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MASS SPECTROMETER STUDY OF TECHNETIUM

BY

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Russell Baldock
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Index No. ORNL-1327

Subject Category: Physics

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August 26, 1952

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ABSTRACT

A sample of approximately five mg of solid ammonium pertechnetate was examined in a mass spectrometer to set the best possible upper limit to the existance of isotopes of masses 97, 100, and 101. Fission product residues were the source of the nearly pure technetium salts. Upper limits were set with respect to Tc 99 as follows: Tc 97, 1/2000; Tc 100, 1/5000; and Tc 101, 1/5000. Incidental to this study several interesting observations were made of the types of ion formation peculiar to technetium compounds as well as on the large number of valence states.

MASS SPECTROMETER STUDY OF TECHNETIUM

John R. Sites, Russell Baldock, and L. O. Gilpatrick

Technetium, the first element to be made artificially, as discovered in 1937 by Perrier and Segre[1] in molybdenum bombarded with neutrons. Lincoln and Sullivan[2] reported in 1945 a fission product activity which was presumed to be a long-lived isotope of element 43 with an estimated half-life of approximately 10^6 years. Late in 1946 Parker, Reed, and Ruch[3] completed experiments using milligram quantities of technetium they had separated from some long-bombarded uranium slugs. In 1948 they reported on investigations on the beta activity, half-life, optical emission spectra, X-ray emission spectra, direct isotopic mass assignment, absorption of visible light, and the chemistry of technetium.

In 1947, Inghram, Hess, and Hayden[4] reported on the direct isotopic mass assignment of technetium. Using the doubly charged mercury ions of masses 99 to 102 as mass standards, they obtained a marked increase in the mass 99 peak while the technetium was distilling into the mass spectrometer source. They also reported that all other possible long-lived fission isotopes of technetium are present to less than 3 per cent of mass 99.

A sample containing 19 milligrams of ammonium pertechnetate (NH_4TcO_4) in an aqueous solution containing ammonia (NH_4OH) and hydrogen perodixe (H_2O_2) was obtained from Parker in 1951. The material was converted to oxide by carefully heating with H_2O_2 at about 150°C. (The following reactions are postulated on the basis of data to be presented.)

$$2(NH_4)TcO_4 \xrightarrow[\sim 150°C]{(H_2O_2)} Tc_2O_7 + 2NH_3 + H_2O$$

$$Tc_2O_7 + H_2O \longrightarrow 2HTcO_4$$

1. Perrier, C. and E. Segre, J. of Chem. Phys. 5, 712 (1937).
2. Lincoln, D. C. and W. H. Sullivan, Atomic Energy Commission Report, CN-3449.
3. Parker, G. W., James Reed, and J. W. Ruch, Atomic Energy Commission Report, AECD-2043.
4. Inghram, Mark G., David C. Hess, Jr., and Richard J. Hayden, Phys. Rev. 72, 1269 (1947).

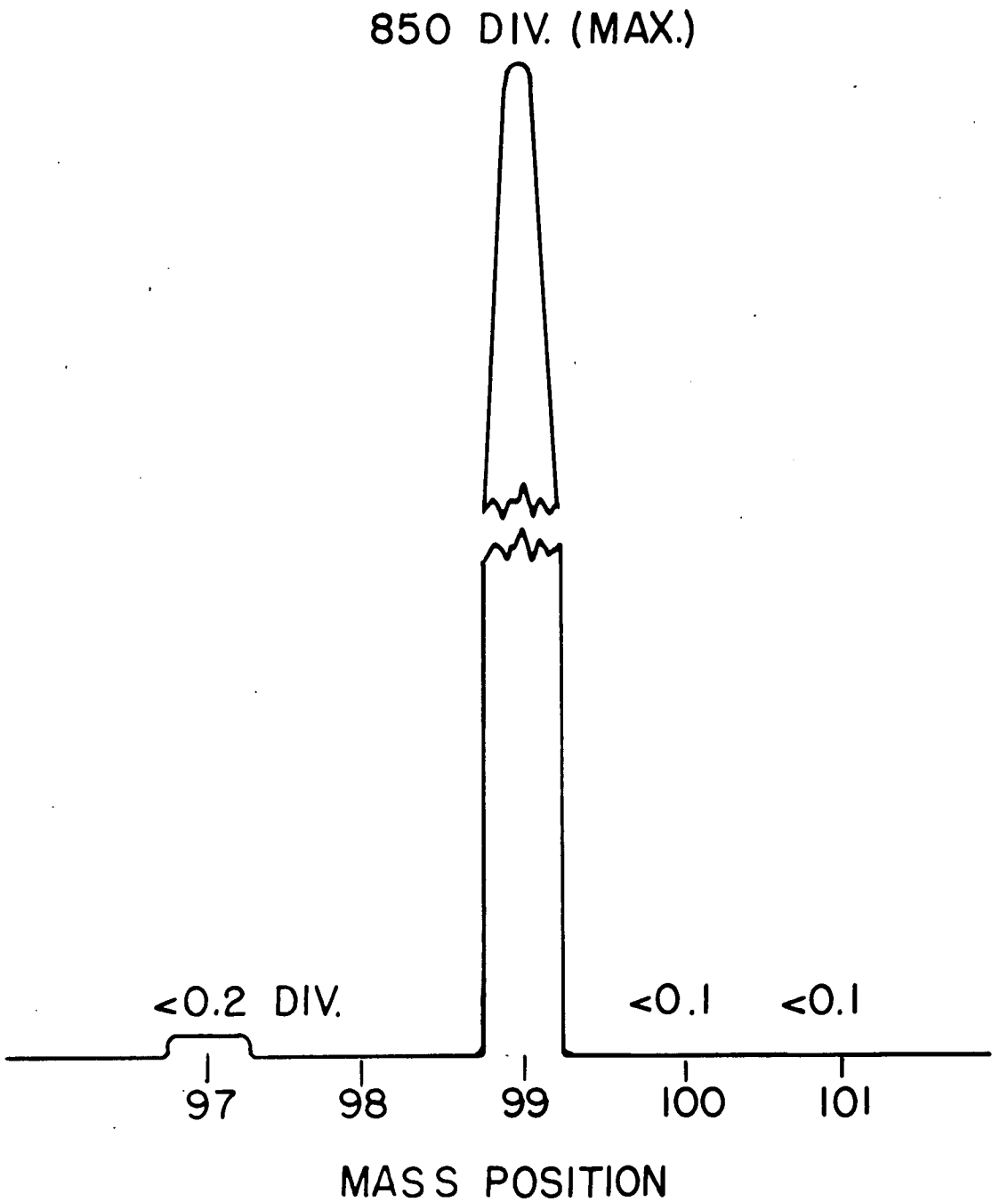
The products of this treatment were put in a small platinum tube which was placed in the ion source of the mass spectrometer. Data were taken for various temperatures of the source oven. The ion accelerating voltage was set at 2000 volts, the ionizing electron voltage at 75 volts, and the trap current at 100 microamperes. The pressure in the mass spectrometer ranged from 1 to 3 x 10^{-6} mm of mercury.

The data are in the form of normalized ion currents with the intensity of one of the mass fragments of a group being set equal to 100 arbitrary units.

During several series of repeated scans through the technetium mass region, it was observed a maximum intensity for the mass 99 peak of 850 divisions on the recorder chart (Fig. 1). It was assumed that a peak 0.1 divisions high could be detected. None were observed at masses 100 and 101. At mass 97 there was a 0.1 to 1.2 division high background peak, probably due to hydrocarbon contamination from the diffusion pump oil. Hence, the upper limit has not been set as high for mass 97 as for masses 100 and 101. The following upper limits of the other isotopes with respect to Tc 99 were found to be: Tc 97/Tc 99, 1/2000; Tc 100/Tc 99, 1/5000; Tc 101/Tc 99, 1/5000. Mass 98 is not reported because of $Se^{82}O^+$ ion contamination.

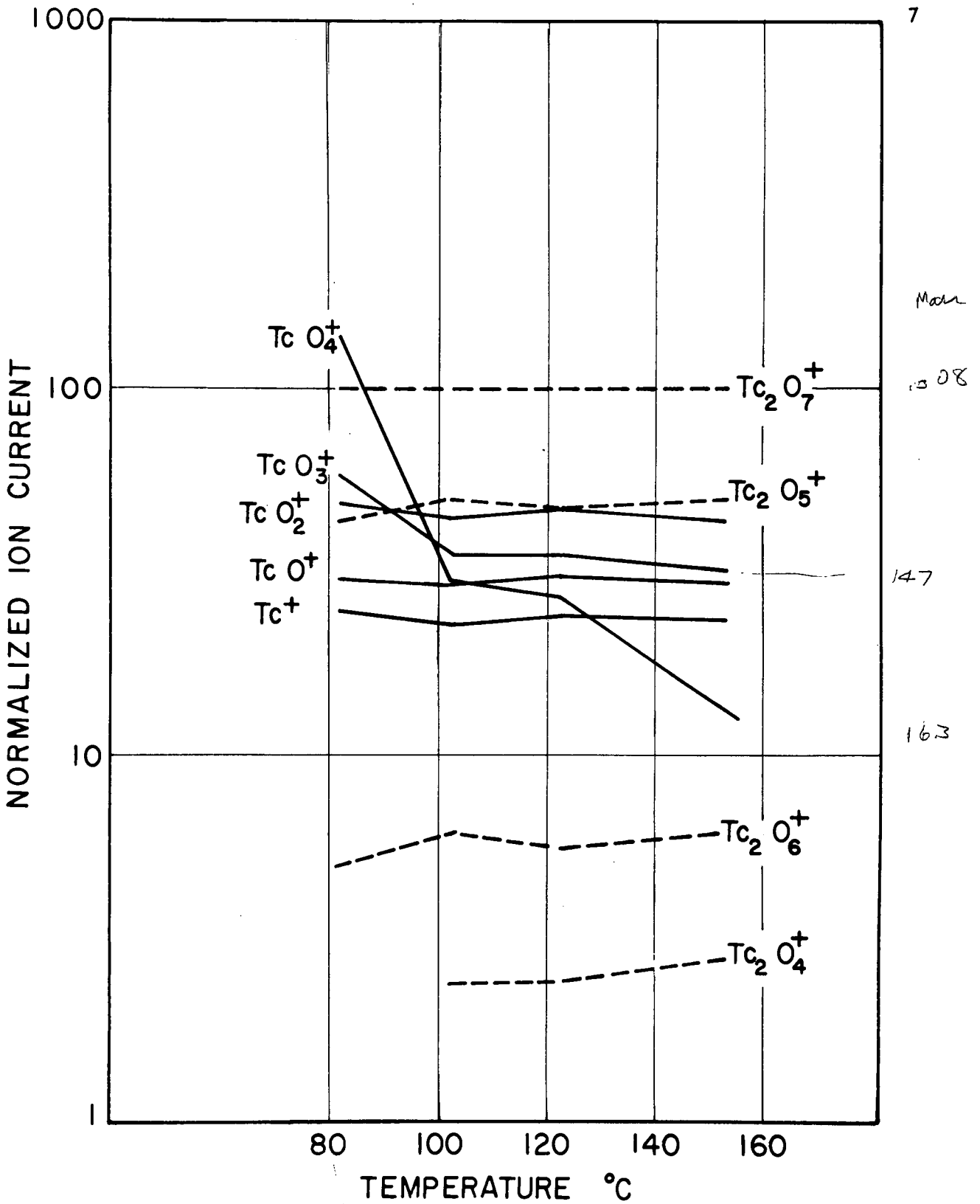
The normalized ion currents for the mass fragments of the heated technetium oxide material from 80° to 160°C are shown in Figure 2. The data are normalized with the most intense ion peak, $Tc_2O_7^+$, equal to 100 units. The parallelness of the ditechnetium oxide curves indicates a common molecular source whose ion mass fragmentation pattern does not change within this temperature range. The drastic decrease in intensity of the TcO_4^+ ion, and the lesser decrease of the TcO_3^+ ion may indicate the thermal decomposition of the postulated $HTcO_4$. The parallelness of the other monotechnetium oxide curves with that of the high temperature tail of the TcO_3^+ ion may indicate the presence of TcO_3 material. The lower ditechnetium oxide ions were of too low intensity to be recorded.

The mass cracking pattern of the technetium oxide material was observed at a temperature of 151°C, with the $Tc_2O_7^+$ ion being set equal to 100 units (Fig. 3). The notation is simplified by identifying each bar on the graph by the number of oxygen atoms related with either one, or two technetium atoms. The prominent ion peaks in the ditechnetium group are $Tc_2O_5^+$ and the $Tc_2O_7^+$, with $Tc_2O_4^+$ and $Tc_2O_6^+$ lower by a factor of ten, and Tc_2^+, Tc_2O^+, $Tc_2O_2^+$, and $Tc_2O_3^+$ lower by a factor of one hundred. The monotechnetium oxide group includes ions of the parent postulated above, $HTcO^+$, $HTcO_2^+$, and $HTcO_3^+$. Prominent between these two oxide groups were two peaks identified as $NH_4TcO_4^+$ and $(NH_4)H_2TcO_4^+$. Several minor ion peaks were identified as being mass fragments of other technetium compounds. The intensities of the monotechnetium oxide group changed much less with



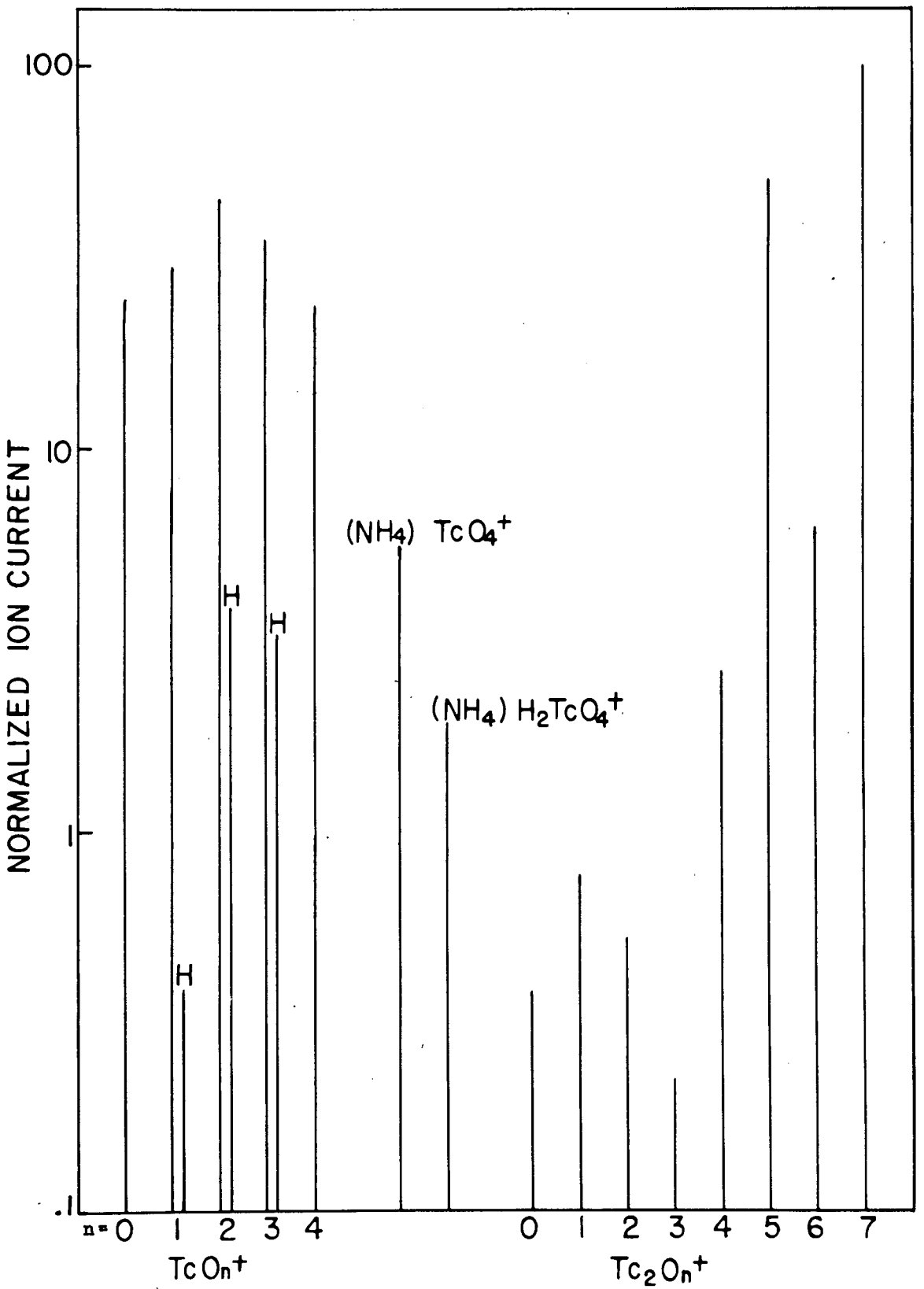
ION PEAKS IN TECHNETIUM MASS REGION

FIGURE 1



TECHNETIUM OXIDE MASS FRAGMENTS
($Tc_2O_7^+$ = 100)

FIGURE 2



TECHNETIUM OXIDE MASS CRACKING PATTERN
($Tc_2O_7^+ = 100$)

FIGURE 3

increasing temperature than did those of the ditechnetium oxide group, indicating that they come from different parent molecules.

Very prominent in the low mass region are SO^+, SO_2^+ ions indicating the presence of sulfates. This is in accord with the recent experiments of Rulfs and Meinke,[5] who reported finding a large amount of ammonium sulfate in their ammonium pertechnetate solution.

At masses of approximately 249.5 and approximately 70, characteristic broad ion peaks indicated the presence of metastable ions. The first corresponds to a $Tc_2O_7^+$ ion losing two oxygens after passing through the accelerating electric field, and going through the magnetic field as a $Tc_2O_5^+$ ion. The second corresponds to a $Tc_2O_7^+$ ion losing a TcO_4 grouping and going through the magnetic field as a TcO_3^+ ion.

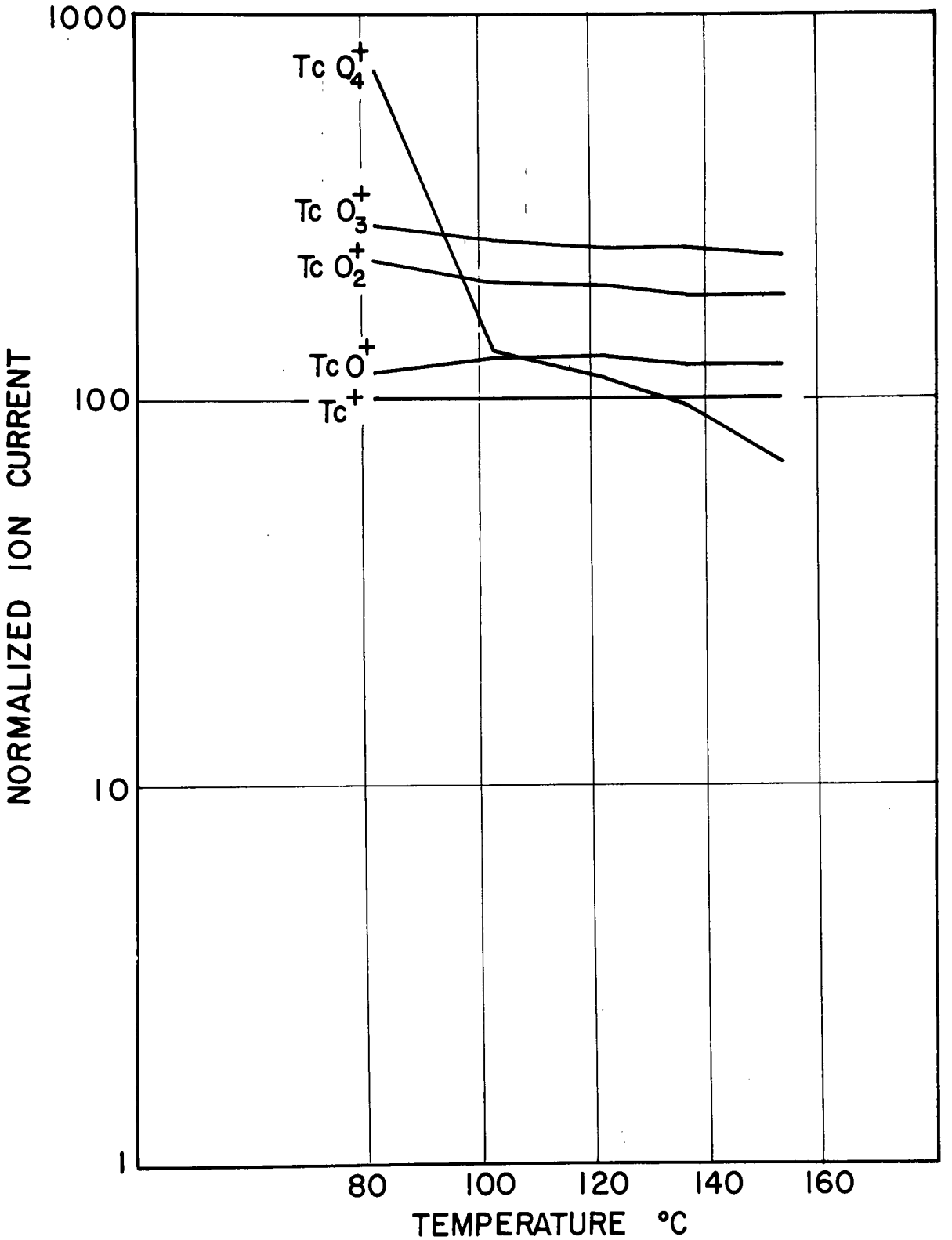
As an additional help in specifying the masses of the higher ditechnetium ions UF_4 was added to the technetium oxide material in the platinum tube. UF_4 was used because its mass cracking pattern had been previoulsy determined, and the masses of its various fragments were close to masses of the ditechnetium oxide fragments. Thus a useful mass dispersion curve could be drawn. However, after the addition of UF_4 not a single peak due to ditechnetium ions appeared during the scans.

The original monotechnetium oxide data shown in Figure 2 were normalized to Tc^+ equal to 100 units and replotted (Fig. 4). Again note the obtuseness of the TcO_4^+ ion, but the TcO_3^+ ion now behaves more like the TcO_2^+ ion.

The monotechnetium data from technetium plus uranium fluoride are also normalized to Tc^+ equal to 100 units (Fig. 5). Before adding the UF_4 the Tc^+ ion was the lowest of its group, but after it is the most intense and there are several technetium oxyfluorides present. There is no TcO_4^+ ion present, nor are there any $Tc_2O_7^+$ ions as stated above. The most abundant ion peaks are those of what apparently is TcO_3F material. The parent peak is of very great intensity, at least more than twenty times that of the next most abundant ions $TcOF^+$ and TcO_2F^+. The TcF^+ ion curve is lower than these by a factor of five.

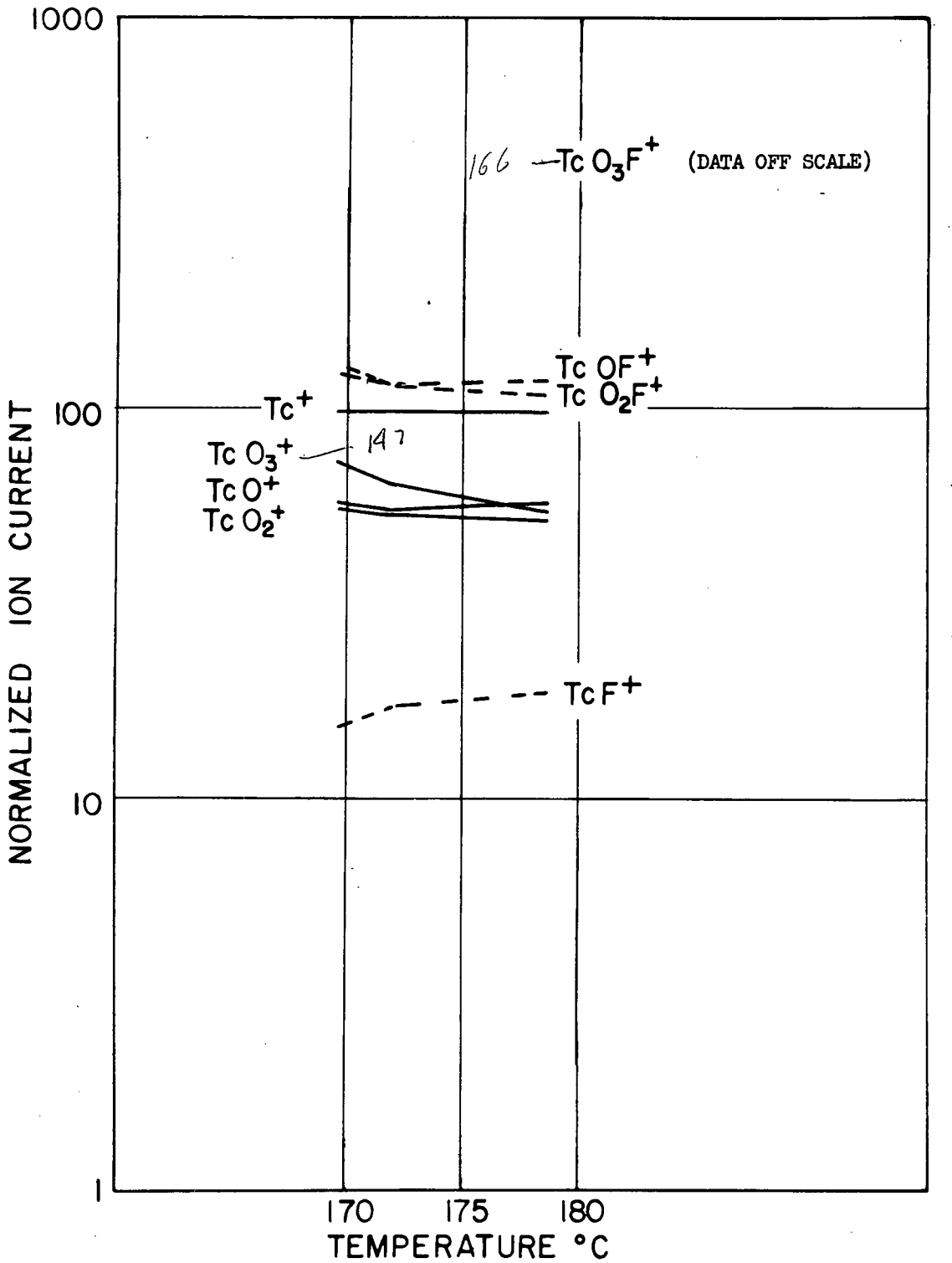
A source of UF_5^+ ions has been detected in UF_4 material. It has been postulated that the source of UF_5 is UO_2F_2 material which reacts with UF_4

5. Rulfs, Charles L., and W. Wayne Meinke, J. of Am. Chem. Soc. 74, 235 (1952).



TECHNETIUM OXIDE MASS FRAGMENTS
(Tc^+ = 100)

FIGURE 4



MASS FRAGMENTS OF TECHNETIUM PLUS URANIUM FLUORIDE
($Tc^+ = 100$)

FIGURE 5

to give UF_5 upon heating. This UO_2F_2 material may also react with the

$$2Tc_2O_7 + UF_4 \xrightarrow{160°C} 4TcO_3F + UO_2$$

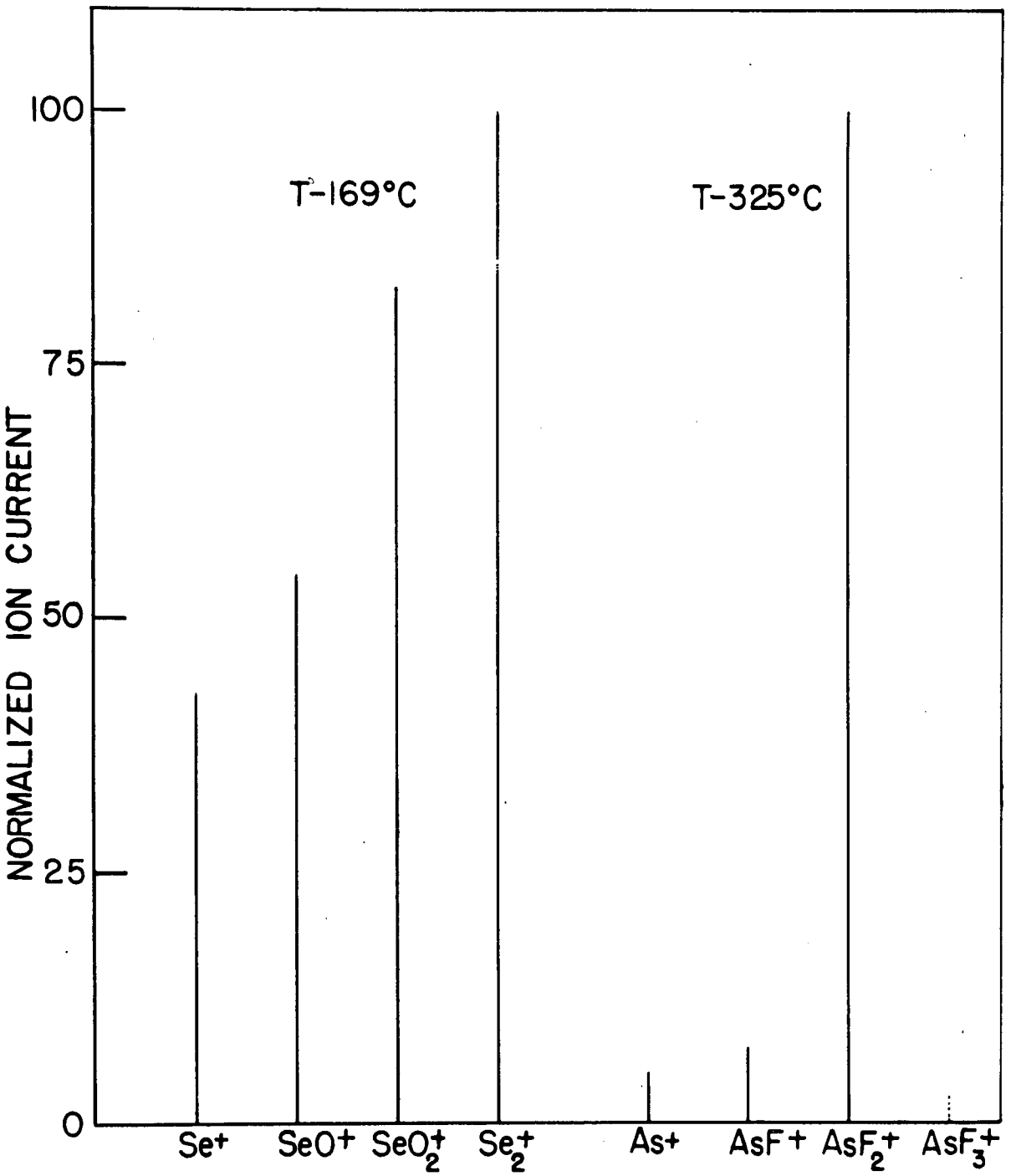
$$2Tc_2O_7 + 2UO_2F_2 \xrightarrow{160°C} 4TcO_3F + 2UO_2 + O_2$$

Tc_2O_7. In this investigation of the technetium with the UF_4 added, the uranium mass fragments were of the UF_5 pattern. These reactions are proposed as possibilities. Tests have not yet been made for the presence of UO_2 in the residue.

Other ion fragments found (Fig. 6) were those identified as coming from selenium oxide and arsenic trifluoride. The Se_2^+ ions were identified by the unique pattern of peaks given by plotting the relative abundances of all the possible two-atom combinations of the six stable isotopes of selenium. It was subsequently learned that the selenium was introduced in one of the early stages of the separation of the fission products. No monoselenium fluorides or oxyfluorides were found, or any diselenium oxides, fluorides, or oxyfluorides. The arsenic is an impurity of unknown source. The AsF_3^+ ion peak is less than two per cent of the AsF_2^+ peak. Neither of these sets of mass fragments have been found in the UF_4 material in subsequent mass spectrometer check runs.

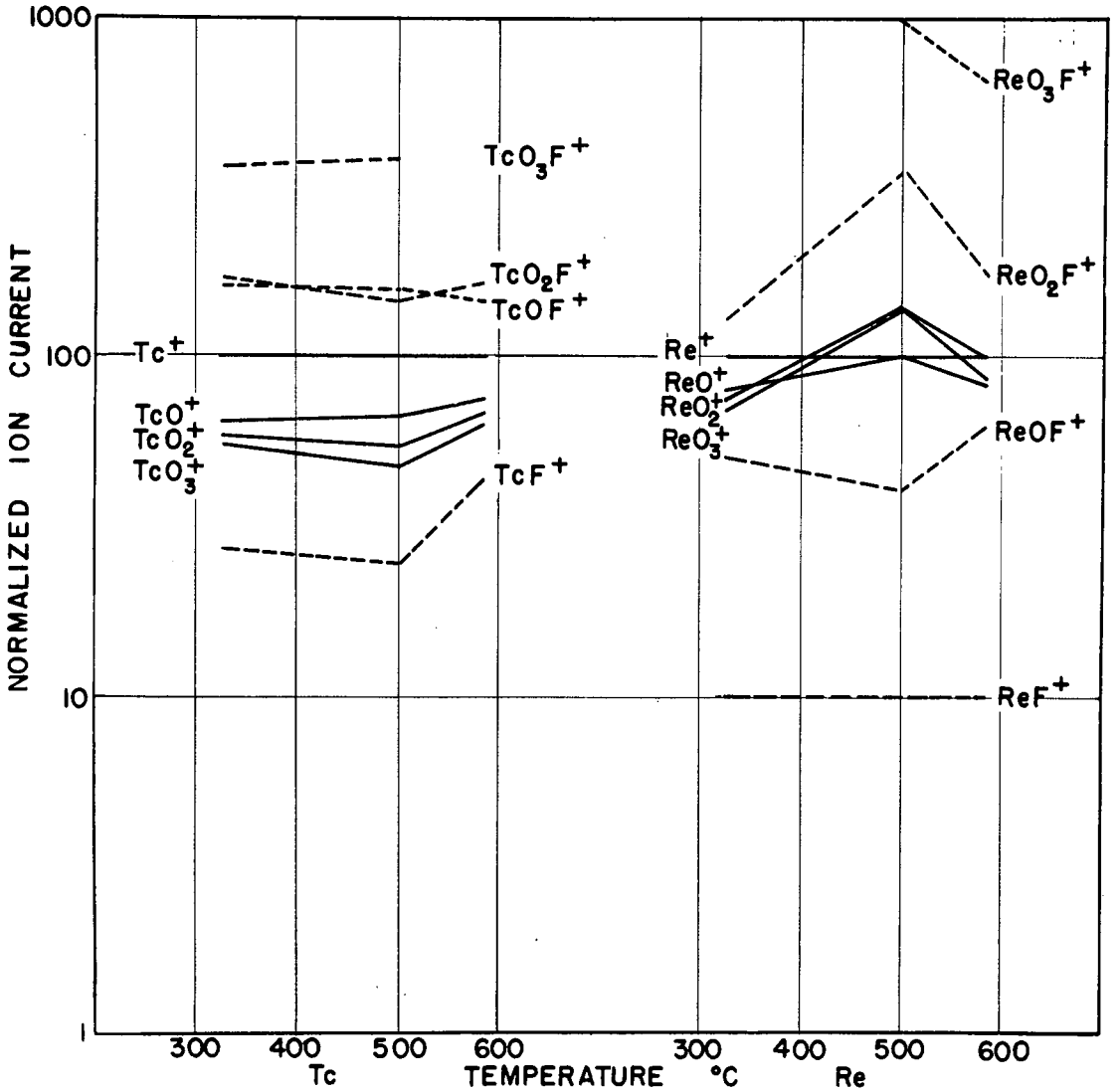
Above 300°C mass fragments of rhenium appeared (Fig. 7). Rhenium, being chemically similar to technetium, had been added in the separation of the fission products as a carrier for technetium and was not completely removed. Here the technetium and rhenium oxyfluoride patterns are normalized to the elemental ion equal to 100 units. The rhenium oxide group of mass fragments is quite similar to the technetium oxide group but the rhenium oxyfluoride mass fragments have a different distribution. The ReF^+ ion is the lowest of the group and it is lower than the TcF^+ ion. The $ReOF^+$ ion is below the oxide group while the $TcOF^+$ ion is above its oxide group and essentially the same as the Tc_2F^+ ion. The ReO_2F^+ ion is similar to the TcO_2F^+ ion. Both the TcO_3F^+ and ReO_2F^+ ions are much more intense than the other mass fragments, with the rhenium ion higher than that of technetium and with an apparently different slope. The scatter in the rhenium data was greater than that of the technetium due to the much smaller intensity of the rhenium mass fragments. The differences in the oxyfluoride patterns and the similarity of the oxide patterns may indicate that two compounds are co-existing, the trioxide and the trioxyfluoride.

These data are based on our preliminary study of technetium and it is planned to continue our investigations.



SELENIUM AND ARSENIC IN TECHNETIUM PLUS URANIUM FLUORIDE

FIGURE 6



COMPARISON OF TECHNETIUM AND RHENIUM IN TECHNETIUM PLUS URANIUM FLUORIDE (Te^+, Re^+ = 100)

FIGURE 7