation of Sewage and Industrial Wastes Association. Standard Methods for the Examination of Water, Sewage, and Industrial Wastes. 9th Ed. New York: American Public Health Association (1946) p. 145.

Principle and Limitations

A measured volume of sample is evaporated to dryness in a tared evaporating dish. The dissolved and suspended solids remain in the dish which is reweighed. The difference in weight is calculated as parts per million total solids.

Equipment

1 Evaporating dish, porcelain, 100 ml
1 Volumetric flask, size of sample aliquot

Procedure

1. Place a clean, dry porcelain dish in a drying oven at 105°C for one hour.
2. Transfer the dish to a desiccator and allow it to cool for 30 minutes.
3. Weigh the dish to the nearest 0.0001 g. Record the weight.
4. Measure the required sample aliquot into a volumetric flask. (See Note 1).
5. Place the tared evaporating dish over the mouth of the flask. Carefully invert the dish and the flask.
6. Place the dish and the flask in this inverted position on the steam bath.
7. Lift the flask slightly to allow 1/4 in. of sample in the dish. Support the flask in this position by means of a ring support.
8. Evaporate the sample to dryness.
9. Transfer the dish to a drying oven at 105°C and allow it to remain in the oven for one hour.
10. Transfer the dish to a desiccator and allow it to cool for 30 minutes.
11. Weigh the dish and residue to the nearest 0.0001 g and record the weight.

Calculations

$$\text{ppm total solids} = \frac{(A - B) \times 10^6}{C(1 + 0.0011\ D)}$$

where

A = weight of evaporating dish and residue, g
B = weight of empty evaporating dish, g
C = volume of sample, ml
D = D_2O concentration of sample, wt %

Note

1. The sample aliquot should be large enough so that the total solids content can be determined to within ±1%.

HEAVY WATER: DISSOLVED MERCURY

Colorimetric Method

References

1. Snell, F. D. and C. T. Snell. Colorimetric Method of Analysis, 3rd Ed., 2. New York: D. Van Nostrand Co., Inc., (1951), pp. 1-8, 70-71.

2. Sandell, E. B. Colorimetric Metal Analysis, 2nd Ed., 3. New York: Interscience Publishers, (1950), pp. 87-112, 444-446.

Principle and Limitations

Dithizone dissolved in carbon tetrachloride will extract mercury from an aqueous solution forming an unstable orange colored complex. The extraction occurs best if the solution is made acidic with sulfuric acid. In an acidic solution silver, copper, gold, and palladium will also develop color with dithizone. The green color of the dithizone reagent absorbs light at a wave length of 620 millimicrons. The color complex is made more stable by the addition of acetic acid. The decrease in the intensity of the green color of the dithizone reagent due to the formation of the mercury complex is measured spectrophotometrically and is the means of determining the mercury content of the sample.

This method is not applicable to turbid samples and therefore can only be used if some means of eliminating turbidity is added as a preliminary step to this analysis.

Equipment

1	Spectrophotometer, Beckman, Model B
3	Cells, absorption, 10 mm light path
3	Flasks, volumetric, 2000 ml
3	Flasks, volumetric, 500 ml
3	Funnels, separatory, large
1	Pipet, Mohr, 25 ml
2	Pipets, volumetric, 10 ml
2	Pipets, volumetric, 5 ml
1	Pipet, volumetric, 2 ml

Reagents

1. Acetic acid, CH_3COOH, 6N
2. Dithizone reagent, 0.001% (diphenylthiocarbazone, CP in CCl_4, CP)
3. Sulfuric acid, H_2SO_4, 25N
4. Carbon tetrachloride, CCl_4, CP

Procedure

A. Calibration

1. Using reagent grade mercuric chloride and distilled water prepare a stock mercury solution containing 100 ppm of mercury (0.1354 g of mercuric chloride per liter).
2. Prepare a working standard solution by diluting 10 ml of the above solution to one liter. (1 ml contains 0.001 mg of mercury).
3. Pipet, carefully, duplicate 2, 5, 7, and 10, and 15 ml samples of the working standard solution into separate 500 ml volumetric flasks, containing 200 ml of distilled water. This represents 0.004 ppm, 0.010 ppm, 0.015 ppm, 0.021 ppm, and 0.031 ppm on the basis of a 480 g sample.
4. Prepare a reference sample in the following manner:
    a. Add 20 ml of 25N sulfuric acid to 400 ml of distilled water in a 500 ml volumetric flask.

    b. Dilute to the mark with distilled water.

    c. Transfer the contents of the 500 ml flask to a 2 liter volumetric flask and add by pipet 5 ml of 6N acetic acid and 10 ml of carbon tetrachloride.

    d. Stopper and shake for 10 minutes.

    e. Transfer to a large separatory funnel and allow the layers to separate.

    f. Fill a clean, dry, 10 mm absorption cell with the carbon tetrachloride layer. This is the "sample reference".

5. To the 500 ml flask containing 2 ml of the standard mercury solution (Step 3), add 20 ml of 25N sulfuric acid and dilute to the mark with distilled water.

6. Transfer the solution to a 2 liter volumetric flask and add by pipet 5 ml of acetic acid and 10 ml of 0.001% dithizone reagent. Stopper and shake for 10 minutes.

7. Transfer to a large separatory funnel and allow the layers to separate.

8. Fill a clean, dry, 10 mm absorption cell with the dithizone layer and immediately measure the absorbancy against the sample reference prepared in Step 4 with the spectrophotometer using a wave length of 620 millimicrons, a sensitivity of 2, and red-sensitive phototube. Record as "sample absorbancy".

9. Repeat Steps 5 through 8 with the other standard solutions.

10. Prepare a blank by following Step 4 but substitute 10 ml of 0.001% dithizone for the carbon tetrachloride.

11. Measure the absorbancy of the blank immediately against the sample reference keeping the absorption cells in the same order and using the same wave length, sensitivity and phototube as in Step A-8. Record as "blank absorbancy".

12. Plot the difference in absorbancy (blank absorbancy - sample absorbancy) as the ordinate vs. the concentration in ppm as the abscissa on standard graph paper.

B. Determination of Sample

1. Prepare a sample reference as under Calibration (Step A-4).

2. Determine the absorbancy of a blank against the sample reference as under Calibration (Steps A-10 and A-11).

3. If the sample to be analyzed is approximately neutral make 1N by adding 20 ml of 25N sulfuric acid to the sample in a 500 ml volumetric flask and fill to the mark with the sample. The final amount of sample to be used is now approximately 480 g. If the sample is not neutral, neutralize with a few drops of concentrated sulfuric acid or sodium hydroxide; then add 20 ml of 25N sulfuric acid and fill to the mark with neutral sample.

4. Transfer the solution to a 2 liter volumetric flask and add by pipet 5 ml of 6N acetic acid and 10 ml of 0.001% dithizone reagent.

5. Stopper and shake for 10 minutes.

6. Transfer to a large separatory funnel and allow the layers to separate.

7. If the green color has not completely disappeared (See Note 1), fill a clean, dry, 10 mm absorption cell with the dithizone layer and measure immediately the absorbancy of the sample against the sample reference with the spectrophotometer using a wave length of 620 millimicrons, a sensitivity of 2 and a red-sensitive phototube. Record as "sample absorbancy".

Calculations

1. (A - B) = difference in absorbancy

where

A = blank absorbancy (Step B-2)
B = sample absorbancy (Step B-7)

2. Using the prepared graph determine the ppm of mercury corresponding to the difference in absorbancy.

Note

1. If the green color of the dithizone is replaced by the orange color, the original sample must be diluted and re-analyzed.

HEAVY WATER: CHLORIDE

Turbidimetric Method

Principle and Limitations

The addition of silver nitrate to a water sample containing chloride, to which has been added methyl alcohol, nitric acid, and sodium sulfate, produces a turbidity that is proportional to the amount of chloride present in the sample.

The procedure will give a straight line standard curve in the range 0.005 to 0.100 mg Cl per 50 ml volume (0.1 ppm to 2 ppm Cl).

The method deviates from Beer's law with increasing concentrations. The particles of silver chloride continue to grow with time and will settle out in higher concentrations. The other halogens interfere.

This method cannot be used for turbid solutions unless some means of removing the turbidity prior to analysis is incorporated. In some cases, it may be necessary to remove any color as well.

Equipment

Preparation of Standard Curve

1	Transfer pipet, 1 ml
1	Transfer pipet, 2 ml
3	Transfer pipets, 5 ml
1	Transfer pipet, 10 ml
4	Volumetric flasks, 50 ml
1	Spectrophotometer, Beckman Model B or equivalent
2	Absorption cells, 50 mm light path

For Analysis of Sample

1	Transfer pipet, 1 ml
2	Transfer pipets, 5 ml
3	Volumetric flasks, 50 ml
1	Spectrophotometer, Beckman Model B or equivalent
2	Absorption cells, with 50 mm light path

Reagents and Chemicals

Sodium chloride standard solution, 0.005 mg as Cl/ml
Methyl alcohol, CP, CH_3OH
Sodium sulfate (0.35M)-Nitric acid (2.3M)
Silver nitrate, 0.075N

Procedure

A. Preparation of Standard Curve

1. Pipet 2, 5, and 10 ml of the 0.005 mg Cl/ml standard into separate 50 ml volumetric flasks. Using distilled water, dilute to approximately 35 ml.

2. Using the standard solutions, follow Steps 2 through 8 of Part B, Analysis of Sample.

3. Calculate the corrected absorbance of each standard reagent solution by subtracting the observed absorbance of the reagent reference from the observed absorbance of each standard reagent solution.

4. Plot the corrected absorbance of the standard reagent solutions as the ordinate vs. the concentration as the abscissa on rectilinear graph paper.

B. Analysis of Sample

1. Pipet an aliquot of sample containing 0.01 to 0.1 mg of chloride into each of two 50 ml volumetric flasks. Using distilled water, dilute to approximately 35 ml. These will be the sample reagent solutions. (See Note 1).

2. To another 50 ml volumetric flask, add approximately 35 ml of distilled water. This will be the reagent reference.

3. Using transfer pipets, add the following to each flask:

   a. 5 ml of methyl alcohol
   b. 5 ml of sodium sulfate-nitric acid solution

4. Mix the solutions well. They should be clear at this point.

5. Using a transfer pipet, add 1 ml of 0.075N silver nitrate to each flask and dilute to 50 ml with distilled water.

6. Mix by slowly inverting and turning the flasks. DO NOT SHAKE VIGOROUSLY.

7. Allow the solutions to stand 10 minutes, but not in excess of one hour.

8. With a spectrophotometer, determine the absorbancies of the sample reagent solutions and the reagent reference compared to distilled water. Use cells with a 50 mm light path and a wave length of 450 mμ. (See Note 2). Record the readings as the observed absorbancies of the sample reagent solutions and the reagent reference.

Calculations

Corrected absorbance of the sample reagent solution = A - B

where

A = observed absorbance of the sample reagent solution
B = observed absorbance of the reagent reference

Using the standard curve, determine the weight (mg) of chloride corresponding to the corrected absorbance of each sample reagent solution.

$$\text{ppm Chloride} = \frac{C \times 1000}{D}$$

where

C = weight of chloride from standard curve, mg
D = volume of sample aliquot taken for analysis, ml (Step B-1) (See Note 3)

Notes

1. If the sample is colored, pipet an equal aliquot of sample into another 50 ml volumetric flask. This will be the sample blank. Follow Steps 3 through 8 of Part B, Analysis of Sample, but omit the addition of silver nitrate in Step 5. If the absorbancy of the sample blank is greater than 0.1, it would be preferable to incorporate some means of removing the color prior to the analysis. To obtain the corrected absorbance of each sample reagent solution, make the following calculations:

   Corrected absorbance of the sample reagent solution
   $= A - (B + E)$

where

A = observed absorbance of the sample reagent solution
B = observed absorbance of the reagent reference
E = observed absorbance of the sample blank

2. For details of operation of the spectrophotometer, refer to the manufacturer's operating instructions for the spectrophotometer.

3. If the sample has been concentrated, calculate the volume of the sample aliquot used for analysis as follows:

   $$\text{Volume of sample aliquot used for analysis, ml} = \frac{H \times F}{G}$$

where

H = volume of original sample used for concentration, ml
F = aliquot of concentrated sample used for analysis, ml (Step B-1)
G = volume to which the sample was concentrated, ml

HEAVY WATER: PERMANGANATE DEMAND
Volumetric Method

References

American Public Health Association, American Water Works Association, and Federation of Sewage and Industrial Wastes Association. Standard Methods for the Examination of Water, Sewage, and Industrial Wastes. 9th Ed. New York: American Public Health Association (1946) p. 122.

Furman, N. H. and W. W. Scott. Scott's Standard Methods of Chemical Analysis, 5th Ed., II New York: D. Van Nostrand Co., Inc., (1950) p. 2053.

Principle and Limitations

The oxidizable matter in the sample is oxidized by refluxing for one hour with potassium permanganate. A distilled water blank is treated in the same manner and the difference between the amount of potassium permanganate consumed by the sample and by the blank is a measure of the oxidizable matter in the sample.

Equipment

1	Graduated cylinder, 100 ml
3	Distilling flasks, round bottom, 300 ml with 20/40 ST ground-glass joint (See Note 1)
2	Burets, 50 ml
1	Buret, 10 ml
	Boiling chips
3	Condensers, straight, water-cooled with 20/40 ST ground-glass joint at neck (See Note 1)
1	Electric heater

Reagents and Chemicals

Potassium permanganate, 0.01N, standardized
Sulfuric acid, 9N
Oxalic acid, 0.01N

Procedure

1. Using a graduated cylinder, add 100 ml of sample to a 300 ml, round bottom distilling flask.

2. Using a calibrated buret, add 10 ±0.01 ml of 0.01N potassium permanganate to the distilling flask. Record the volume of potassium permanganate added.

3. Add, from a buret, 5 ml of 9N sulfuric acid to the flask.

4. Add several boiling chips to the flask to prevent bumping. Attach the condenser and turn on the condenser water. (See Note 2).

5. Using an electric heater, reflux the sample gently for one hour. The sample should reflux approximately 2 inches into the condenser.

6. Cool the sample below the boiling point, but not under 80°C. Disconnect the condenser.

7. Using a buret, add 40.0 ml of 0.01N oxalic acid to the distillation flask. Swirl the flask gently until all the color and any precipitate has disappeared.

8. Using a buret, titrate the excess oxalic acid with 0.01N potassium permanganate to the first faint pink color that persists for one minute. (See Note 3). Record, to the nearest 0.01 ml, the volume of potassium permanganate required for the titration.

9. Run a blank by following Steps 1 through 8, substituting 100 ml of distilled water for the sample.

Calculations

$$\text{Potassium permanganate, g/ml} = \frac{[(A + B) - (C + D)] \times E \times F}{G}$$

where

A = volume of potassium permanganate added to the sample, ml (Step 2)
B = volume of potassium permanganate required for the titration of the excess oxalic acid in the sample, ml (Step 8)
C = volume of potassium permanganate added to the blank, ml (Step 2)
D = volume of potassium permanganate required for the titration of the excess oxalic acid in the blank, ml (Step 8)
E = normality of potassium permanganate
F = gram milliequivalent weight of potassium permanganate $= \frac{158.03}{5 \times 1000} = 0.0316$
G = volume of sample, ml

Notes

1. The distilling flasks and condensers can be obtained from Eck and Krebs, Inc., 27-09 40th Ave., Long Island City 1, New York.

2. To prevent contamination, all connections must be free from grease, oil, and other oxidizable material.

3. The temperature of the sample must be maintained between 80 and 90°C during the titration.

HEAVY WATER: TRITIUM
Vibrating Reed Electrometer Method

References

Palevsky, H., R. K. Swank, and R. Grenchik, "Design of Dynamic Condenser Electrometers", *Review of Scientific Instruments*, *18*, pp. 298-314, (1947) May, No. 5.

"Instruction Manual for Vibrating Reed Electrometer, Model 30," Applied Physics Corporation, Pasadena, California.

Principle and Limitations

A water sample is decomposed by metallic calcium, using calcium chloride as a catalyst. The gaseous products are collected in an ion chamber across which a potential of 300 volts is applied. The resulting current flow between the two electrodes is proportional to the tritium radioactivity present in the sample. Standard curves are prepared by analyzing samples of known concentration. A sample of greater than 400 µc/ml is diluted to within this range.

Equipment (See Note 1)

1	Vibrating Reed Electrometer and Accessories (Figure VI-1)
2	Reaction flasks, 125 ml, "Pyrex", with 24/40 \$ joint
2	Y-Adapters, "Pyrex", with two 24/40 \$ joints and one 14/20 \$ joint
2	Sample burets, "Pyrex", with 14/20 \$ joint
1	Vacuum pump
1	Vacuum gage, 0-30 inches of mercury
1	Battery, 300 volts

Reagents and Chemicals

Calcium, CP, Ca
Calcium chloride, CP, $CaCl_2$
Silica gel, $SiO_2 \cdot xH_2O$

Procedure

A. Preparation of Standard Curve

1. Using four tritium standards, between 10 and 400 μc/ml follow Steps 1 through 15 of Part B, Analysis of Sample.

2. Using equations (a) and (b) in the Calculations section, calculate the corrected current flow in amperes.

3. Plot, on rectilinear graph paper, the corrected current flow in amperes against the concentration of tritium in microcuries/ml.

B. Analysis of Sample

In the analysis of a single sample, run duplicate determinations.

1. Place approximately 3 g of calcium and 3 to 4 granules of calcium chloride in a clean, dry, 125 ml reaction flask.

2. With the meter switch in the center position and the turret switch in the GROUND position, assemble the glassware. Use stopcock grease on all joints.

3. Open stopcocks A, B, and C. Close stopcock D. (See Figure VI-2). Make certain that water is circulating in the condenser.

4. Start the vacuum pump and evacuate the system until the vacuum gage reads approximately 30 inches of mercury.

5. Close stopcock A and observe the vacuum gage for one minute. A decrease in the reading on the gage indicates a leak. (See Note 2).

6. If no leak is observed, slowly open stopcock D until the system reaches atmospheric pressure as indicated by a zero reading on the vacuum gage. Close stopcock C.

7. Set the turret switch to the GROUND position. Connect the terminal leads to the 300 volt battery. Set the range selector on 1000. Place the meter switch in the NEGATIVE position and zero the meter by adjusting the zero knob.

8. Move the turret switch to the 1, 2, and 3 position until a reading on the millivolt meter is obtained.

9. If no reading can be obtained, return the turret switch to the GROUND position and change the range selector to the 100, 10, or 1 position. Re-zero the meter after each change in selector position. Repeat Step 8 after each change of range until a reading is obtained on the millivolt meter.

10. Record, to the nearest 0.01 millivolt, the meter reading. Record the turret setting and the range selector setting. After the readings are recorded, return the turret switch to the GROUND position and the range selector to the 1000 position.

11. Repeat Steps 3, 4, and 5.

12. Add approximately 5 ml of sample to the sample buret.

13. Introduce the sample by slowly opening stopcock D and allowing the sample to enter the reaction flask dropwise until the pressure of the system is at atmospheric pressure as indicated by the vacuum gage. (See Note 3).

14. Close stopcock C.

15. Remove the apparatus containing the sample from the system.

16. Repeat Steps 7, 8, and 9.

17. Record, to the nearest 0.01 millivolt, the meter reading. Record the turret setting and the range selector setting.

Calculations

To determine the current flow (amperes) of the background or the sample, use the following equation.

$$\text{Current flow, amperes} = \frac{A \text{ x } B \text{ x } 10^{-3}}{C} \qquad \text{(a)}$$

where

A = recorded meter reading, (Step 10 for background; Step 17 for sample)
B = range selector setting (Step 10 for background; Step 17 for sample)
C = resistance, ohms (See Note 4)

To determine the corrected current flow (amperes), use the following equation:

Corrected current flow, amperes = D - E (b)

where

D = current flow of the sample, amperes (From equation a)
E = current flow of the background, amperes (From equation a)

Using the corrected current flow, determine from the standard curve the microcuries of tritium/ml corresponding to the corrected current flow in amperes. (See Note 5).

Notes

1. The glass assembly and ion chamber of the equipment are housed in a glove box equipped with an exhaust to carry tritium away from personnel zones.

2. If a leak is present, open stopcock D and disassemble the apparatus. Regrease all stopcocks and reassemble the apparatus. Repeat Steps 3, 4, and 5.

3. Pressures above or below atmospheric pressure will give inaccurate results.

4. The resistance for each turret setting is recorded on the turret head.

5. If the corrected current flow exceeds the maximum corrected current flow of the standard curve, dilute the sample with distilled water and repeat the analysis. Multiply the value obtained from the curve by the dilution factor.

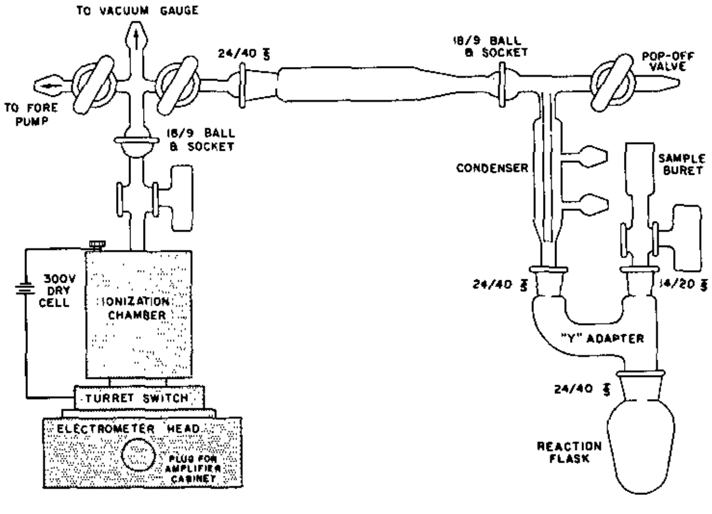

FIG. VI-2 VIBRATING REED ELECTROMETER

HEAVY WATER: GROSS BETA-GAMMA ACTIVITY
Geiger-Mueller Counting Method

References

Prohaska, C. A., The SRP Standard Geiger-Mueller Counter, E. I. du Pont de Nemours & Co., Aiken, S. C. AEC Research and Development Report DP-61, 27 pp. (1954).

Principle and Limitations

The gross beta-gamma activity of a sample is determined by evaporating a suitable aliquot to dryness and counting the activity in a Geiger-Mueller counter. The determined activity is based upon calibration of the counter with a Radium(D + E) standard source.

The precision of the method depends upon the amount of activity and the length of time the sample is counted.

Equipment

2	Dishes, Type 304 stainless steel
1	Infrared heater
1	Pipet, size of sample aliquot
1	Tweezers
	Cellophane tape
2	Holders, dish
1	"Lucite" carrier
1	Geiger-Mueller counter consisting of:
1	Geiger-Mueller tube, Tracerlab Model TGC-2/1B84, or equivalent
1	Scaler, Tracerlab Model CC-10, or equivalent
1	Lead shield for tube, Technical Associates Inc., Model AL14A, or equivalent

Reagents and Chemicals

Acetone, CP

Determination of Sample

In the analysis of a sample run duplicate determinations.

1. Clean the stainless steel dish by washing it with acetone and drying it with absorbent tissue.

2. Place the dish under an infrared heater and pipet the prescribed aliquot of the sample into the dish. (See Note 1)

3. Turn on the infrared heater to low heat. Adjust the heater to such a height that the sample evaporates without spattering.

4. Allow the sample to evaporate to dryness and then turn off the lamp.

5. After the dish has cooled, place it in a dish holder and secure the dish to the dish holder by means of cellophane tape. (See Note 2).

6. Determine the counting rate of the sample on the dish by means of the Geiger-Mueller Counter. (See Note 3). Record the registered counts and the length of time the sample was counted.

Calculations

$$\text{Gross beta-gamma disintegrations/min/ml} = \frac{D(J + H)}{E}$$

where

$$J = \frac{A}{B} - C$$

and:

A = uncorrected count for sample and background
B = time sample counted, minutes
C = background, counts per minute, c/m
D = normalizing factor = F/G
E = volume of sample, ml
F = Ra(D + E) d/m, theoretical for standard
G = Ra(D + E) c/m, determined in the Geiger-Mueller counter
H = counter coincidence correction

Notes

1. The sample size is determined by the expected activity and the precision desired.

2. Completely cover the dish with tape. This prevents any material from falling or blowing from the dish and contaminating other areas.

3. The count is determined with the source on the second shelf. The time of counting will be determined by the expected activity.

HEAVY WATER: GROSS ALPHA ACTIVITY
Counting Method

References

Rider, B. F., *Selected Analytical Methods for Purex Process Control*. General Electric Co., Schenectady, N. Y., Knolls Atomic Power Lab., AEC Research and Development Report KAPL-890, (1954), p. 51.

Rodden, C. J., *Analytical Chemistry of the Manhattan Project*. *National Nuclear Energy Series*. NNES VII-1, New York: McGraw-Hill (1950), p. 665.

Principle and Limitations

Samples for determination of gross alpha activity are evaporated on flat, stainless steel plates and counted for alpha activity in a methane proportional counter. A thin layer of collodion is applied to each plate after the sample evaporation to hold the dried material on the plate. The thin film of collodion has a negligible absorption for alpha particles and does not affect the counting rate of the sample. The instrument is set to operate in the alpha plateau and below the beta threshold, thus discriminating against beta activity. The count so obtained is designated as gross alpha since the instrument is not designed to distinguish between different alpha emitters.

The sample size is limited primarily by the activity of the sample. Alpha activity of the plate should not exceed 1×10^5 d/m. The beta activity is limited primarily by the danger of exposure of counting personnel to radiation.

Equipment

1	Forceps, 4 in. long
4	Dishes, stainless steel, 304
4	Plates, flat, stainless steel, 1-7/16 in. diameter
2	"Transite" boards or asbestos mats
4	Rings, stainless steel, 3/4 in. diameter
1	Infrared heater
	Micropipets, 1 set
2	Shielded pipet controls
1	Brush, camel's hair, 1/8 in. diameter
1	Disc ringer

1	Bunsen burner
1	"Transite" board tongs
4	Holders, dish
1	"Lucite" carrier
1	Alpha counter consisting of:
1	Proportional counter, Nuclear Measurement Corp., Model PCC-10, or equivalent
1	Scaler, Tracerlab, Model CC-10, or equivalent

Reagents and Chemicals

Nitric acid, 2M
"Zapon" solution, 1 part "Zapon": 3 parts thinner
Collodion solution, 0.5 mg solids/ml

Procedure

In the analysis of a single sample, run duplicate determinations.

1. Make any necessary preliminary sample dilutions.

2. Using forceps, place a clean, flat, stainless steel plate on either a "Transite" board, asbestos mat, or a stainless steel ring which is beneath an infrared heater.

3. Using a small brush and disc ringer, paint a "Zapon" ring on the plate.

4. Pipet the prescribed sample aliquot onto the center of the plate and inside the "Zapon" ring.

5. If a micropipet is used, rinse the pipet twice with 2M nitric acid and add the rinsings to the plate. All of the liquid should remain on the plate at this point. (See Note 1)

6. Turn on the infrared heater and evaporate the sample to dryness.

7. Turn off the heater and remove the plate from beneath the heater.

8. Using a Bunsen burner, flame the plate to a dull red heat and allow the plate to cool to room temperature on a "Transite" board.

9. Add 2 drops of collodion to the plate and allow the collodion to spread over the surface. (See Notes 2 and 3)

10. After the plate has air dried for 5 minutes, count in a methane proportional counter for at least three minutes. (See Note 4)

Calculations

Alpha disintegrations/min/ml = A x B x C

where

A = alpha counts/minute (from counting room)
B = dilution factors (if any)
C = geometry factor for proportional counter (determined from standards).

Notes

1. When the sample size is excessive, use a transfer pipet for the sample and omit rinsing the pipet.

2. The plate must be cool at this point, otherwise the collodion will form an uneven deposit due to rapid evaporation. When this happens, erratic results may be obtained due to absorption of the alpha particles in the thick portions of the collodion film.

3. The drops of collodion must be evenly spaced on the surface of the plate.

4. The counting period required to ensure analytical reliability will depend on the total alpha activity of the plate and should be determined after the approximate activity is observed.