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FINAL ISOLATION AND PURIFICATION OF
THE TRANSPLUTONIUM ELEMENTS FROM
THE TWELVE CAMPAIGNS CONDUCTED AT TR
DURING THE PERIOD
AUGUST 1967 — DECEMBER 1971

R. D. Baybarz
J. B. Knauer
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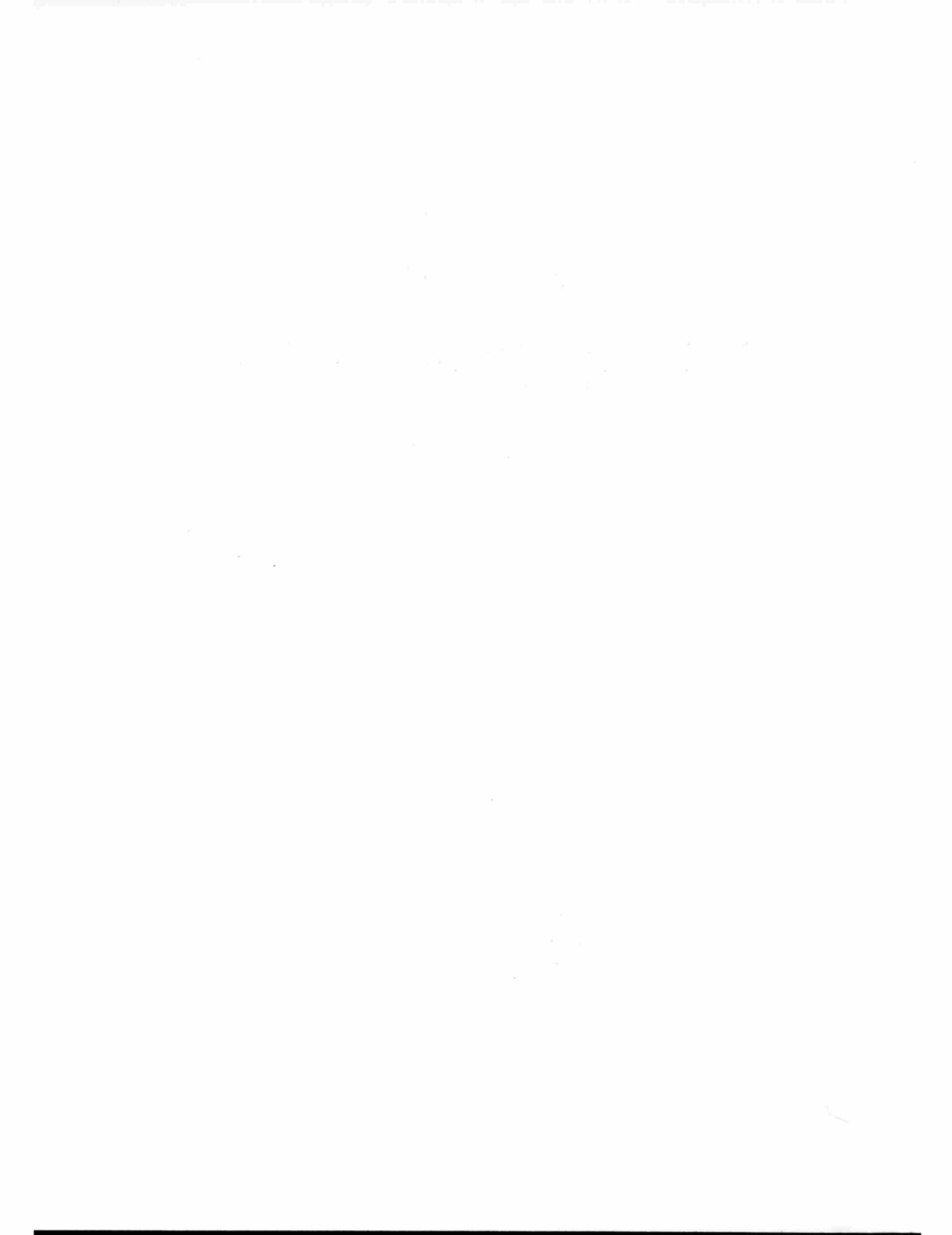
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APRIL 1973

OAK RIDGE NATIONAL LABORATORY
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ABSTRACT

Problems previously encountered in the final purification and isolation of the transplutonium elements have largely been resolved by the development of new equipment and techniques. Control of the LiCl anion exchange process has been assumed by TRU Operations, and the cation exchange process has been improved by use of the pressurized system. A new Californium Facility has become operational, making possible the isolation of pure ^{248}Cm . A total of 313 mg of ^{252}Cf , 1140 μg of ^{253}Es , 30 mg of ^{249}Bk , 1.7 mg of ^{249}Cf , 7.8 mg of ^{248}Cm , and 4.5×10^9 atoms of ^{257}Fm were isolated and purified in the 12 campaigns carried out during the period from August 1967 to December 1971.

1. INTRODUCTION

This report covers the progress made in the final isolation and purification of the heavy actinides during the period August 1967-December 1971.¹ This time interval has seen three major modifications in the procedure for the final processing of the transplutonium elements. In August 1967, the LiCl anion exchange partitioning of these elements was scaled up about threefold and transferred from cubicle 5 to cubicle 6 of the Transuranium Processing Plant (TRU). Responsibility for this process was assumed by the TRU Operations Group. The second change was the development of the pressurized cation exchange system by Campbell and Buxton,² and our subsequent adaptation of this system to high-activity-level processing. The third modification involved the startup of the Californium Facility located in the Thorium-Uranium Recycle Facility (TURF). Equipment racks, which contained the temporary glassware formerly used in purification of the actinides, have been replaced by racks containing pressurized ion exchange columns, extraction chromatography

columns, high-pressure pumps, glass storage pots, and bottle storage racks.

Initial processing of the HFIR irradiated targets, which is done by TRU Operations, has also undergone modifications and improvements.

The following is a list of the steps comprising the procedure currently being used at TRU:

1. The aluminum-clad targets are dissolved in NaOH-NaNO₃, and the NaAlO₃ is removed by filtration.
2. The actinide oxides are dissolved in HCl or HNO₃.
3. Plutonium and zirconium are removed by batch solvent extraction using di(2-ethylhexyl)phosphoric acid (HDEHP) in diethylbenzene (DEB) diluent.
4. Metallic impurities are removed by batch solvent extraction of the actinides with HDEHP in Amsco 125-82 diluent.
5. Most of the fission products are removed by batch solvent extraction^{3,4} using Adogen 364 HP in DEB diluent.
6. Partitioning of the actinides and further fission product removal are accomplished via LiCl anion exchange.⁵
7. The transcurium products from the LiCl anion exchange runs are precipitated as hydroxides, which are subsequently filtered, dissolved in nitric acid solution, and transferred to cubicle 5 for separation.

Progress reports describing the main-line processing are published on a semiannual basis; the most recent one in the series is ORNL-4833.

In the 12 campaigns made from August 1967 through December 1971, 237 targets were processed:

- (1) twelve ^{242}Pu HFIR targets, which had been irradiated in both the HFIR and an SRP reactor,
- (2) thirteen ^{242}Pu HFIR targets,
- (3) six ^{244}Cm - ^{243}Am HFIR targets,
- (4) seven ^{242}Pu HFIR targets and one-half ^{244}Cm - ^{243}Am HFIR target,
- (5) seven ^{242}Pu HFIR targets and one-half ^{244}Cm - ^{243}Am HFIR target,
- (6) seven ^{242}Pu and two ^{244}Cm - ^{243}Am HFIR targets,
- (7) thirty-five ^{244}Cm - ^{243}Am SRP target slugs,
- (8) thirty-two ^{244}Cm - ^{243}Am SRP target slugs,
- (9) thirty ^{244}Cm - ^{243}Am SRP target slugs,
- (10) thirty-two ^{244}Cm - ^{243}Am SRP target slugs,
- (11) thirty-five ^{244}Cm - ^{243}Am SRP target slugs,
- (12) thirteen ^{242}Pu and five ^{244}Cm HFIR targets.

2. DESCRIPTION OF EQUIPMENT

2.1 Primary-Isolation Purification Equipment, Cubicle 5, TRU

Figure 1 is a photograph of the right-hand rack that replaced the temporary glass-equipment rack previously used. Like the earlier one, the replacement rack had the dimensions 69 x 34 x 16.5 in.; however, being of a more permanent nature, it was used for three years. In June 1970, this rack was replaced by the further improved version depicted in Fig. 2. The basic equipment in the new rack consists of a pressurized, hot-water-jacketed ion exchange column 3/8 in. in outer diameter by 4 ft long; a hot-water-jacketed ion exchange column 1/2 in. in outside diameter by 4 ft long; and a pressurized column 1/2 in. in outside diameter by 8 in. long. A variable-speed, variable-stroke, high-pressure piston pump with associated piping and valves of stainless steel

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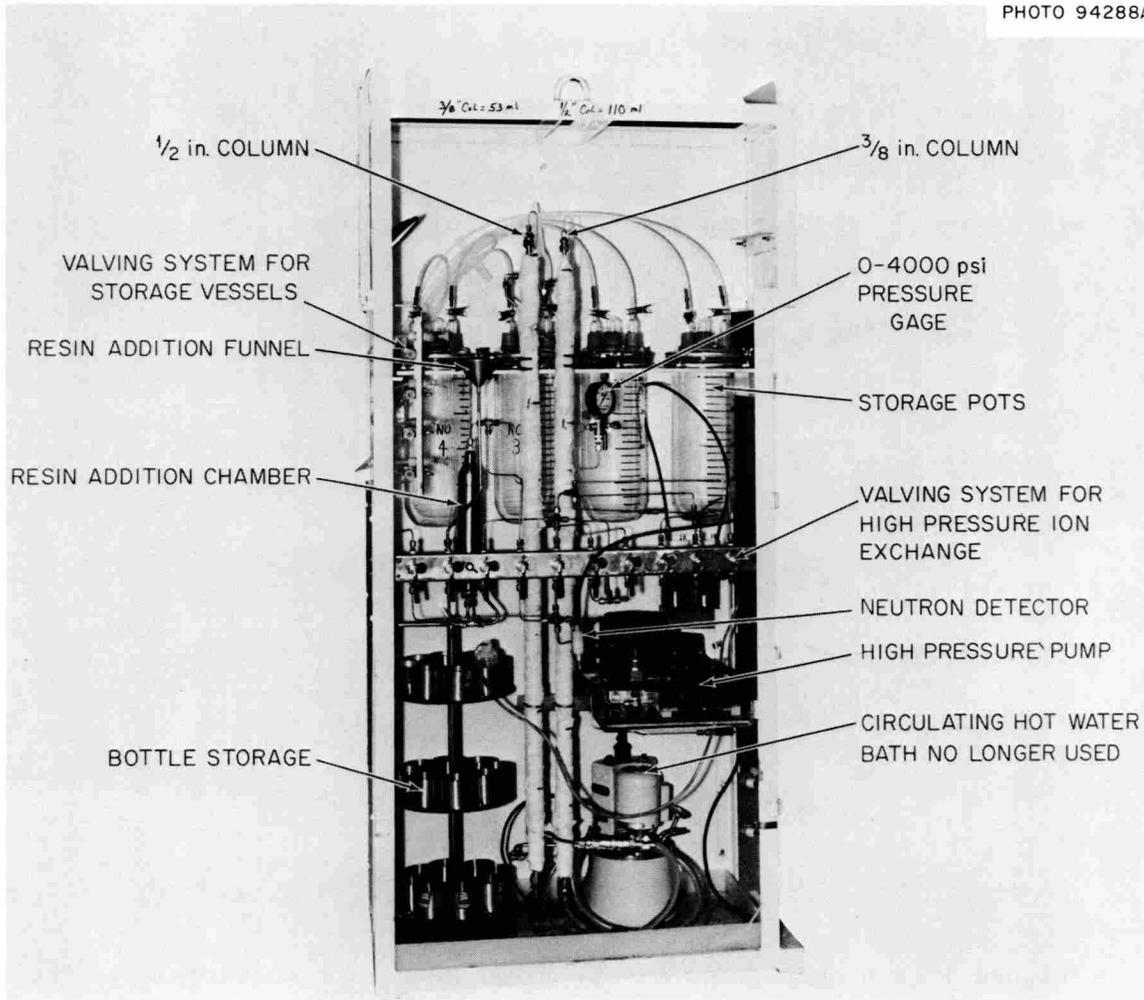


Fig. 1. First Pressurized Ion Exchange Rack Installed at TRU.

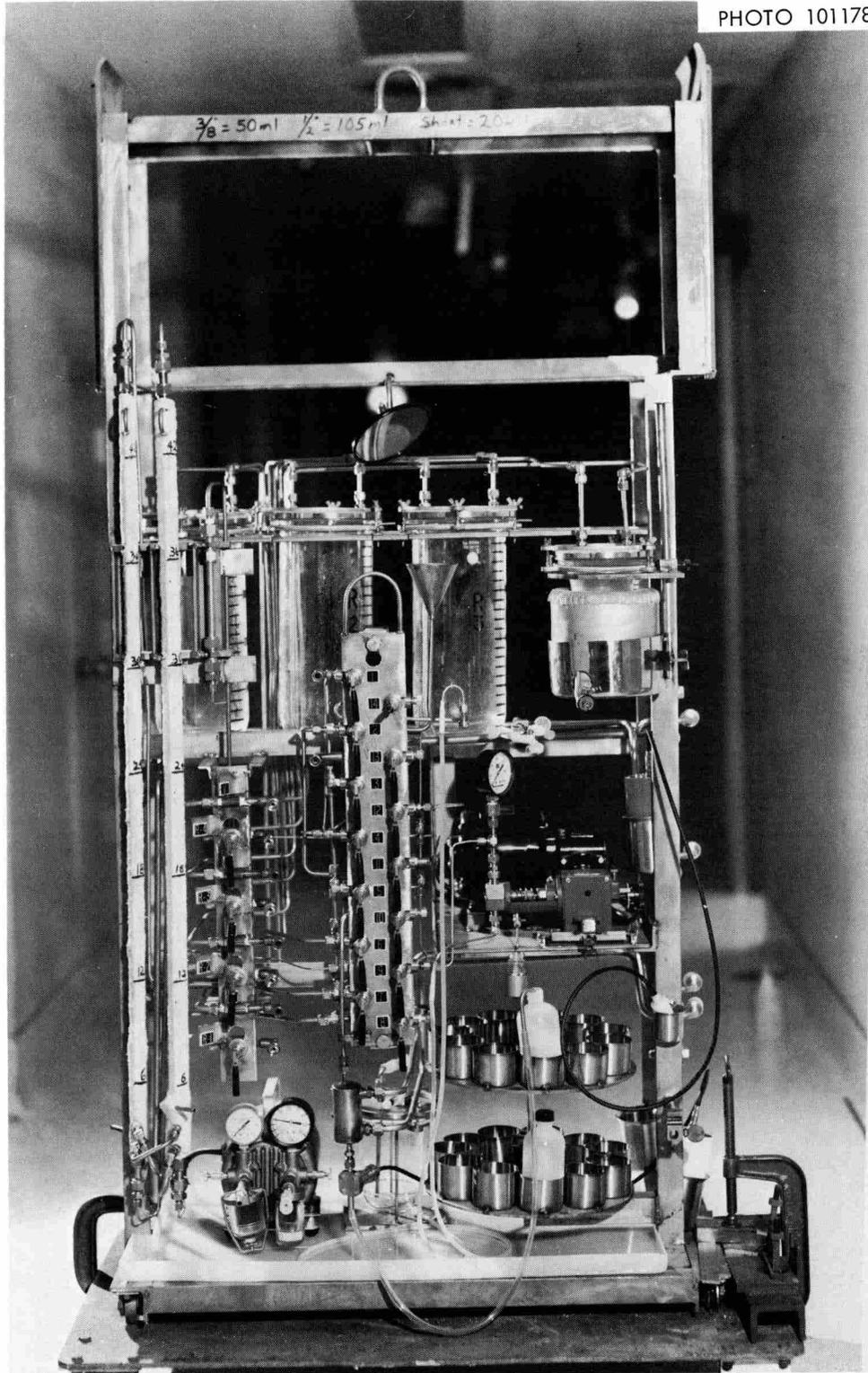


Fig. 2. Present Pressurized Ion Exchange Processing Rack.

is employed to operate the column system; discharge from the system is routed through a flow-through alpha detector⁶ to fraction collection bottles held in a two-tier, rotating bottle rack. Hot water (80°C) is supplied to the columns.

Three 4-liter glass pots, each equipped with dip legs and vent lines of stainless steel, are used for solution transfer and storage. They are mounted near the top of the equipment rack. A fourth glass pot, equipped with vent line, dip leg, and removable heating mantle, is used to degas concentrated feeds prior to loading onto the pressurized columns.

The back rack (shown in Fig. 3) which contains equipment designed for multiple processing procedures, was installed in cubicle 5, TRU, in July 1970. The column system of this rack consists of two pressurized, hot-water-jacketed ion exchange columns (one of which is 1 in. in inside diameter by 4 ft long and the other is 1/2 in. in inside diameter by 4 ft long) and a loading column 1 in. in inside diameter by 8 in. long. A Lapp Pulsafeeder variable-speed pump with associated stainless steel piping and valves is used to operate the column system. The loading column can be operated alone or in series with either of the other two columns; the discharge is routed through an in-line alpha detector. The TRU Facility system supplies hot water to the jacketed columns. The rack is also equipped with three 4-liter glass pots with dip legs and vent lines for solution transfer and storage. Two additional 4-liter pots, each of which is equipped with an electric stirrer and ball valve in order to make solvent extractions and phase separations, are installed near the top of the rack. A laboratory centrifuge and a precipitation pot are also mounted in this rack.

2.2 Purification Equipment, Laboratory 111, TRU

Laboratory 111 in TRU contains two hot cells, junior caves A and B, and a 6-ft alpha glove box. Equipment in each cave (cave B is shown in Fig. 4) consists of a pressurized, hot-water-jacketed ion exchange column (3/8 in. ID by 4 ft in junior cave A and 1/4 in. ID by 4 ft in junior cave B), a variable-stroke and -speed piston pump with associated piping,

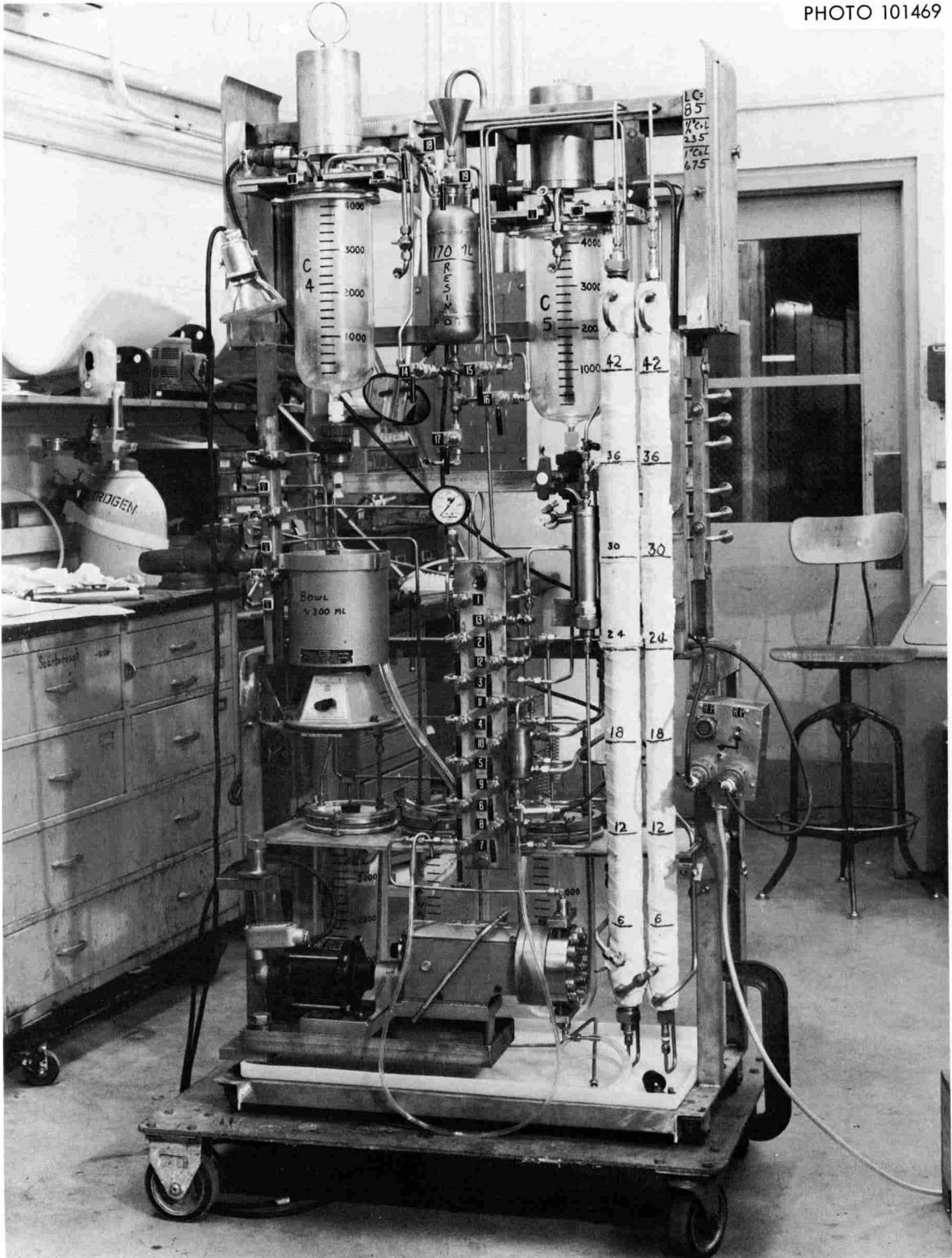


Fig. 3. Multiple-Processing Final Separations Rack.

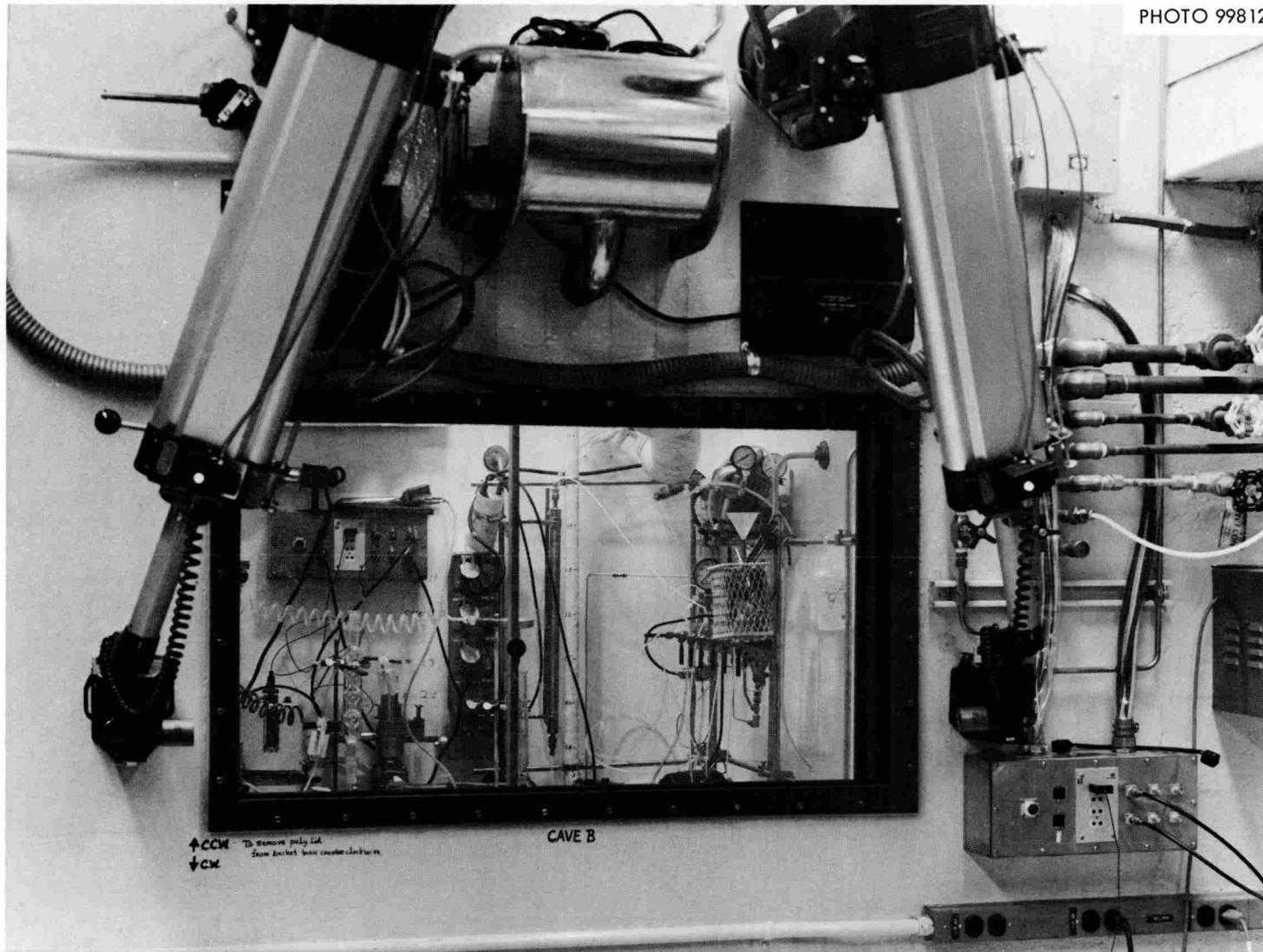


Fig. 4. Junior Cave B with Pressurized Ion Exchange Equipment.

and a valve manifold for operation of the column system. Each cave also contains a 3/8-in.-OD by 2-ft-high pressurized extraction chromatography column and a 1-in.-ID by 6-in.-high concentration column. These columns are not water-jacketed. Each cave is equipped with a neutron probe, consisting of a silicon diode detector with a polyethylene face, which is used in conjunction with a count-rate meter to detect californium in solutions and to follow the ^{252}Cf band movement on the columns. All columns in the systems are discharged through a flow-through alpha detector to product fraction bottles held in portable bottle racks. A thermostatically controlled circulating water bath with a 2-liter capacity is used to maintain the temperature of the ion exchange columns at 80°C . Small diaphragm vacuum pumps, equipped with a soda-lime trap ahead of the pump to prevent vapors from corroding the pump mechanism, are used for liquid transfers and filtrations.

The solvent extraction equipment located in junior cave A consists of a standard 1-liter separatory funnel equipped with an air-drive stirring motor for contacting organic and aqueous phases. This system is used in the first- and/or second-cycle separation of ^{249}Bk from ^{244}Cm and ^{252}Cf . Extractions of this type are not done in junior cave B, since it is desirable to keep this area free of ^{244}Cm contamination.

A special feature incorporated into junior cave B is a hydraulic transfer system connected directly to the HFIR reactor pool. This system permits specially irradiated HFIR targets to be transferred rapidly to junior cave B for processing and subsequent separation and purification of the HFIR-produced isotopes.

The 6-ft alpha glove box is equipped with a 1/4-in.-ID by 2-ft-high pressurized, hot-water-jacketed ion exchange column, a 1/4-in.-ID by 6-in.-high concentration column, a variable-speed and -stroke high-pressure pump and associated piping, and a valve manifold for operation of the columns. An alpha probe, consisting of a silicon diode detector with a 0.005-in. Mylar window coupled with a count-rate meter, is used to detect the alpha activity in each drop of effluent. This makes it possible to obtain exact

product fractions. Hot water (80°C) is supplied to the ion exchange column by a circulating hot-water bath located outside the glove box.

2.3 Purification Equipment Located in the TURF Californium Facility

Figures 5 and 6 show the equipment racks in cubicles 1 and 2, which were installed in cell G at TURF. These racks became operational in March 1970. The basic equipment on the rack in cubicle 1 consists of two pressurized hot-water-jacketed ion exchange columns (one 3/8 in. ID by 4 ft high and the other 1/4 in. ID by 4 ft high), a 1/4-in.-ID by 2-ft-high extraction chromatography column, a 3/8-in.-diam by 6-in.-high loading column, a high-pressure pump with associated piping, and a valve manifold for the column system. Two 2-liter and two 4-liter glass pots with stainless steel tops, dip legs, and vent lines, used for feed adjustment and storage, are mounted at the top of the rack. Transfers to and from these pots are made using a small diaphragm vacuum pump operated through a valve manifold of stainless steel lines and toggle valves. A liquid trap is located ahead of the vacuum pump to protect it from corrosive liquids.

The equipment rack in cubicle 2 is basically the same as the rack in cubicle 1 except that the storage pot system is not included. Also, it contains a "utility site," which is used for the operation of concentration columns, extraction chromatography columns, the loading of californium shipping capsules, and the loading of californium neutron sources. Both racks utilize flow-through alpha detectors and neutron probes to aid in making fraction cuts and in locating ^{252}Cf in solution or on the columns. Each cubicle is equipped with three rotating bottle racks, each for a different size of fraction collection bottle.

A pneumatic transfer system from the decontamination facility in TRU to the TURF Californium Facility (cell G of TURF) has recently become operational. This transfer system provides a method of rapid transfer of californium to TURF for further decontamination from ^{244}Cm and eliminates the need for using a shielded carrier. The purified ^{252}Cf , packaged in

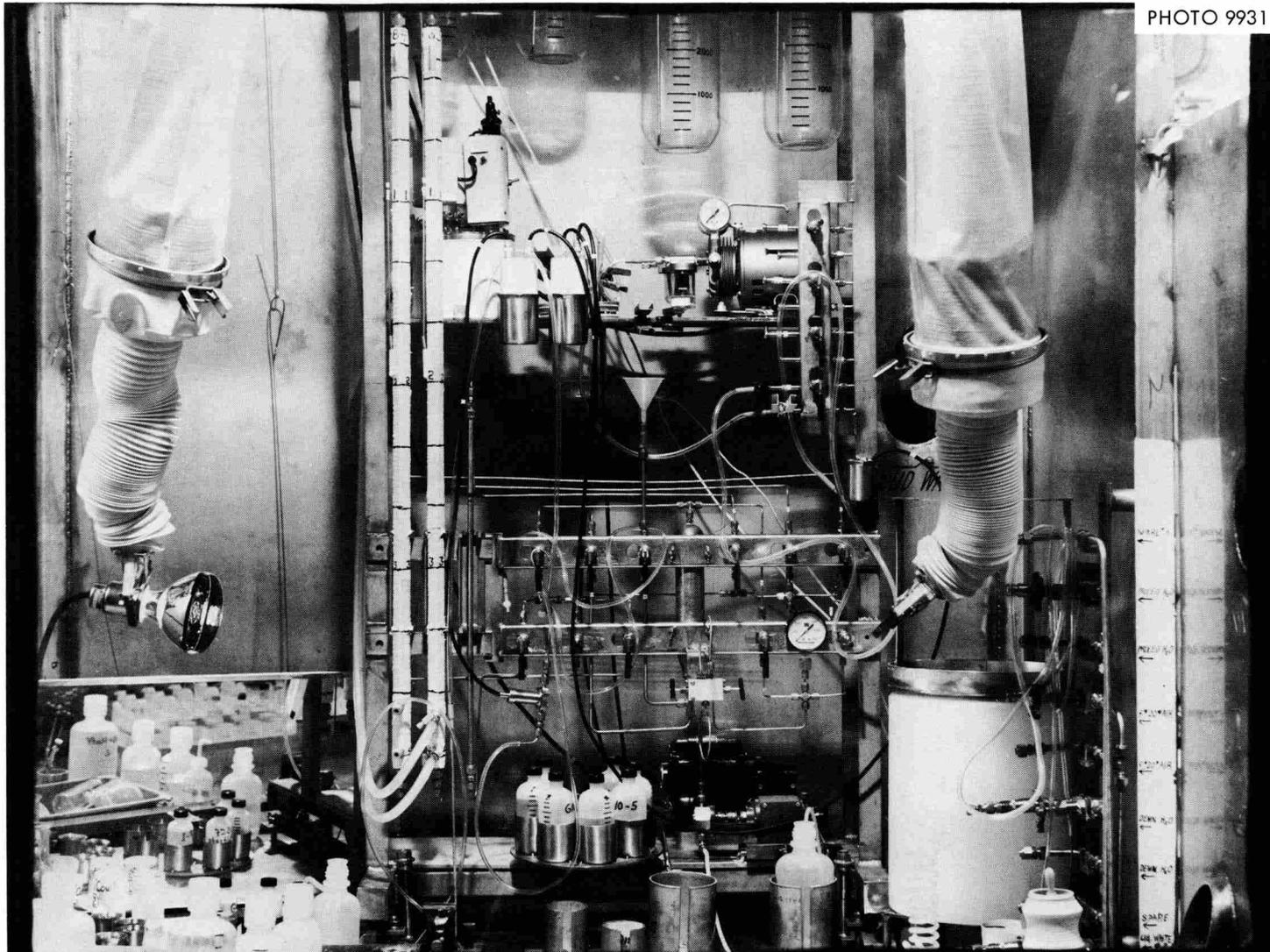


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Fig. 5. Pressurized Ion Exchange Equipment in Cubicle 1, TURF Californium Facility.

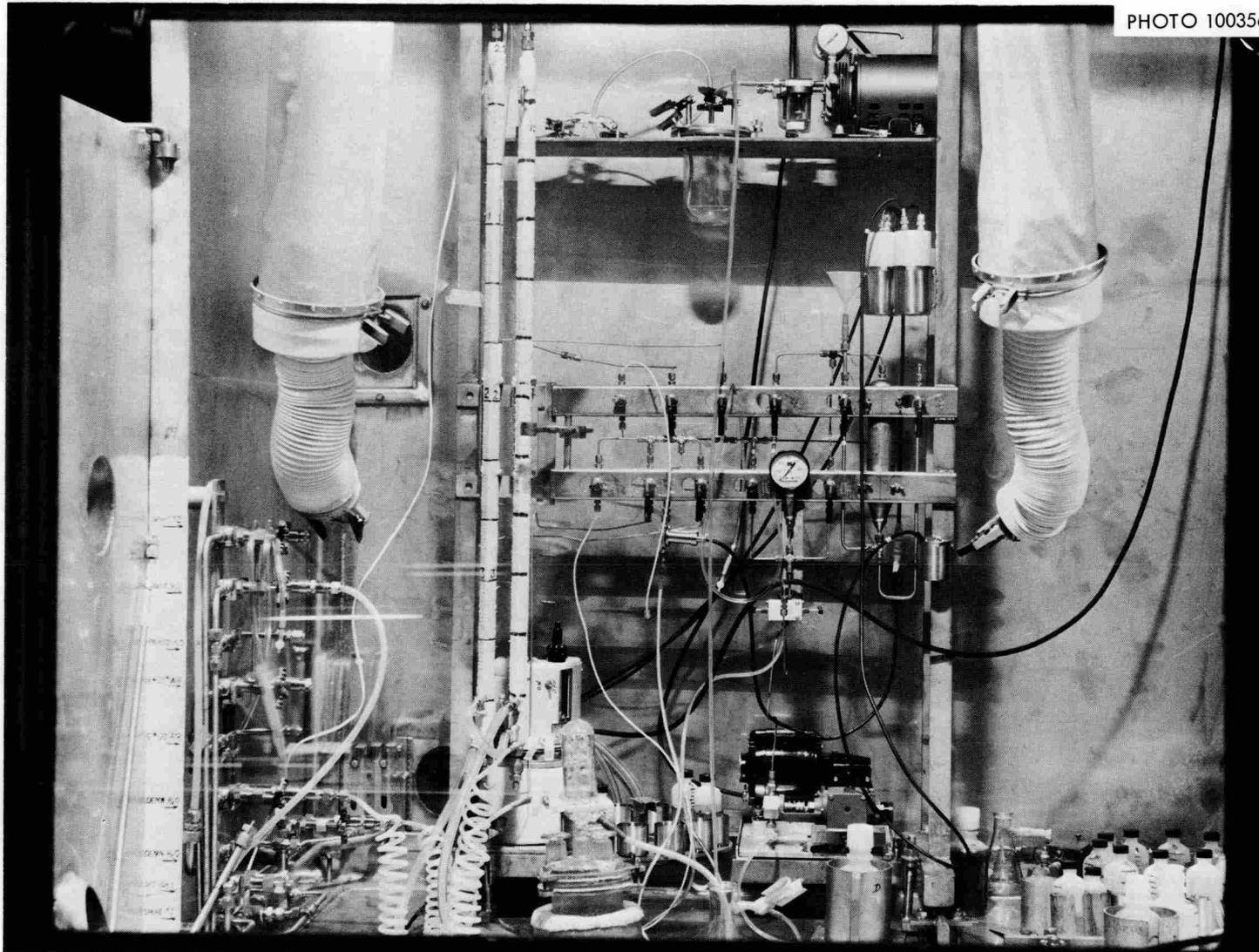


Fig. 6. Pressurized Ion Exchange Equipment in Cubicle 2, TURF Californium Facility.

either shipping capsules or neutron sources, may also be returned to TRU from TURF via this system for decontamination, calibration, and shipment.

2.4 Final Micropurification Equipment, Building 3508

The final separations performed in Building 3508 consist of ion exchange, extraction chromatography, and solvent extraction operations, all of which are carried out in glove boxes. The columns used for the chromatographic elution with α -hydroxyisobutyrate (AHIB) solution are 4 mm in diameter by 8 cm high and glass-jacketed; they are heated by a small recirculating water bath maintained at 80°C. The solution flow rate through the resin bed is maintained at approximately $10 \text{ ml cm}^{-2} \text{ min}^{-1}$ by application of pressure with argon. The final ion exchange columns are 4 mm and 2 mm in diameter by 8 cm high and are made of quartz. Quartz equipment is used in the final separation steps in order to minimize cationic impurities in the transplutonium-element product. The extraction chromatographic columns are 4 mm in diameter by 8 cm high and made of glass. Solvent extraction of the berkelium is performed in a 1-liter separatory funnel in which the phases are mixed with an air-motor-stirred impeller.

The columns and collection cones used in the final ion exchange separations are leached prior to use. The glass and quartzware are cleaned with detergent, rinsed in distilled water, and then leached in concentrated reagent-grade HCl for one to two weeks. After the HCl leach, the vessels are rinsed twice, first in ordinary distilled water and then in water that has been distilled in quartz apparatus. The glassware is then dried in an oven at 110°C and stored in a dust-free container.

The reagents used in the microscale purifications are prepared and maintained in an ultraclean state. Baker ultrahigh-purity "Ultex" Grade HCl and HNO_3 are used to prepare acid solutions. The α -hydroxyisobutyric acid is double-vacuum-sublimed in order to obtain a high-purity reagent. Water that has been triply distilled from quartz apparatus is used in all the solutions. Spark-source mass spectrometry of the reagent solutions has routinely indicated less than 0.5 ppm of total metal ion impurities.

3. FLOWSHEETS

Figure 7 presents a schematic diagram of the procedures employed in the overall processing operation required to isolate and purify the heavy actinides. Details of the major processing steps are shown in Figs. 8-10.

4. DESCRIPTION OF THE PROCESSING

4.1 Processing in Cubicle 5, TRU

Transcurium elements partitioned by LiCl-based anion exchange were precipitated by the addition of lithium hydroxide, filtered, dissolved in dilute nitric acid, and transferred to cubicle 5 by TRU operations. In cases where the transcurium-element fraction contained very little curium, up to 200 mg of iron was added as a carrier to ensure quantitative precipitation of the transcurium elements. The most significant radioactive contaminant in this product was ^{144}Ce , although the entire spectrum of fission products was present in small quantities (since they are continuously formed by spontaneous fissioning of ^{252}Cf).

Suitable feed for the cation exchange column was obtained by filtering the solution of transcurium elements to remove particulates and diluting to obtain a nitric acid concentration of about 0.3 M. In the later campaigns in which larger numbers of targets were processed, difficulties were experienced as a result of the presence of colloidal material (presumably zirconia from corrosion of TRU plant equipment). In these cases, it was necessary to pretreat the solutions to remove the zirconium by solvent extraction and/or precipitation. The total chemical equivalents of polyvalent ions present determined which of the two pressurized ion exchange columns was used for the initial separation. Generally, as much as 300 mg of actinides could be separated on the 3/8-in. column (resin volume, 50 ml) and approximately 750 mg on the 1/2-in. column (resin volume, 105 ml).

As the ^{252}Cf content of the feeds increased, various problems arose. First, radiolytic gassing of the more-concentrated californium feeds caused the high-pressure pumps to air-lock. This difficulty was circumvented

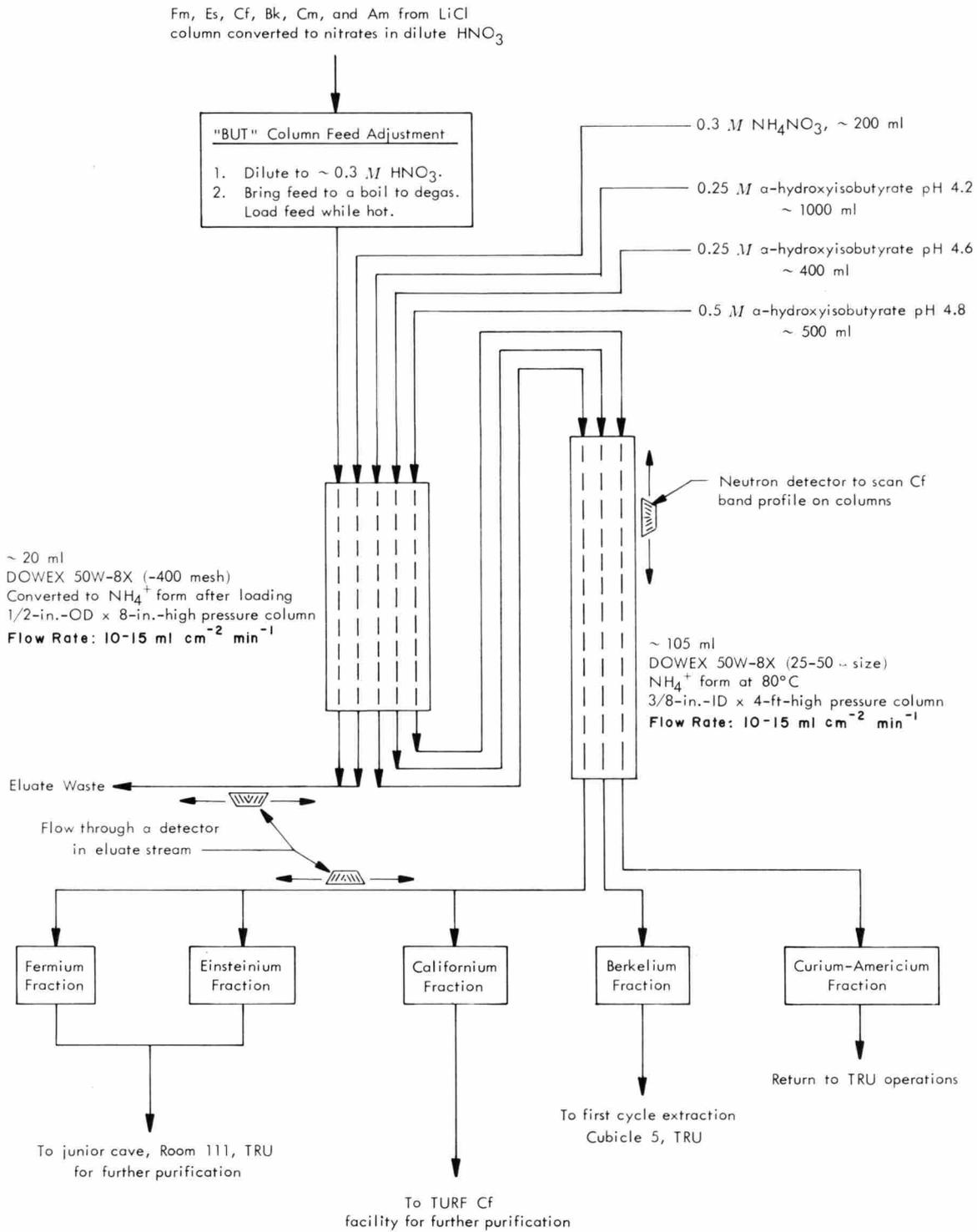


Fig. 8. Initial Isolation of Fm, Es, Cf, Bk, and Cm-Am Fractions by Chromatographic Elution with α -Hydroxyisobutyrate on Cation Exchange Resin.

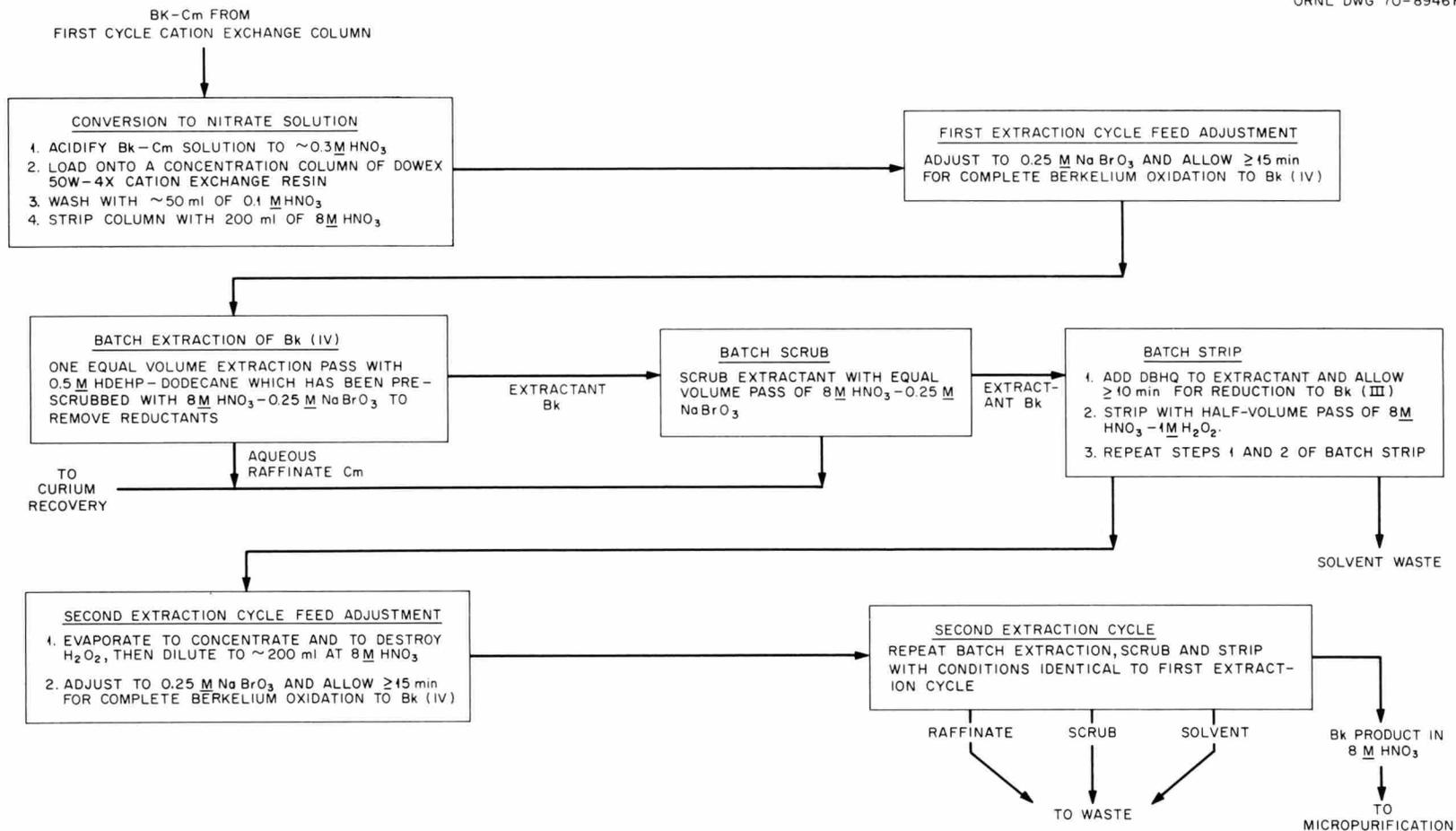


Fig. 9. Separation of Berkelium from Residual Curium and Californium by Selective Extraction of Tetravalent Berkelium.

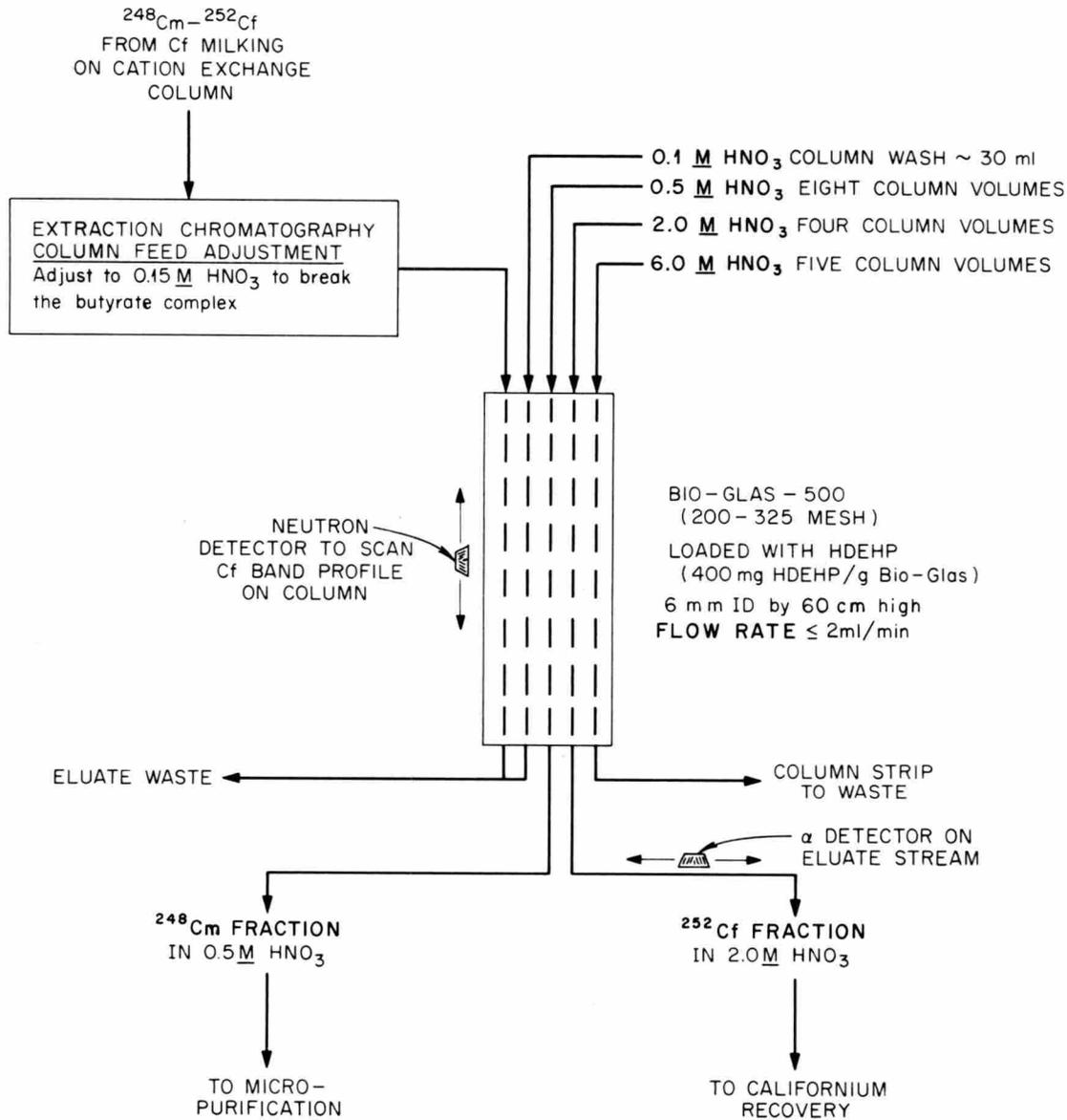


Fig. 10. Isolation of ^{248}Cm from ^{252}Cf by Extraction Chromatography.

by gently boiling the feeds just prior to loading and keeping the solution hot during the loading step. Second, radiolytic degradation of the cation resin occurred in the pressurized columns, resulting in decreased flow rates and severely increased pressures. This problem was solved by incorporating 3/8-in.-ID by 8-in.-high loading columns into the pressurized column systems. The use of a loading column, which was operated alone during loading and conversion and in series with the pressurized column during elution, permitted increased flow rates during loading and a reduced volume of 0.3 M NH_4NO_3 for conversion because of its smaller resin content. The standard run time for a pressurized ion exchange separation was decreased by 1-1/2 to 2 hr when such a column was used. This decrease permitted elution to proceed before the intense radiation from the californium in the loaded actinide band could significantly damage the resin.

Regardless of the acid concentration of the feed, an H^+ band always loads below the actinide band when the feed is pumped through the column of NH_4^+ -form resin. With subsequent chromatographic elution, the formation of the actinide bands is disrupted by this H^+ band, the severity of the disruption depending on the acid concentration of the feed solution. Initially, the H^+ band was displaced by pumping 0.3 M ammonium formate (pH 4.0) solution through the column after the actinides had been loaded. The NH_4^+ ions displaced the H^+ barrier; however, in the process, the actinides were forced down the column 1 or 2 in. It was subsequently found that a 0.3 M NH_4NO_3 solution (pH 5.5) pumped through the column would accomplish the same purpose with little or no movement of actinide bands; hence the procedure now calls for this method of removing the H^+ barrier prior to chromatographic elution of the actinides.

The actinides, which were loaded onto the loading column at a flow rate of approximately 15 ml/min and a pressure of less than 1000 psi, formed a tight band at the top of the resin bed. Following the conversion of the resin to the NH_4^+ form, the loading column was valved in series with the proper pressurized column. Band formation and elution were accomplished using 0.25 M AHIB (pH 4.2) until all the Fm, Es, and Cf were eluted from the column; at this time, the eluent was changed to 0.25 M AHIB (pH 4.6).

(The higher pH accelerates the elution of berkelium.) After the Bk fraction had been collected, the Cm, Am, and Ce were stripped from the column by elution with 0.5 M AHIB (pH 4.8). Figure 11 shows a typical elution curve (as recorded by the alpha flow-through detector) for the initial separation of the actinides by selective elution with AHIB from cation exchange resin. The products from this primary isolation-purification step were then transferred to the other facilities for final purification and cleanup.

4.2 Processing in Laboratory 111, TRU

The Fm, Es, and Bk-Cm fractions were transferred to junior cave A, using a shielded carrier called "The Mule" (see Fig. 12). The fermium and einsteinium fractions were combined, acidified to 0.25 M HNO_3 to break the AHIB complex, and loaded at a flow rate of 6 to 8 ml/min onto a 3/8-in.-ID by 4-ft-high pressurized cation exchange column.

Following loading and conversion of the resin to the NH_4^+ form with 0.3 M NH_4NO_3 , the actinides were selectively eluted with 0.25 M AHIB (pH 4.2) at a flow rate of 4 to 5 ml/min. The fermium fraction was collected with the aid of the in-line alpha detector; at this point the ^{252}Cf was located (as indicated with the in-cell neutron probe) about 20 in. from the bottom of the column. The einsteinium fraction came off the column when the ^{252}Cf was 8 to 10 in. from the bottom. When the californium band was about 1 in. from the bottom of the column, collection of the einsteinium fraction was ended and the californium fraction was started. After the californium had been eluted, the column was stripped with 0.5 M AHIB (pH 4.8) to remove curium and/or any residual actinides remaining on the column.

The fermium fraction was then transferred to Building 3508 for micro-purification, packaging, and shipment. Final processing of the einsteinium fraction was carried out in the alpha glove box, Laboratory 111, TRU. If the quantity of ^{252}Cf remaining in the einsteinium was significant, a third pressurized cation exchange column run was made. If less than 0.2 μg of ^{252}Cf remained in the einsteinium fraction, only a

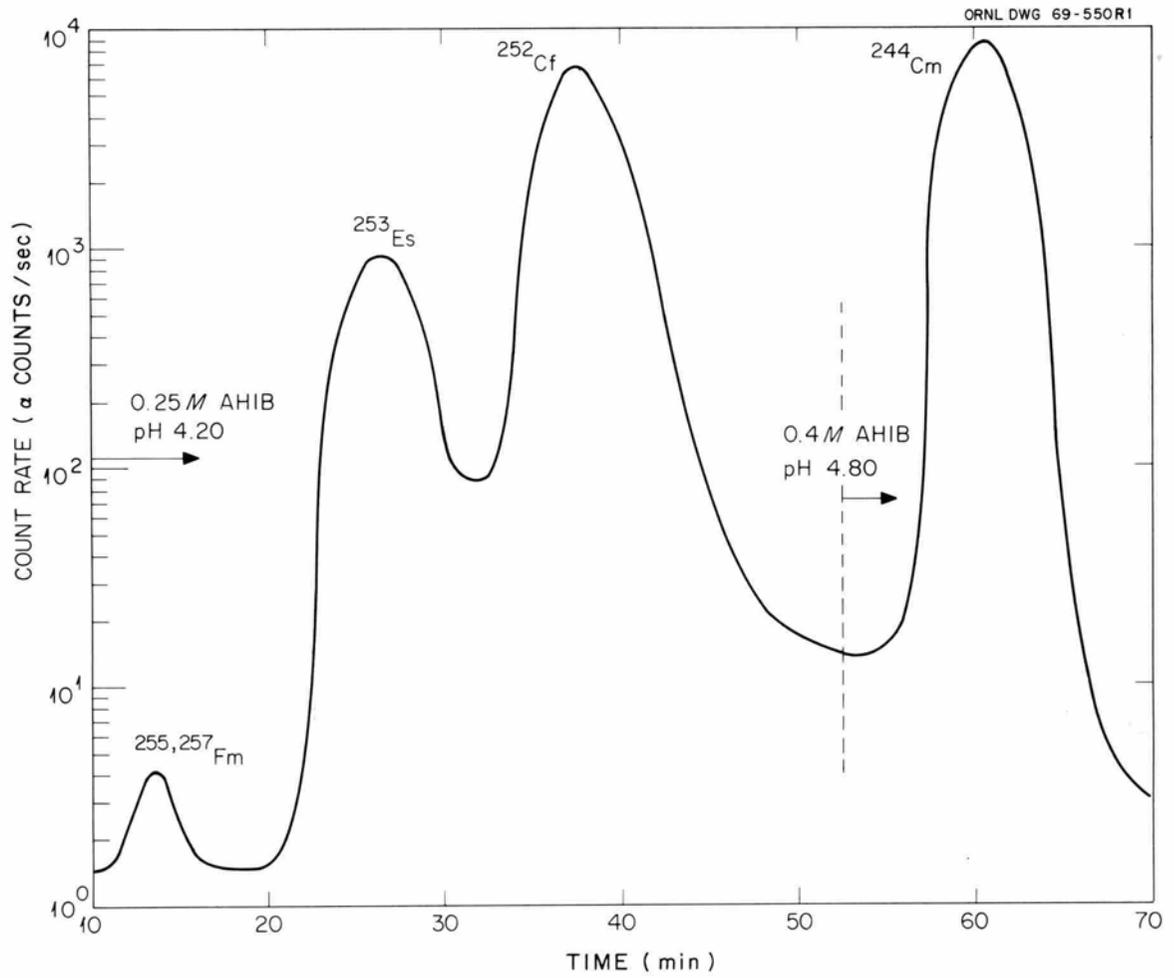


Fig. 11. Elution Curve Drawn by Alpha Flow-Through Detector.

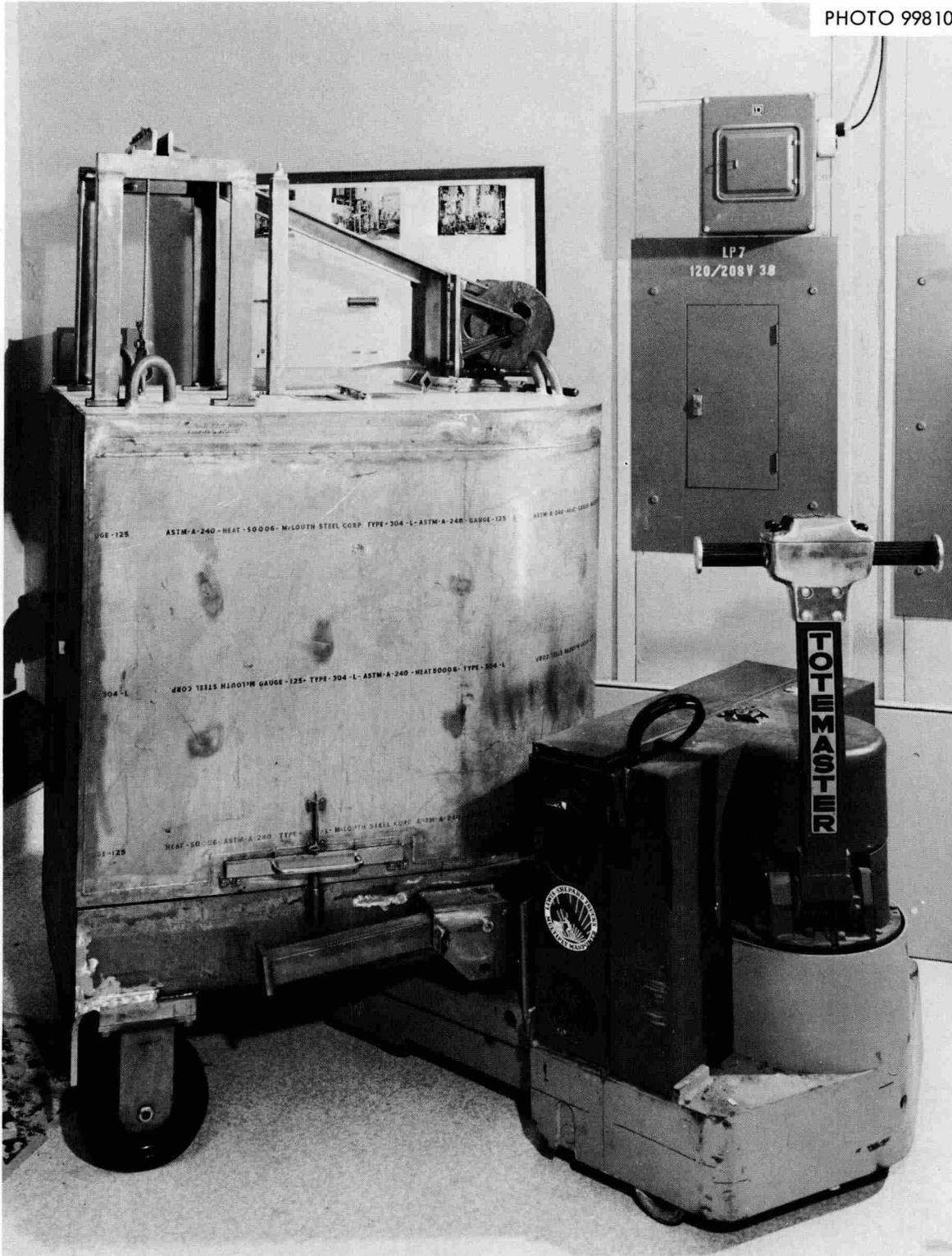


Fig. 12. Intracell Transfer Shielded Carrier, "The Mule."

final cleanup column run was made. This involved acidifying the butyrate solution and loading the einsteinium onto a 1/4-in.-ID by 6-in.-high stainless steel column containing Dowex 50W-X4 cation exchange resin. The column was washed with 0.1 M HNO_3 to remove the butyrate and with 2 M HNO_3 to remove ionic contaminants such as iron. At the first indication of the presence of einsteinium in the effluent, the eluent was changed to 6 M HNO_3 , which stripped the ^{253}Es in a relatively small volume (6 to 8 ml). The einsteinium product was divided according to customer requests, taken to dryness under an argon purge in leached-quartz or -Pyrex cones using an infrared heat lamp, and packaged for shipment.

The Bk-Cm fraction was converted from the butyrate to the nitrate form by acidifying the fraction to 0.3 M HNO_3 and loading the Bk and Cm onto a 1/2-in.-ID by 6-in.-high cleanup (or conversion) column containing cation exchange resin. The loaded column was then washed to remove butyrate, and the Bk and Cm were stripped with 8 M HNO_3 as part of the feed adjustment for the Bk extraction.

The 8 M HNO_3 containing the Bk and Cm was transferred to a separatory funnel equipped with an air-motor stirrer, adjusted to 0.25 M in NaBrO_3 , and agitated gently for 15 min to allow oxidation of the Bk to Bk(IV). This aqueous phase was contacted 20 min with an equal volume of 0.5 M HDEHP--dodecane that had been prescrubbed with 8 M HNO_3 --0.25 M NaBrO_3 to remove any reductants. The phases were separated, and the organic phase, which contained the berkelium, was scrubbed for 10 min with an equal volume of 8 M HNO_3 --0.25 M NaBrO_3 .

Following scrubbing and separation of the phases, 2,5-di-tert-butylhydroquinone (DBHQ) was added to the organic phase and gently stirred for about 15 min to reduce the Bk(IV) to Bk(III). The Bk(III) was subsequently stripped from the organic phase with two half-volume portions of 8 M HNO_3 --1 M H_2O_2 ; a contact time of 15 min was used for each strip. The berkelium strip product was transferred to Building 3508 for the second-cycle extraction, micropurification, milking of ^{249}Cf , and packaging for shipment.

The californium products from the primary isolation were either left in cubicle 5 for loading into capsules for shipment or were transferred to other areas — junior cave B or the TURF Californium Facility — for decontamination from residual ^{244}Cm . Since junior cave B is limited by its shielding effectiveness to a maximum of 2 mg of ^{252}Cf , separation of ^{248}Cm and fabrication of neutron sources from more than 2 mg of californium were performed in the TURF Californium Facility.

4.3 Processing in the TURF Californium Facility

The butyrate solutions of californium from the primary isolation in Cell 5 were acidified and loaded into small shipping capsules, which consisted of 3/8-in.-OD by 1-in.-high stainless steel cylinders containing 1.5 to 2 ml of cation exchange resin each. End plugs were placed in the fittings that held the capsule during loading. Each capsule was decontaminated to remove ^{244}Cm from its exterior and transferred to Cell G, TURF, via the pneumatic rabbit transfer system. (Approximately 15 sec is required for the transfer from TRU to TURF.)

Upon receipt of the californium capsules at TURF, the end plugs were removed and the capsule was piped into the equipment rack of cubicle 1. The californium was then stripped from the capsule using 0.5 M AHIB (pH 4.8). Any californium remaining in the capsule (<1%) was recovered by elution with 8 M HNO_3 and was subsequently reprocessed.

The californium was separated from any residual ^{244}Cm remaining after the primary isolation in TRU by means of pressurized ion exchange techniques. The californium product fraction was stored in cubicle 2, TURF, and allowed to decay for 1 month prior to the first milking of second-growth ^{253}Es and ^{248}Cm . It was essential that cubicle 2 remain completely free of ^{244}Cm so that pure ^{248}Cm could be isolated.

The californium was separated from the isotopically pure, second-growth ^{253}Es and the ^{248}Cm by selective elution with 0.25 M AHIB (pH 4.2) from cation exchange resin contained in a pressurized column. The ^{253}Es fraction required an additional ion exchange run to reduce the ^{252}Cf

activity to a sufficiently low level to permit transfer of the fraction to the alpha glove-box facility at Building 3508 for micropurification, packaging, and shipment.

Pressurized extraction chromatography⁷ was used to decontaminate the ^{248}Cm fraction from ^{252}Cf (Fig. 10). This process involved adjusting the nitric acid concentration of the ^{248}Cm fraction to 0.15 M and passing the fraction through a 6-mm-diam by 60-cm-high stainless steel column containing 20 ml of porous silica (Bio-Glas 500) that had been preloaded with HDEHP. The Bio-Glas contained 400 mg of HDEHP per gram of silica. As the dilute acid solution passed through the column, the ^{248}Cm and ^{252}Cf were quantitatively extracted into the organic phase absorbed in the Bio-Glas. The column was washed with 0.1 M HNO_3 to remove the butyrate, and the ^{248}Cm was selectively eluted from the column with approximately five column volumes of 0.5 M HNO_3 . Figure 13 shows a typical elution curve for the separation of ^{248}Cm from ^{252}Cf by extraction chromatography using Bio-Glas as the support matrix.

During the elution with 0.5 M HNO_3 , the californium did not move down the column more than 6 in. from its loading position. The californium was stripped from the column with 2 M HNO_3 , and the column was then treated with 6 M HNO_3 to clean it for reuse. At this point in the processing, the residual ^{252}Cf activity level was so low that the ^{248}Cm was taken to an alpha glove-box facility in Building 3508 for final micropurification, packaging, and shipment.

After the californium had been milked of ^{248}Cm and ^{253}Es , it was loaded into californium shipping capsules (see Fig. 14), or fabrication of neutron sources was begun.

The primary container of a shipping capsule consisted of a 3/8-in.-OD by 1-in.-high platinum tube filled with cation exchange resin. Platinum frits were rolled into each end to completely encapsulate the resin. Capsules of this type were piped into the equipment rack of cubicle 2 and loaded by passing a dilute acid solution of californium through the resin bed. The californium-loaded capsules were calcined with air flowing through the resin at 650°C for 3 hr. Following the calcination procedure, end

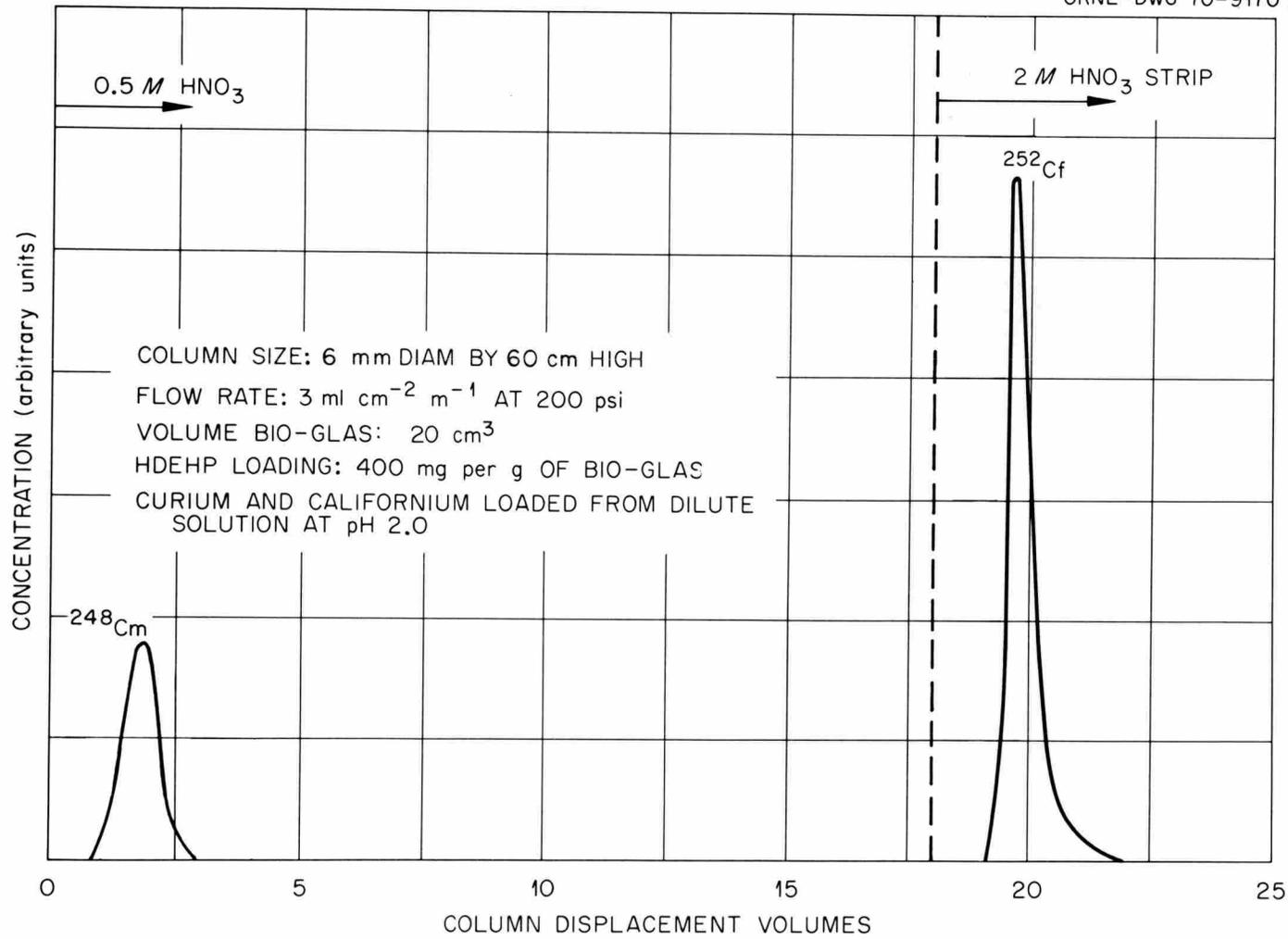


Fig. 13. Extraction Chromatographic Elution Curve for ²⁴⁸Cm and ²⁵²Cf.

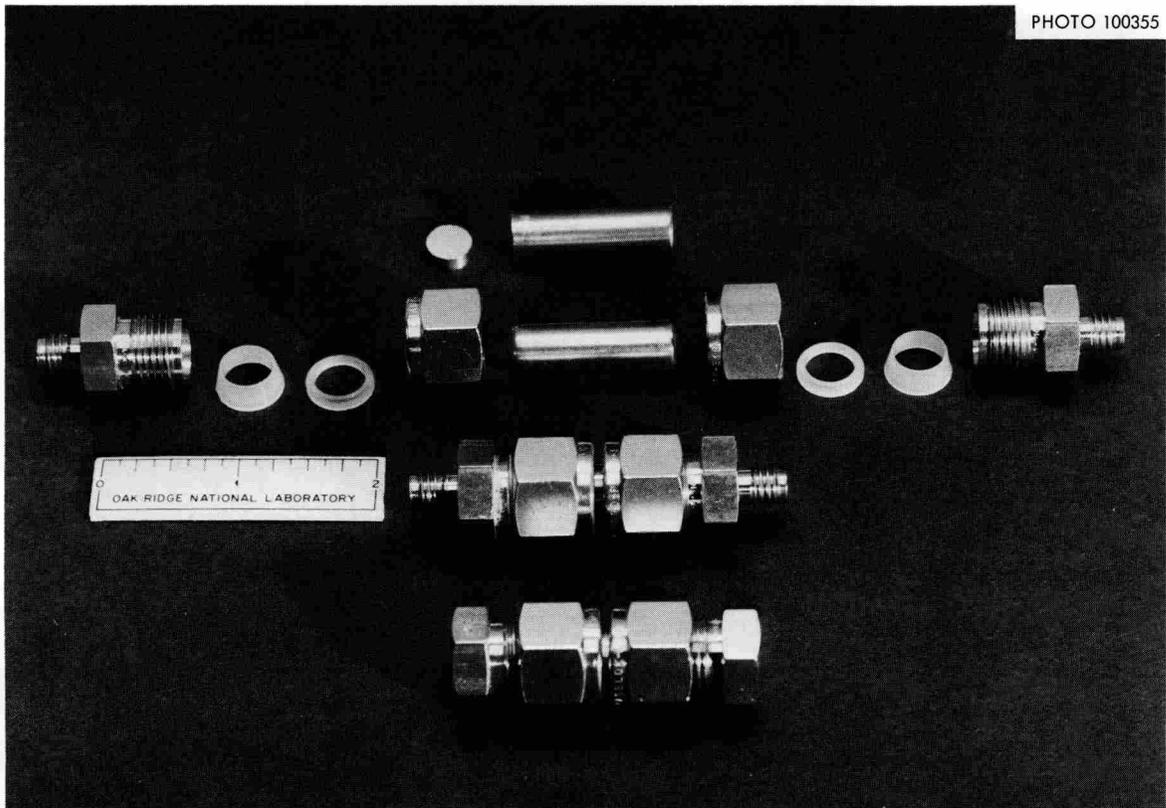


Fig. 14. Platinum Shipping Capsule for ^{252}Cf .

plugs were placed on each capsule, and the capsule was welded into a secondary stainless steel container.

Californium neutron sources were fabricated by a pressed aluminum-resin technique,⁸ which is shown schematically in Fig. 15. The basic container is a 1/4-in.-OD aluminum can with a series of small holes in the bottom. A porous aluminum frit is pressed onto the bottom to support the resin bed. The can is filled with 0.25 ml of Bio-Rad cation exchange resin (50W-X8, 25-50 μ); then a layer of aluminum powder is placed on top of the resin. The resin is loaded by forcing a dilute nitric acid solution of californium through the prepared container. The californium loads quantitatively (>99.9%). Following loading, the aluminum container is rinsed with dilute nitric acid and flushed with ethanol to remove excess acid solution. The aluminum can containing aluminum powder and californium-loaded resin is then calcined at 450°C to decompose the resin, and aluminum powder is placed on top to provide an aluminum cap when pressed. Subsequently, the aluminum can is pressed to 95% of the theoretical density of aluminum metal. To complete fabrication of the source, the pressed aluminum pellet is welded into a secondary stainless steel container.

Each californium shipping package and neutron source was transferred to TRU (via the pneumatic rabbit transfer system), decontaminated, calibrated, and shipped. Figure 16 shows the "cannonball" carrier, which served to transport californium neutron sources and shipping packages to customers at the various AEC laboratories.

4.4 Micropurification in Building 3508

4.4.1 Recovery of ^{257}Fm

The longest-lived isotope of fermium produced in HFIR irradiations is ^{257}Fm , which has a half-life of 94 ± 10 days. The next longest-lived isotope is ^{255}Fm , which has a half-life of 20.07 hr. The most desirable isotope is ^{257}Fm , because of its longer life. Unfortunately, it is produced at a rate of only 1.5×10^7 atoms per milligram of ^{252}Cf produced.

ORNL DWG 70-6322

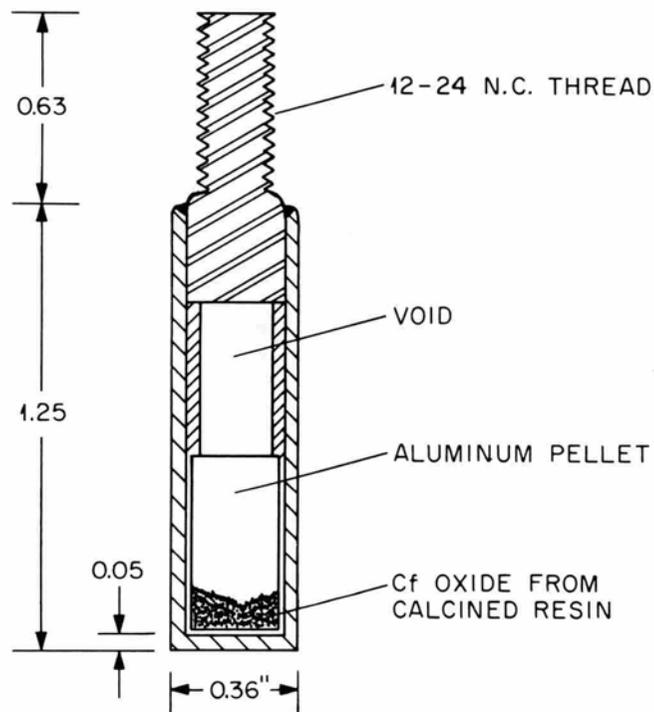
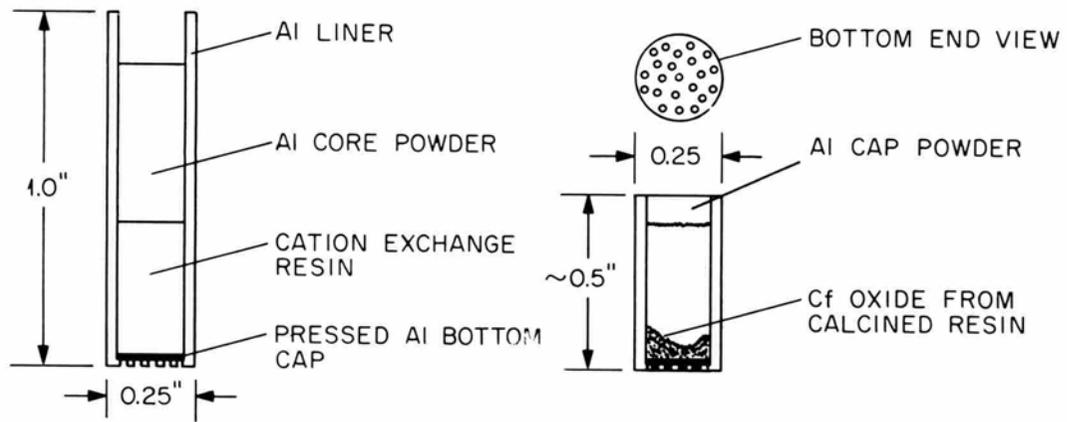


Fig. 15. Schematic Diagram Showing the Various Steps in the Fabrication of Neutron Sources.

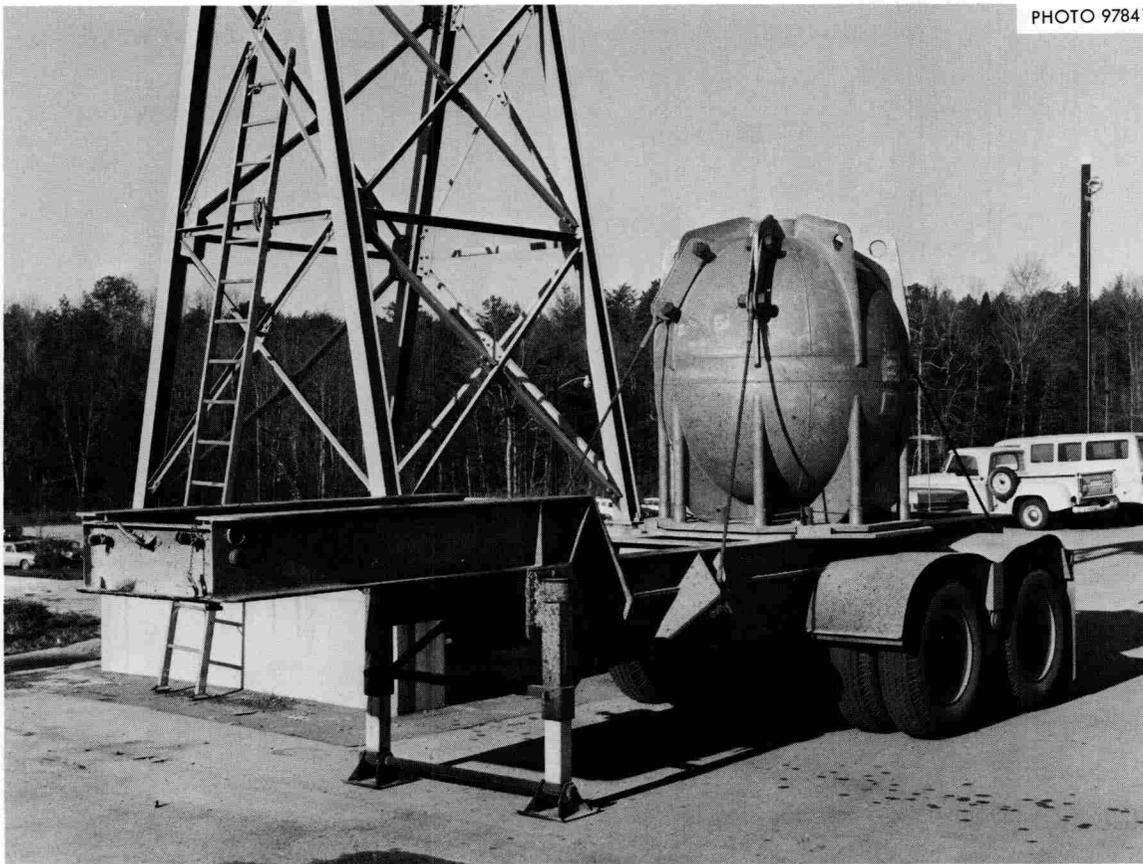


Fig. 16. Shielded Carrier, "Cannonball," Used to Transport ²⁵²Cf.

This quantity of ^{257}Fm corresponds to an alpha count rate of 78 α dis/min. Considering that ^{252}Cf has an alpha count rate of 1.15×10^{12} α dis min^{-1} mg^{-1} , it becomes obvious that the recovery and purification of ^{257}Fm constitute a formidable processing procedure.

As was mentioned earlier in the text, the fermium and einsteinium effluent fractions from the first AHIB pressurized ion exchange column are combined for additional processing. This is to ensure that no loss of the fermium occurs during the initial separation of the transcurium elements. The Fm-Es fractions are transferred to the junior cave in Laboratory 111, where a second AHIB pressurized ion exchange run is made. A Fm-Cf decontamination factor (DF) of approximately 1×10^7 is achieved over the two ion exchange runs. At this point, ^{255}Fm is the predominant alpha activity in the fermium fraction. This fermium fraction is then transferred to the glove-box facility in Building 3508 for final purification.

In order to ensure that a radiochemically pure ^{257}Fm fraction is isolated, a third AHIB pressurized ion exchange run is made immediately in the glove box. In this run, a 4-mm-diam by 6-cm-high glass ion exchange column containing Dowex 50W-X8 (20-40 μ) resin is used. The alpha activity of ^{255}Fm at this point, approximately 1×10^5 α dis/min, completely masks the alpha activity of ^{257}Fm . The purified fermium is allowed to decay for about ten half-lives of ^{255}Fm and is then passed through an AHIB ion exchange column that is 1 mm in diameter by 3 cm high and contains approximately 25 μl of Dowex 50W-X8 (10-20 μ) resin. The effluent is collected as single drops on platinum plates, which are subsequently evaporated to dryness under a heat lamp, counted for alpha activity, and analyzed by pulse-height techniques. The ^{257}Fm plates are selected, and the evaporated AHIB is dissolved in a few drops of 0.25 M HCl and loaded onto a 1-mm-diam by 3-cm-high column containing Dowex 50W-X4 (25-50 μ). The AHIB is washed off the column with 0.5 M HCl, and the ^{257}Fm is stripped with 6 M HCl. The resultant ^{257}Fm product is radiochemically pure; other alpha-active transplutonium elements contribute less than 1% of the total alpha activity.

4.4.2 Recovery of ^{249}Bk and Production of ^{249}Cf

The berkelium extraction strip product from the hot-cell facilities was contained in 200 to 500 ml of 8 $\underline{\text{M}}$ HNO_3 --1 $\underline{\text{M}}$ H_2O_2 . This solution was transferred to the glove-box facilities in Building 3508, where the H_2O_2 was destroyed by gently bringing the solution to a boil and evaporating to approximately half the volume. The solution was then readjusted to the composition 8 $\underline{\text{M}}$ HNO_3 --0.25 $\underline{\text{M}}$ NaBrO_3 , and a second oxidation-extraction-reduction-strip cycle, similar to that described earlier in the text, was performed. The resulting berkelium product was free of any residual ^{252}Cf ($\text{DF} > 10^8$). The strip solution from the second-cycle extraction was radiochemically pure except for fission product cerium, which was extracted along with the berkelium (if it was not completely removed in the Tramex extraction or by the LiCl anion exchange column). The residual HDEHP extractant was removed from the strip solution by two half-volume scrubs of xylene. The strip product was then evaporated to dryness to remove the 8 $\underline{\text{M}}$ HNO_3 . The berkelium was dissolved in 0.1 $\underline{\text{M}}$ HNO_3 for the final ion exchange purification steps.

If ^{249}Cf is required, the berkelium is allowed to decay for the necessary time interval to build up the desired quantity of californium. (The ^{249}Bk decays to ^{249}Cf at a rate of about 6.5% per month.) The ^{249}Cf is then separated from the remaining berkelium by chromatographic elution with AHIB, using a 4-mm-diam by 8-cm-high column of Dowex 50W-X8 (20-40 μ) resin.

There are several methods available for separating ^{249}Cf from ^{249}Bk , for example, reoxidation of Bk(III) to Bk(IV) and extraction with HDEHP. However, this method leaves the ^{249}Cf product in a 8 $\underline{\text{M}}$ HNO_3 --0.5 $\underline{\text{M}}$ NaBrO_3 solution, which is somewhat difficult to process for californium recovery. Other methods have been proposed, including oxidation of berkelium with PbO_2 (ref. 9) or with NaCr_2O_7 (ref. 10) and extraction of the Bk(IV) with HDEHP. After evaluating these various methods, we found the AHIB chromatographic elution to be preferable since the resulting solutions are readily adjusted for subsequent steps and no cationic impurities (which must be subsequently removed) are deliberately introduced.

The final purification steps for ^{249}Bk and ^{249}Cf are identical and involve the alcoholic-HCl elution from Dowex 50W-X4 resin and the final cleanup and concentration step, which is accomplished on an ion exchange resin column. These final separations make use of preleached quartzware and ultrapure reagents.

During the various stages of processing, some rare-earth elements are carried along with the transplutonium products. For instance, in the AHIB chromatographic elution, Tb is eluted with Es, Gd with Cf, and Eu with Bk. Also, cerium is carried along with the berkelium in the oxidation-reduction-extraction with HDEHP. Rare-earth contaminants may also be picked up from reagents and from leaching of glassware. The alcoholic-HCl column is employed in one of the last separation steps for the transplutonium elements. In this step, the transplutonium elements are eluted ahead of the rare-earth elements and a group separation is achieved.

The transplutonium elements are loaded from approximately 0.1 M HCl solution onto a 4-mm-diam by 8-cm-high quartz column containing 1.0 ml of Dowex 50W-X4 (20-40 μ). The column is washed first with approximately five column volumes of 0.25 M HCl and then with one-fourth of a column volume of 2 M HCl. (The 2 M HCl displaces the dilute wash solution and causes the resin bed to shrink due to the increased HCl concentration; however, since it will cause the transplutonium and rare-earth elements to move slowly down the column, only a small amount is used.) The transplutonium elements are then eluted in approximately four to five column volumes of cold 20% ethanol that has been saturated with HCl gas just prior to use. The HCl concentration is about 13.5 M under these conditions. Although extensive gassing occurs during this elution step, excellent transplutonium-lanthanide element group separations have been achieved. It is absolutely necessary that the HCl concentration be greater than 13 M because, at lower HCl concentrations, the rare earths are eluted along with the transplutonium elements. The rare earths are then stripped from the resin in approximately five column volumes of 6 M HCl. The transplutonium elements are evaporated to dryness in the quartz cone with an argon purge and an infrared heat lamp.

The cleanup-concentration ion exchange column is used as the final processing step. The evaporated product from the alcoholic-HCl column is taken up in approximately 1 ml of 0.1 M HCl and loaded onto a 2-mm-diam by 8-cm-high quartz column containing 250 μ l of Dowex 50W-X4 resin (20-40 μ). The cone is washed with an additional 1 ml of 0.1 M HCl, which is subsequently loaded onto the ion exchange column. The column is then washed successively with about ten column volumes of 0.5 M HCl and ten column volumes of 2 M HCl. The effluent of the resin column is monitored for alpha and beta emissions, which arise from the ^{249}Cf and the ^{249}Bk respectively. As soon as the first trace of activity is detected in the 2 M HCl effluent, the eluent is changed to 6 M HCl, and product is stripped from the column into a quartz cone. The resulting product solution is then evaporated to dryness with an argon purge and an infrared heat lamp. The cleanup-concentration column removes essentially all of the alkali metals and alkaline earths and most of the transition metal ions, giving an ultrapure product. Analysis of the final product solution by spark-source mass spectrometry has shown that the product routinely contains less than 0.05 at. % rare earths and is at least 99.8 at. % pure with regard to all cations.

4.4.3 Recovery and Purification of ^{248}Cm

The curium product obtained by extraction chromatography in the TURF Facility usually consists of 50 to 100 ml of 0.5 M HNO_3 containing the light rare-earth fission products produced by the spontaneous fissioning of californium and less than 0.1 μg of residual ^{252}Cf . The extraction chromatography product is diluted to 0.25 M HNO_3 and loaded onto a 4-mm-diam by 8-cm-high concentration column filled with Dowex 50W-X4 (20-40 μ) resin. Most of the ionic contaminants are removed by extensive elution with 2 M HCl, which slowly forces the ^{248}Cm down the column. When the curium band approaches the bottom of the column, the eluent is changed to 6 M HCl, which strips the curium from the resin in less than 5 ml of solution.

The final Cm-Cf separation is made using a 4-mm-diam by 8-cm-high extraction chromatographic column of HDEHP-loaded Bio-Glas. Since new equipment is used for this step, a californium DF of greater than 10^6 is achieved. The flowsheet used is essentially the same as that shown in Fig. 10, except that the column size and volumes are smaller. The product from this column contains only the fission product rare earths mentioned above, which are subsequently removed by use of the alcoholic-HCl cation exchange system. A final 2-mm-diam by 8-cm-high quartz cleanup column using Dowex 50W-X4 (as described above) yields an ultrapure ^{248}Cm product that contains less than 0.05 at. % rare earths and is at least 99.8 at. % pure with regard to all ionic impurities, as determined by spark-source mass spectrophotometric analysis.

Table 1 shows the composition of a typical ^{248}Cm product following the ion exchange separations and the two extraction chromatographic runs. The overall californium DF was greater than 10^{10} , and it can be seen that the ^{252}Cf contributed less than 0.1% of the total alpha activity of the final product. Through December 1971, a total of 7.8 mg of ^{248}Cm has been isolated and purified using the procedures described above.

5. SUMMARY

During the 12 campaigns conducted at TRU during the period August 1967 - December 1971, 313 mg of ^{252}Cf , 1.1 mg of ^{253}Es , 30 mg of ^{249}Bk , 1.7 mg of ^{249}Cf , 7.8 mg of ^{248}Cm , and 4.5×10^9 atoms of ^{257}Fm were isolated and purified. These materials were distributed in 345 separate shipments to more than 50 investigators at AEC sites and at universities. Over 50 neutron sources, varying in size from 10 μg to 10 mg of ^{252}Cf , have been fabricated. All of these sources were thoroughly decontaminated with regard to residual ^{244}Cm content, so that the ^{248}Cm produced by the alpha decay of ^{252}Cf will be of high quality. As of December 31, 1971, these sources contained 11.7 mg of ^{248}Cm , which is recoverable and of the quality reported in the text.

Table 1. Composition of a Typical ^{248}Cm Product Following Separation from ^{252}Cf by Ion Exchange and Two Extraction Chromatographic Separations

Isotope of Curium	Content (at. %)	Percent of Total Alpha Activity
244	0.001	~5
245	0.010	-
246	2.27	~61
247	0.009	-
248	97.71	~34
<hr style="border-top: 1px dashed black;"/>		
^{252}Cf	$<2 \times 10^{-8}$	≤ 0.1

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