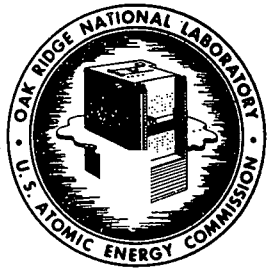


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FROM: W. A. Brooksbank, Jr., R. J. Carter, M. F. Osborne

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Abstract

A preliminary study of the volatility behavior of molybdenum indicated that MoF_5 was converted to MoF_6 by F_2 ; MoF_6 and Tc fluoride are absorbed on NaF at 100° ; technetium fluoride is more strongly held than molybdenum fluoride on NaF; MoF_6 may not be completely trapped by a dry ice trap. The behavior of volatile fission product fluorides was such that (a) Ru and Nb fluorides were volatile from fused salts during fluorination, (b) Mo and technetium were not volatile during hydrofluorination but were in excess F_2 $> 100^\circ\text{C}$.

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The Chemical Technology Division of ORNL has been investigating a non-aqueous, high temperature process for the recovery and purification of uranium from spent fuel. The process consists of three main steps: the dissolution of metallic fuels in a fused fluoride bath in the presence of HF, the volatilization of UF_6 from the melt by gaseous F_2 and the decontamination of the crude UF_6 by means of adsorption-desorption on NaF beds. The product UF_6 is recovered by cold trapping. Aged fission product mixtures have been studied in detail (1), but the data are incomplete for many of the short-lived fission products.

The Solid State Division has been engaged in a study of these processes to better understand fission product behavior in fused salt media.

The study of the volatility process involved three experiments. The first was essentially a duplication of that used by Cathers, et al. This was done to familiarize personnel with high-temperature fluorine technology, and to evaluate in-line radioactivity measurement instruments.

The second experiment was designed to evaluate the behavior of a short-lived fission product, Mo^{99} , during the HF dissolution step.

The third experiment was the study of the behavior of tracer MoF_6 on the NaF adsorption columns.

The gamma scintillation spectrometer was adapted to in-line monitoring of gaseous activities. It consisted of a 1" x 1½" NaI (Tl) crystal optically coupled to a DuMont 6292 photomultiplier tube, an A-1-B cathode follower pre-amplifier, and an A-1-D linear amplifier with pulse height discrimination (Q1151). Pulse height versus intensity data were displayed either on a 0-10 MV Brown recorder fed by a linear count rate meter (Q-1511) or by counting the

In-Line Spectrometer

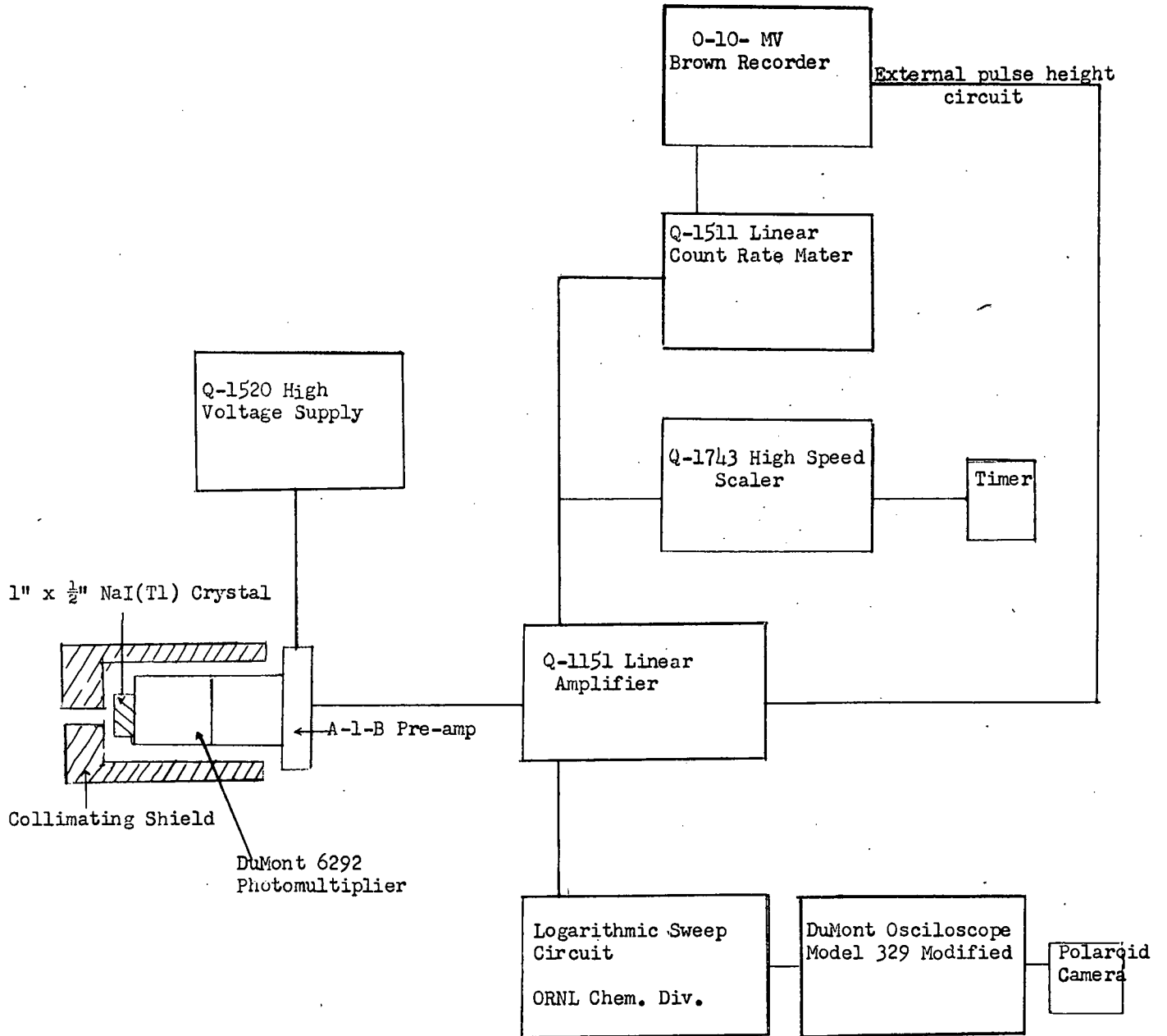


Figure 1

pulses by means of a high speed counter (Q-1743). High voltage was furnished by a very stable negative supply (Q-1520). The crystal was shielded by one inch of lead on the sides and two inches on the front. A slit, 0.125 x 1.00 inches, acted as a collimator. The head was mounted on a table and could be traversed in one axis by a screw drive. Positioning in the other two axes was accomplished by pivoting the table and drive mechanism through 90° and/or by rotating the table and drive on the circular central support (Figure 1). The collimating slit and shield are shown in Figure 2.

This mounting arrangement enables the detector to be placed at any location in the experiment. The experiment must be designed to allow clearance for the detector. The traversing mechanism, in conjunction with an X-Y recorder is used to give activity versus distance plots along system components.

This equipment was modified for experiments 2 and 3 by the addition of a grey wedge analyzer. This device permitted a spectrum of a transient activity to be recorded on a photographic film in less than 15 seconds. The data could then be interpreted at some later time. The components of the spectrometer are shown in Figure 3.

The first experiment consisted of four parts: (1) a ten hour sparge of the salt with He, (2) ten hour sparge with HF at a flow rate of 50 cc/min, (3) ten hour sparge by HF at a flow rate of 110 cc/min, and (4) fluorination and adsorption for one hour at 110 cc/min followed by a four hour desorption step.

Active feed consisted of an in-pile loop fuel, cooled six months. Data on the activity in the exit lines were taken by use of the gamma scintillation spectrometer with a collimating slit in its shield. These measurements were recorded continuously. The equipment used for the preliminary study of volatility is shown in Figure 4. The spectrometer was positioned at the exit

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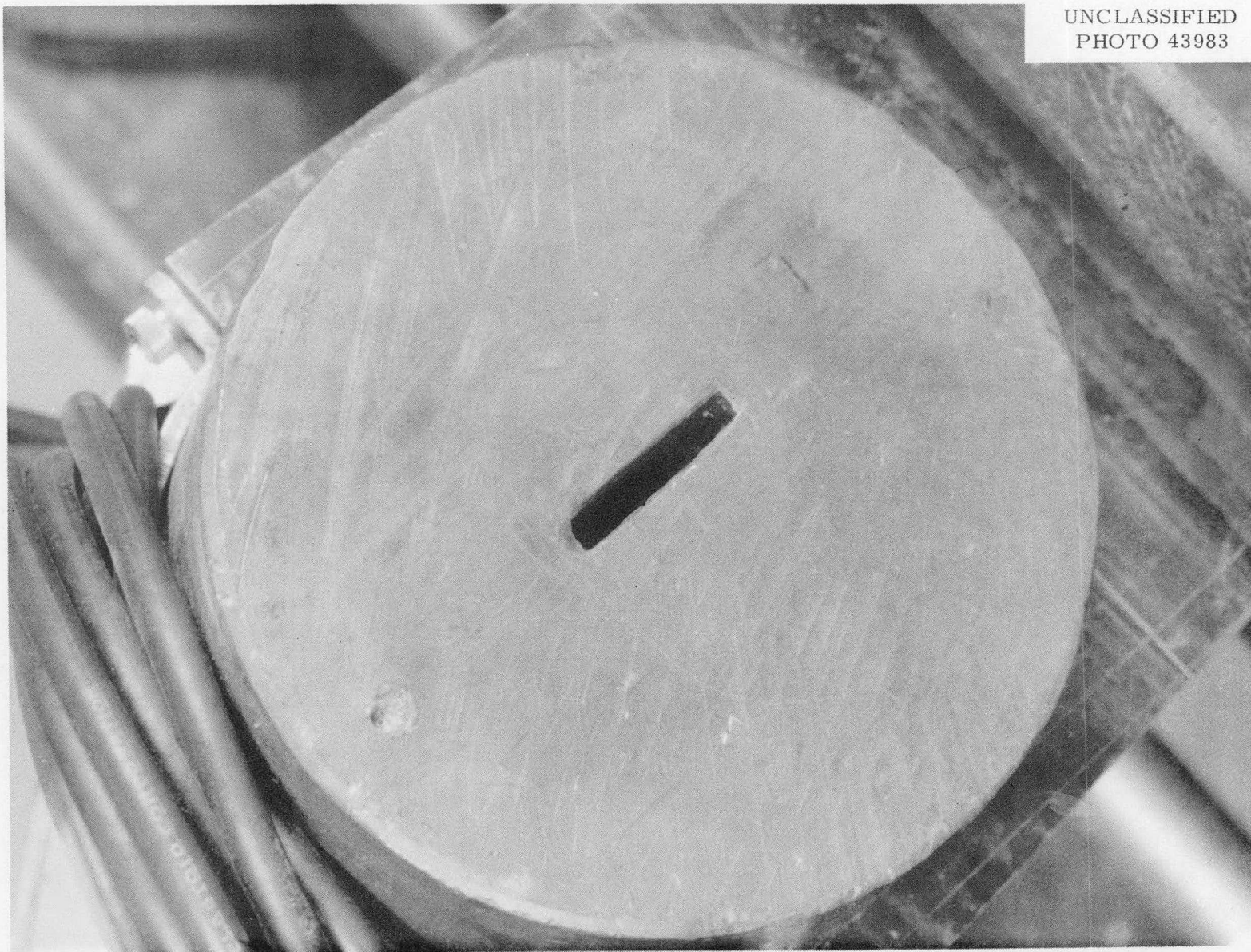


Figure 2 Shield and Collimating Slit

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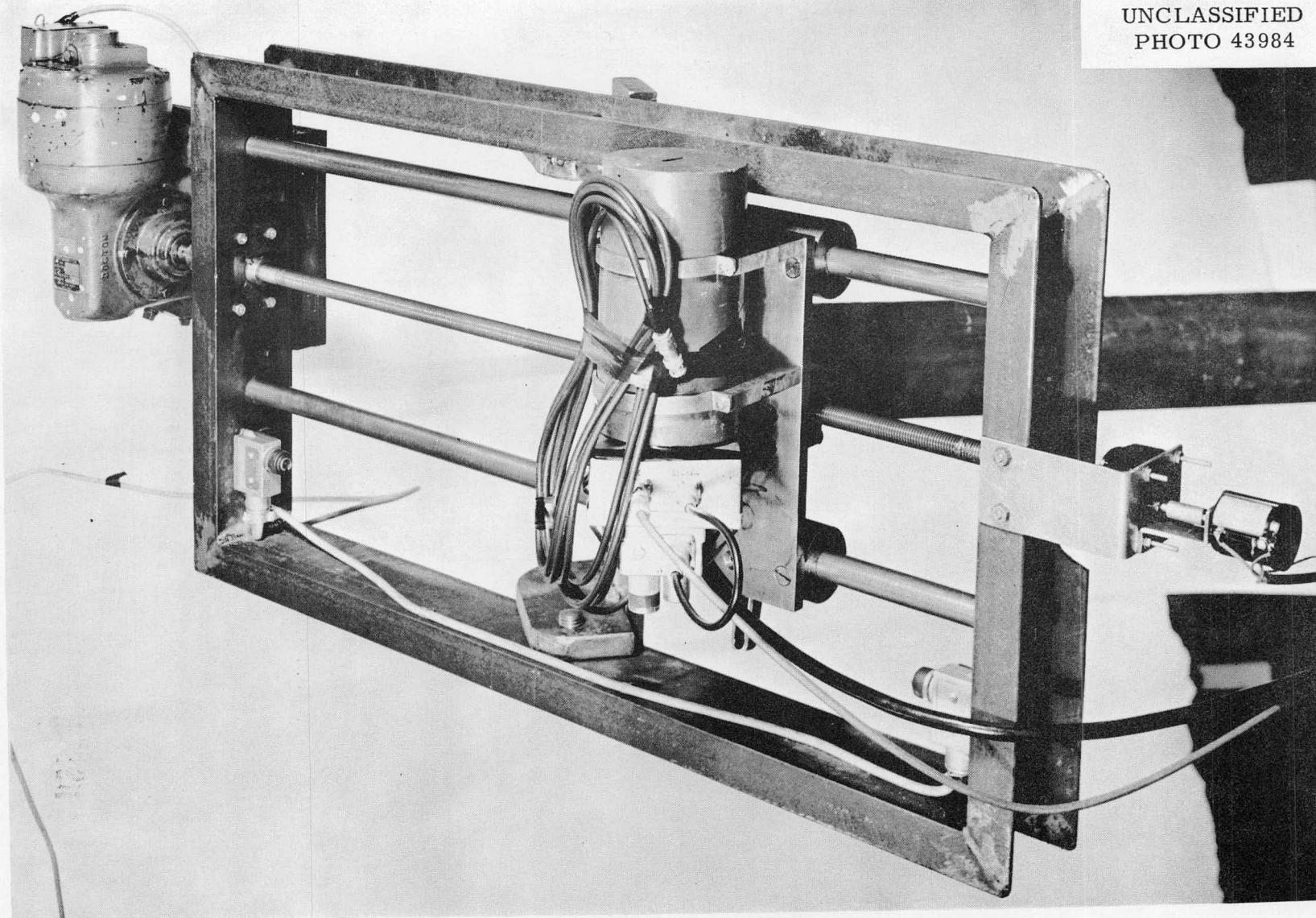


Figure 3 Spectrometer Positioning Assembly

1. F₂ flow meter
2. HF flow meter
3. He flow meter
4. Hydrofluorinator
5. Fluorinator
6. Nickel filter
7. NaF column # 1
8. NaF column # 2
9. UF₆ cold trap
10. Fission product cold trap
11. F₂ waste trap (soda lime)
12. HF waste trap (soda lime)
13. Hood exhaust
14. Hydrofluorinator furnace, 650°C
15. Salt transfer, 700°C
16. Fluorinator furnace, 650°C
17. Filter oven, 100°C
18. No. 1 NaF column furnace, 100°C - 400°C
19. No. 2 NaF column furnace, 100°C - 400°C

line from the hydrofluorination vessel (#4, Figure 4), for the first three steps of the experiment. For the fluorination and subsequent desorption step it was adjacent to the exit line from the fluorination vessel (#3, Figure 4).

Radiochemical analyses were made on the feed, waste salt, bottom and top of the NaF columns, the waste traps, and acid washes from the fission product and UF₆ cold traps.

The nickel filter was examined by means of a scintillation spectrometer, and when sufficient activity was present, by radioautography.

Spectrochemical analyses were conducted on the filter deposits.

Uranium on the UF₆ trap, waste salt, and the NaF columns was determined by fluorimetric methods.

For the activity measurements on the exit gas streams, the spectrometer was adjusted to count all gammas having an energy greater than 50 Kev. The activity level during the He sweep remained constant, except for a burst of activity at about 3.6 hours after startup. This burst was so rapid that it could only have come from a particle of active material being swept by the gas stream. The activity was not identified. After a four hour induction period during the HF sweep the activity gradually increased from 46,000 to 54,000 c/m. There was a two hour induction period during fluorination; then the activity in the exit line from the fluorinator rapidly increased from 8000 to 39,000 c/m. The activity build-up showed no leveling off, but continued to grow until the conclusion of the experiment. The radioactivity in the gas stream at the end of the fluorination was identified gamma spectrometrically as Nb⁹⁵.

The filter was removed at the conclusion of each gas sweep and examined by mounting it on the crystal of a 2" x 2" NaI (Tl) scintillation spectrometer in a low background area. The results are as follows:

1. He sweep - Zr⁹⁵-Nb⁹⁵, Ru¹⁰³, La¹⁴⁰ and probably Te¹²⁹
2. HF sweep - very low activity - possibly U²³⁵ - data uncertain
3. Second HF sweep - very low activity - Possibly U²³⁵ - data uncertain
4. F₂ sweep - activity at least 100 times greater than He sweep, spectrometrically pure Nb⁹⁵

A yellow deposit collected on the filter during the fluorination was shown by spectrochemical analysis to be mainly Cr and Mn. A radioautograph localized the Nb⁹⁵ activity to the area of the deposit (Figure 5).

Radiochemical analysis failed to detect activity in the cold traps, NaF columns and the waste traps. The percentage of the fission product remaining in the waste salt in the reaction vessel were Zr⁹⁵ - 72%, Nb⁹⁵ - 32%, TRU - 82%, Sr - 90%, and Cs¹³⁷ - 100%.

As an indication of the tracer level involved, typical fission product activities in the feed were: Cs¹³⁷ - 0.031 millicuries, Zr⁹⁵ - 2.54 millicuries, and Nb⁹⁵ - 2.79 millicuries. The uranium content was 230 mg. Three grams of zirconium and one hundred grams of NaF-ZrF₄ were also present.

The object of the second experiment was to produce Mo⁹⁹ tracer and study its behavior in the hydrofluorination step. The equipment used for the experiment is shown in Figure 6. The molybdenum activity was prepared by irradiating a small piece of foil in the LITR at a high flux for 60 hours. The foil (~ 10 mg) was dropped into the reaction vessel and the HF flow started. The spectrometer was adjusted to count all gammas having an energy greater than 50 Kev, and installed on the outlet line of the reaction vessel. Grey wedge photographs were made at 30 minute intervals, and whenever a sharp activity increase was noted. The flow of HF was continued for twenty-four hours at 10.6 gms/hr. The activity versus time plot is shown in Figure 7.

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Figure 5 Radioautograph of Filter

Mo⁹⁹ Volatility From Fused Salt Experiment

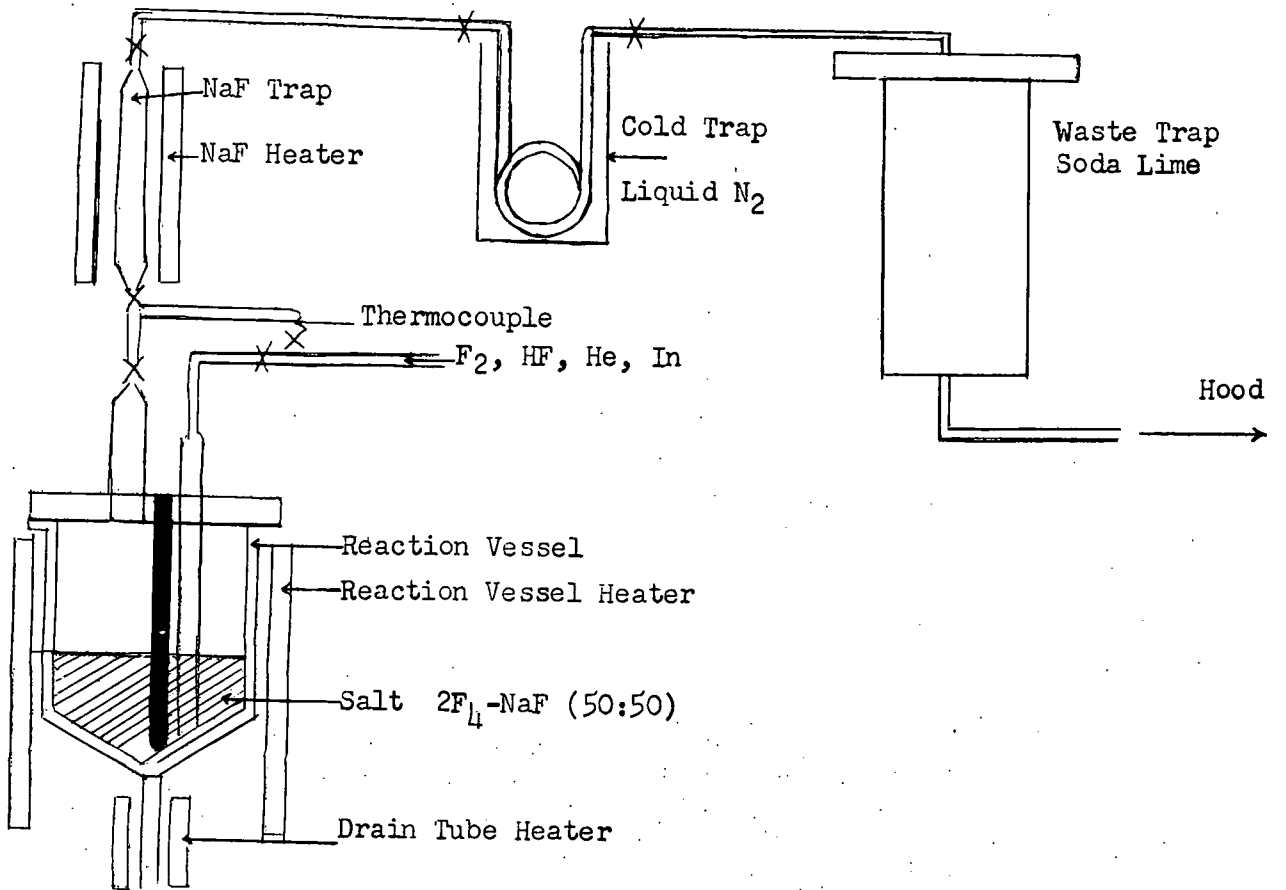
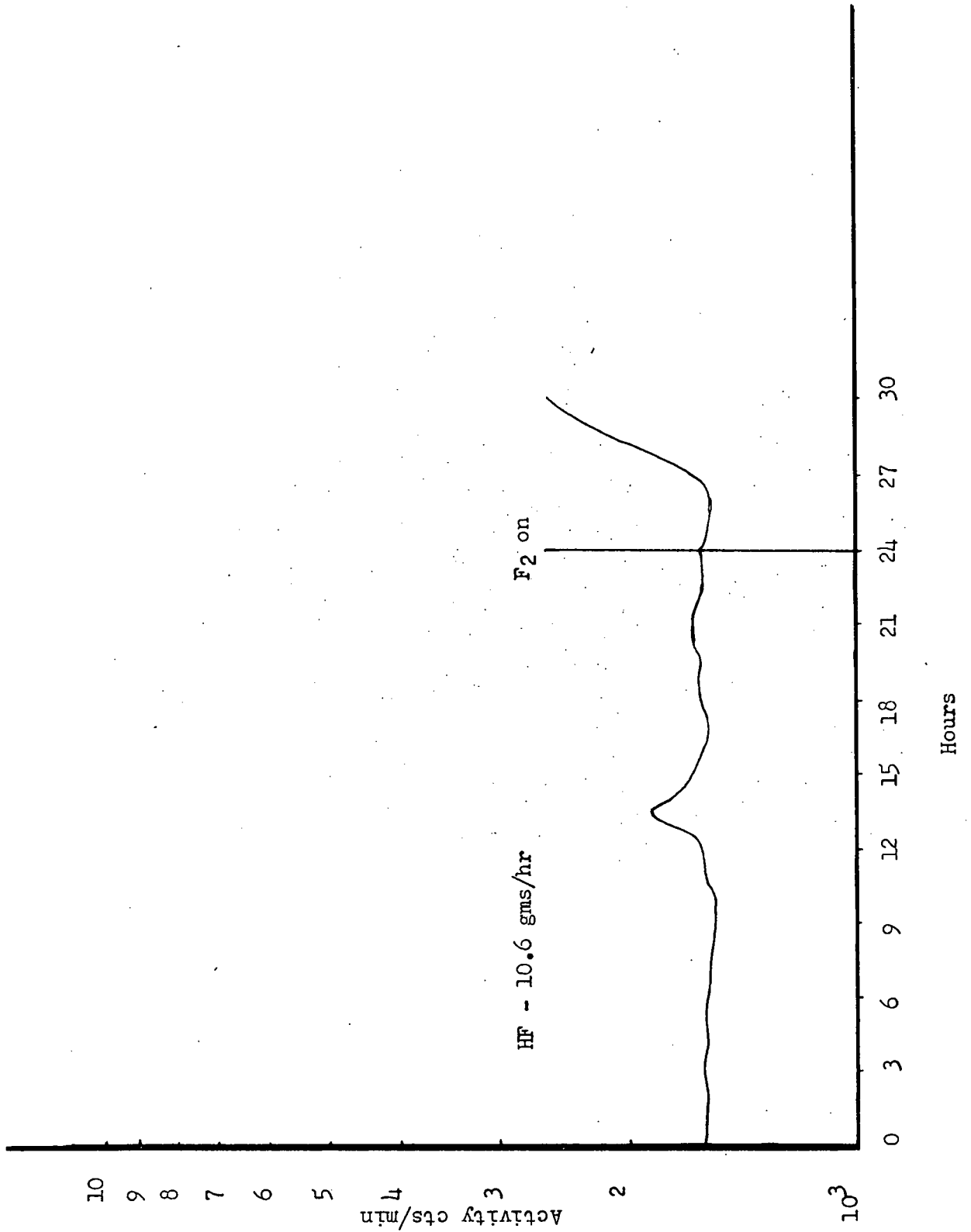


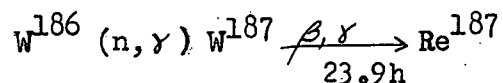
Figure 6

Mo⁹⁹ Volatility from Fused Salt

Figure 7



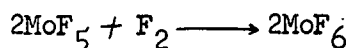
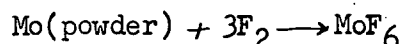
Grey wedge spectra taken on the peak at thirteen hours were inconclusive, since the actual activity increase was only one-fifth of background. Indications were that it was probably W^{187} which was induced in the Mo metal by the neutron bombardment by the following reaction on a tungsten impurity:



The gamma energies of the W^{187} are comparable to the main gammas in Mo^{99} (134 Kev for W^{187} , 140 Kev for Mo^{99}). However, after several days this activity peak could not be located in the equipment, probably indicating decay.

Assuming that it were Mo^{99} , it would amount to much less than 0.1% of the tracer added. The run was terminated at thirty-one hours when the cold trap plugged.

In order to study the behavior of MoF_6 on the NaF column, the final experiments involved the production of $Mo^{99}F_6$ tracer from:



The equipment is shown in Figure 8. It was made of copper tubing, with brass "swage-lok" fittings. The reaction vessel was lined with a tube made from platinum sheet. The NaF column was constructed of brass 1" nickel tubing, and contained 28 grams of 20 mesh C.P. NaF. All tubing which would carry MoF_6 was maintained at about $100^\circ C$ with heating tapes. The system was swept with He, the reaction vessel was closed off from the system and 10 mg of the irradiated Mo powder added. Fluorine was passed over the heated metal for 80 minutes at a flow rate of 5.3 gms/hr. The activity remained in the reaction vessel until the temperature was raised to $300-400^\circ C$. The $Mo^{99}F_6$ condensed in the dry ice cooled reservoir. Fluorine was passed through this container for an additional five hours. No transport of activity was detected by the spectrometer, and the run was discontinued.

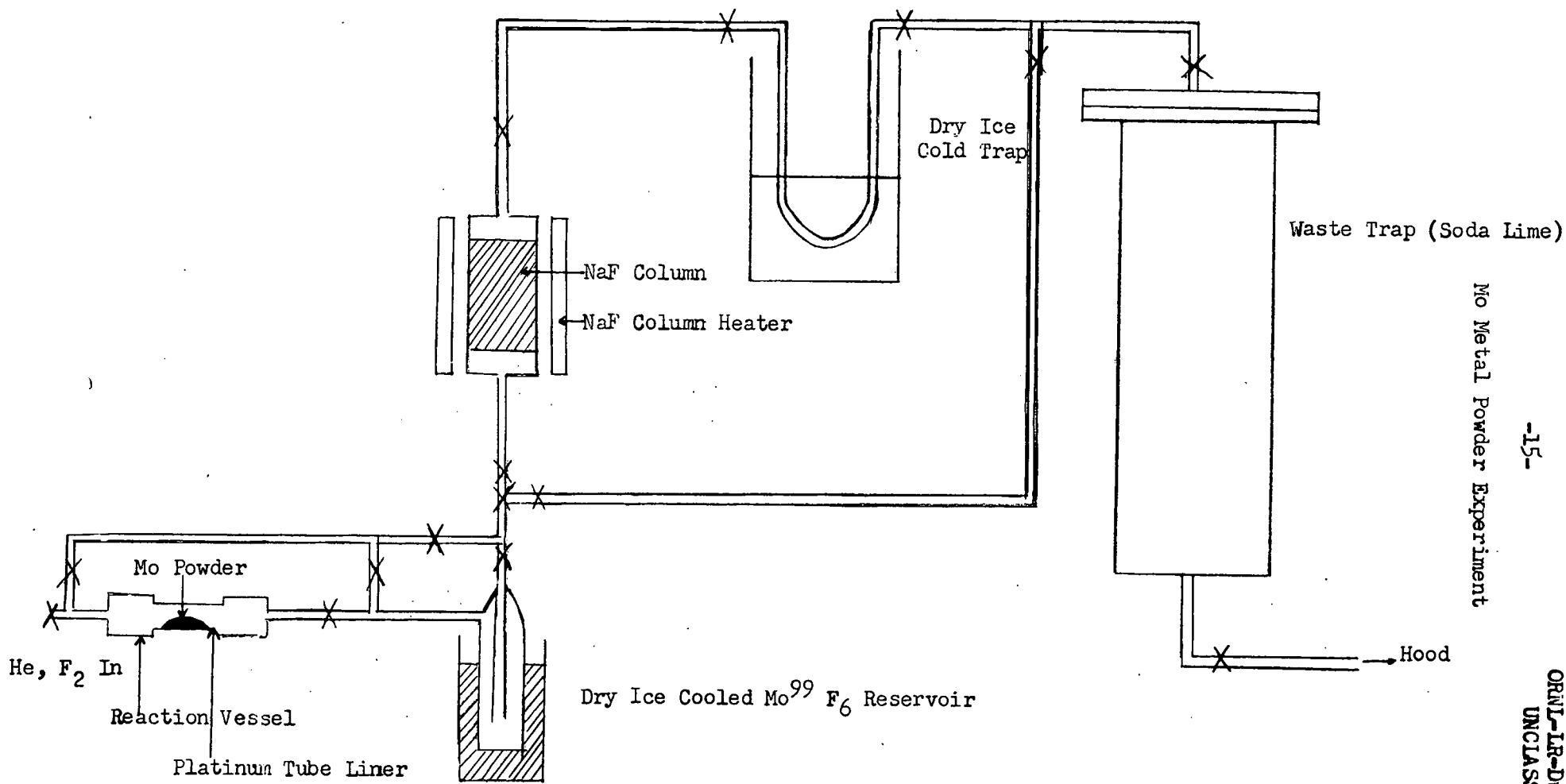
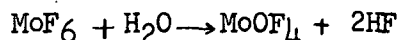
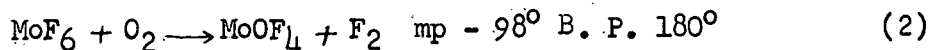


Figure 8

Mo Metal Powder Experiment

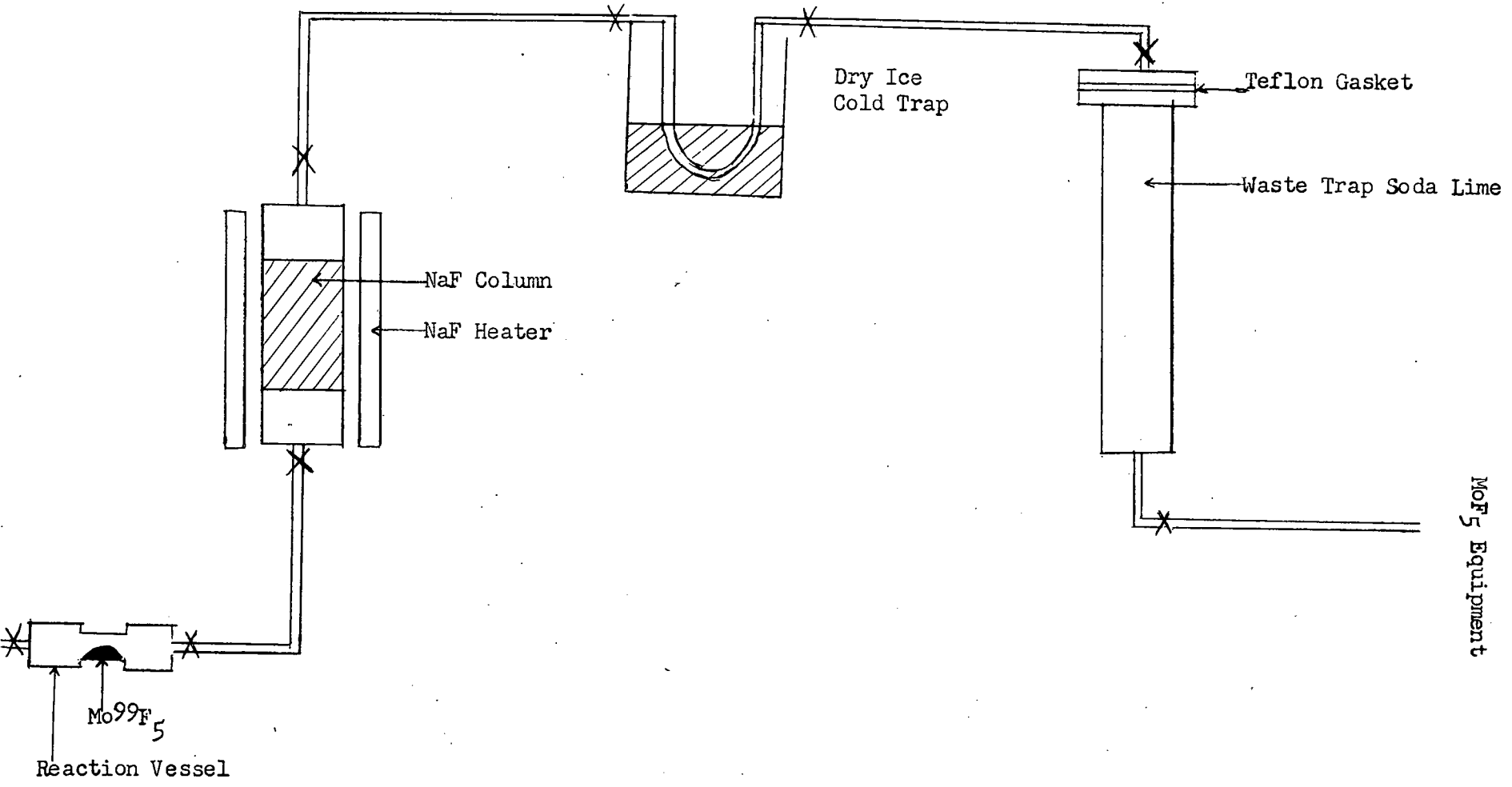
Since the above activity was volatile at 300-400°C and not at 120°C, it must be assumed that the Mo reacted to give fluorides other than MoF₆, or that the MoF₆ formed reacted with water or oxygen to give oxyfluorides.



In order to insure the production of MoF₆ in the highest yield possible, 250 mg of pure MoF₅ was irradiated in the water cooled facility of the graphite reactor and transferred in a He atmosphere to the reaction vessel.

The equipment for the final experiment was modified as shown in Figure 9. All lines were heated to 60-70°C. The spectrometer was installed to monitor the inlet line to the cold trap. A fluorine flow of 6.7 gms/hr was maintained for six hours. The Mo⁹⁹ activity was transferred to the NaF column operating at 100°C. The cold trap was replaced, and the spectrometer placed to monitor the outlet of the new cold trap.

The desorption of the Mo⁹⁹F₆ was started by raising the temperature of the NaF trap to 400°C and continuing the F₂ flow at a rate of 6.7 gms/hr for an additional five hours. The activity versus time plot is shown in Figure 10. Radiochemical Mo⁹⁹ analyses were obtained on the reaction vessel, NaF trap after desorption, the cold trap after absorption at 100°C, the cold trap after desorption at 400°, the teflon gasket at the top of the waste trap, and the upper half of the soda lime from the waste trap; The results are given in Table I.



MoF₅ Equipment

Figure 9

Mo⁹⁹ F₆ Absorption and Desorption on Sodium Fluoride Column

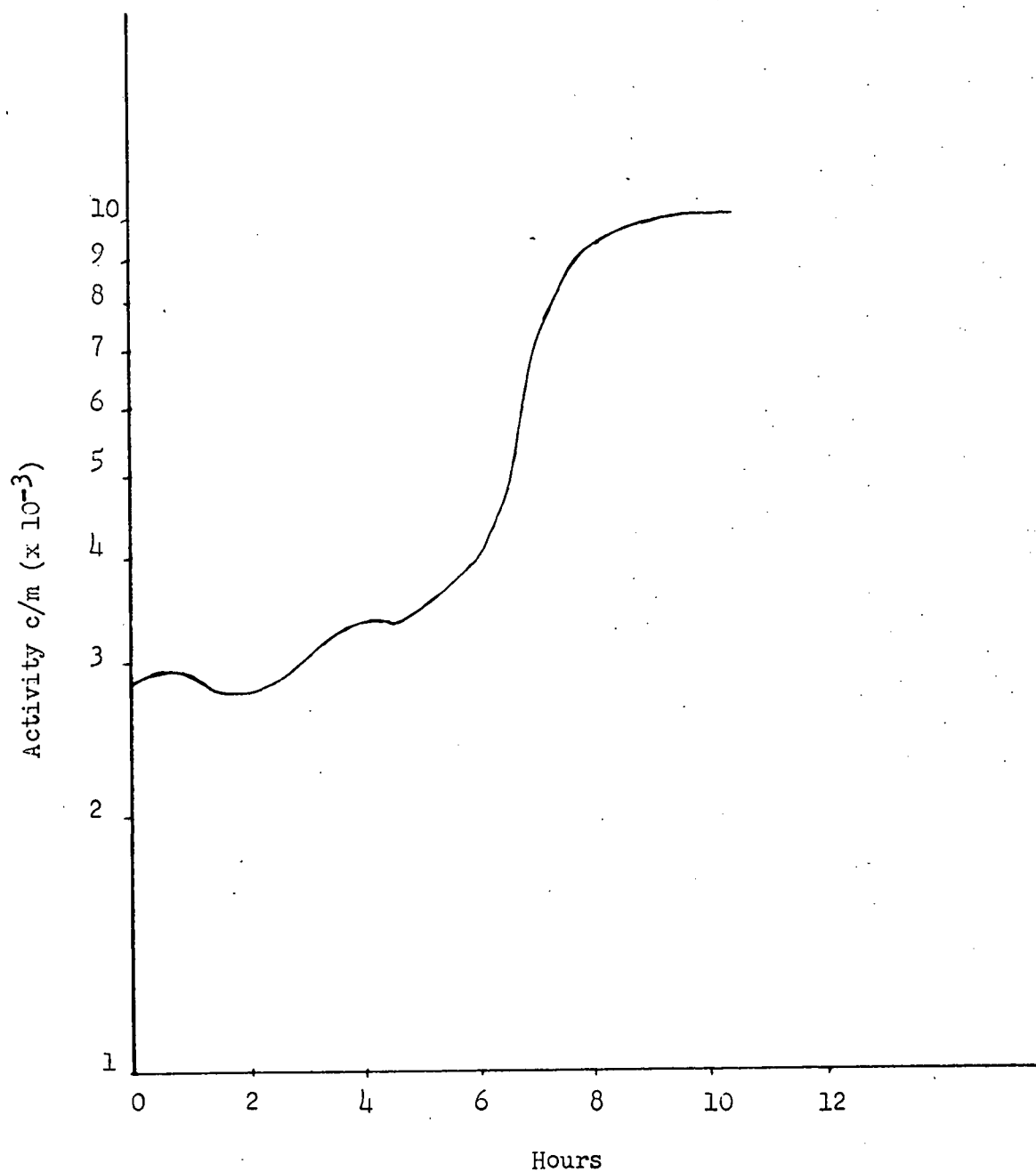


Figure 10

Table I

Distribution of Tracer Mo

	<u>Gross Gamma</u>	<u>Mo</u>	<u>% Gross</u>	<u>% Mo</u>
Reaction Vessel	9.9×10^5	6.2×10^5	8.8	10.3
NaF Column	2.7×10^6	$\sim 5 \times 10^5$	23.9	8.2
Cold Trap after Absorption	2.2×10^4	$< 2.2 \times 10^4$	0.2	0.4
Cold Trap after Desorption	4.5×10^6	3.0×10^6	39.8	49.7
Waste Trap Gasket	2.0×10^6	1.8×10^6	17.7	29.8
Waste Trap	1.1×10^6	1.0×10^6	9.7	16.6

The following conclusions are based on the radiochemical analyses:

1. Most of the MoF_5 was converted to MoF_6 , which volatilized into the NaF column (90%)
2. MoF_6 and Tc fluoride are strongly absorbed on NaF at 100°C . There is less than 0.4% which is not absorbed.
3. The technetium is more strongly held than the molybdenum on the NaF.
4. MoF_6 may not be completely trapped by a dry ice trap because of its vapor pressure of approximately 0.3 mm. at -100°C .

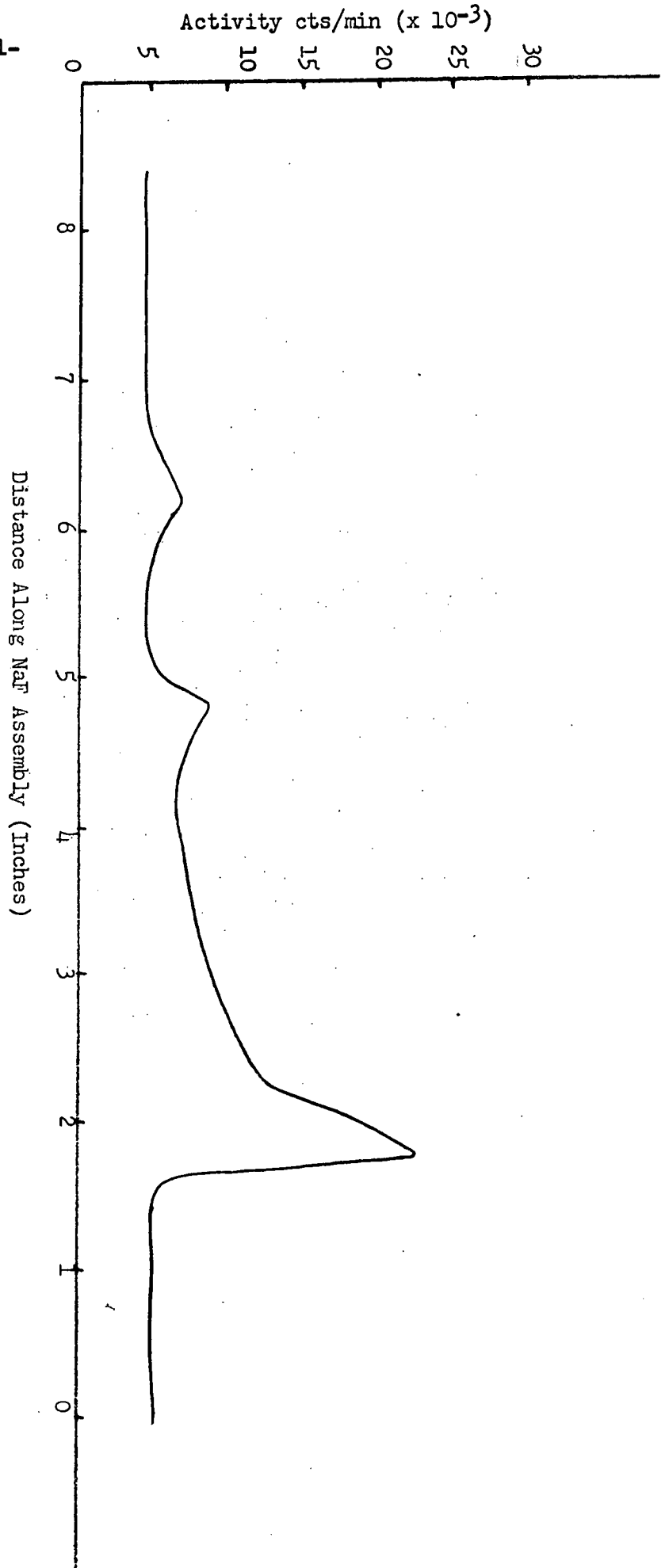
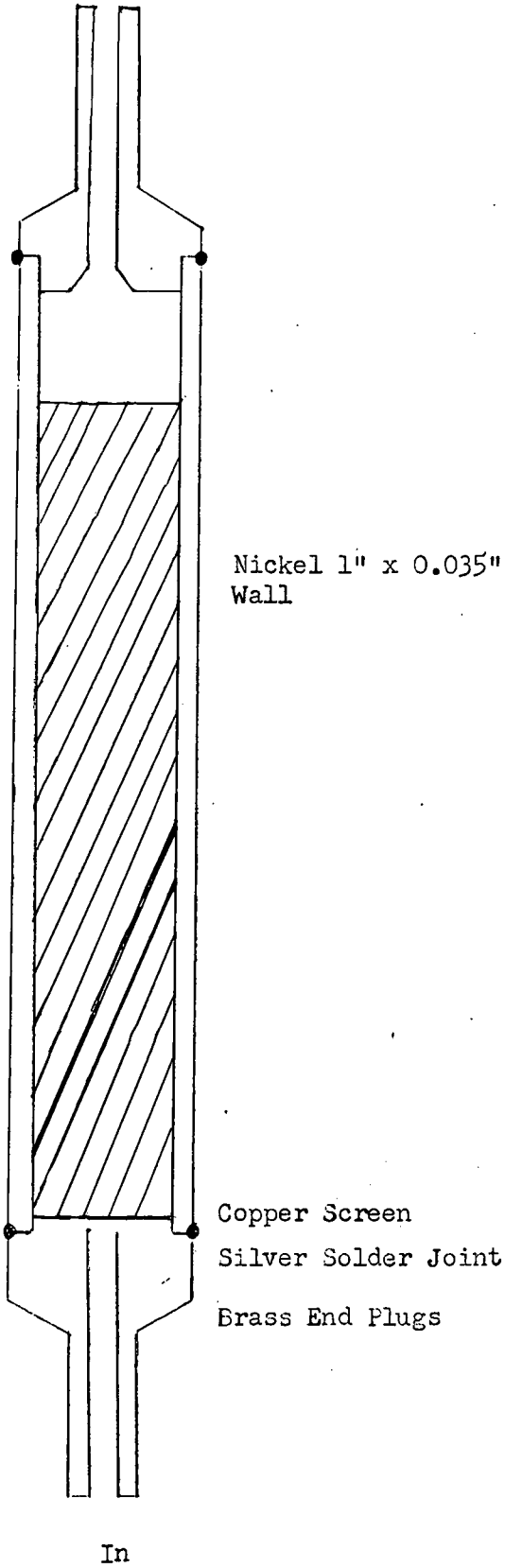
The NaF column was examined by means of the collimated spectrometer. The plot of activity versus distance is given in Figure 11. The multiple peaks may be explained as follows: The largest peak is Tc^{99} , strongly absorbed, which was retained at first contact with the NaF. The second peak is that Mo^{99} which has not yet been displaced from the column. The third peak is activity, Mo^{99} plus Tc^{99} , which was trapped in the crevices of the upper plug.

The behavior of volatile fission product fluorides investigated may be summarized as follows:

1. Ru and Nb fluorides are volatile from fused salts during fluorination.
2. Molybdenum and technetium are not volatile during the hydrofluorination step in fused salt at 630°C .
3. Molybdenum is easily removed from the NaF, while technetium is not.
The MoF_6 is not completely trapped with dry ice - $\text{C}_2\text{H}_3\text{Cl}_3$.
4. Molybdenum and technetium fluorides are volatile in excess F_2 at less than 100°C but are absorbed strongly on NaF.

Future investigations should include studies of the volatile oxyfluorides of Mo.

Figure 11.



The equipment and techniques which were used in the final experiment may be applied to the study of the reaction between any volatile fission product and the NaF bed with a minimum of redesign.

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