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# ABSORPTION SPECTRA OF PLUTONIUM AND IMPURITY IONS IN NITRIC ACID SOLUTION

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JULY 31, 1956

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July 31, 1956

HANFORD ATOMIC PRODUCTS OPERATION
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# ABSORPTION SPECTRA OF PLUTONIUM AND IMPURITY IONS IN NITRIC ACID SOLUTION

## INTRODUCTION

The determination of the valence states of plutonium is desirable in various parts of the process for the separation and purification of plutonium. During the early history of plutonium chemistry, a considerable amount of work was done on the spectra of plutonium ions in various valence states and some of the complexes. With the exception of studies summarized by Hindman,(1) most of this work was done with solutions other than nitric acid. Since the separations process is carried out in nitric acid solutions, and little is reported on the spectra of many of the impurities which are present in the process, an investigation was undertaken to determine the absorption coefficients for plutonium valence species in nitric acid, and for some of the impurities found in process streams. A Beckman DK-2 recording spectrophotometer was used.

## SUMMARY AND CONCLUSIONS

The absorption spectra for plutonium(III), (IV), (VI), and the red plutonium(IV) - peroxy complex were determined in nitric acid solution. Extinction coefficients for the above species of plutonium were measured. Temperature has little effect on the spectra, but variation of acidity causes shifting of absorption peaks and some changes in the extinction coefficients.

The absorption spectra and extinction coefficients in the region 390-1200 mμ were measured for chromic, nickelous, manganous, calcium, lanthanum, aluminum, ferrous, ferric, and permanganate ions in nitric acid solutions. In addition, the effects of nitrite, oxalic acid, sulfamic acid, hydrogen peroxide, and various nitric acid concentrations on the extinction coefficients of some of these ions were determined. The chromic, nickelous, ferrous, and permanganate ions, and ferric ion with oxalic acid, have sufficiently high extinction coefficients to cause inaccuracies in valence determinations of plutonium in solutions containing high concentrations of these ions, unless corrections are made.

## EXPERIMENTAL

### Valence Adjustment

A solution of plutonium nitrate containing 100 per cent plutonium(IV) was prepared by adding hydrogen peroxide (final concentration, three per cent by volume) to pure stock solution (500 g/l plutonium, 4 M $HNO_3$) and allowing the mixture to react completely (ca. twenty minutes). Plutonium (III) was prepared from plutonium(IV) by reduction with stoichiometric amounts of ferrous ion, using 0.1 M sulfamic acid as a holding agent. Plutonium(VI) was prepared by boiling a 1.0 M nitric acid solution of plutonium(IV) (30 g/l plutonium) for several hours under reflux. Plutonium (IV)-peroxy complex was obtained by adding hydrogen peroxide (final concentration, 0.27 M) to plutonium(IV) solution (0.5-1 g/l plutonium) at 0 C.

### Equipment

A Beckman DK-2 Recording Spectrophotometer, with 10 mm square Corex cells, was used for all experiments. A special sample chamber utilizing quartz windows was used to prevent contamination of the spectrophotometer.

### Analysis

All analyses were made in the 234-5 Control Laboratory. Plutonium was determined by radio-assay. Experiments were run at 21-25 C except those with the peroxy complex, which were run at 10-15 C.

## RESULTS AND DISCUSSION

### Plutonium

As previously reported,(1) plutonium(III), (IV), and (VI) follow the Beer-Lambert law in their light absorbing characteristics. The plutonium(VI) peak at 829 mμ, however, deviates markedly, as shown in Figure 1. The absorption spectra of these three valence states are shown in Figure 2, and DK-2 plots of the valence states are shown in Figures 6, 7, and 8, respectively. For all of the absorption peaks except the 829 mμ, an average extinction coefficient was determined from absorption measurements made over the concentration range 0.5-3 g/l plutonium.

The absorption spectra of the plutonium(IV)-peroxy complex does not differ greatly from the plutonium(IV) spectra at wavelengths greater than 650 mμ but has very strong absorption in the shorter wavelength region, as shown in Figure 9. The peroxy complex extinction coefficients were determined at plutonium concentrations of 0.5 and 1 g/l. At the nitric acid concentration used (2 M), a very large peroxide to plutonium(IV) ratio (approximately 135/1) was necessary for complete complexing of the plutonium(IV). Further addition of peroxide resulted in no change in absorption. The red peroxy complex had an absorption spectrum similar to that previously reported.(1) No brown peroxy complex was observed in 2 M nitric acid. The extinction coefficients obtained for the plutonium(IV) peroxy complex hold over the range 0.5-135 moles of peroxide/mole of plutonium, as shown by material balances. Uncomplexed plutonium(IV) can be determined quantitatively in the presence of complexed plutonium(IV) from the 475 mμ peak.

Table I shows the molar extinction coefficients of plutonium(III), (IV), (VI), and the red plutonium(IV)-peroxy complex, as determined for the DK-2 used. These values may vary slightly for other machines because of different characteristics of the individual spectrophotometers. No correction for ferric iron absorption is made on the plutonium(III) peaks, since the absorption is negligible for the small amount of iron (0.5 g/l) present.

Concentrations as low as 0.1, 0.05, 0.01, and 0.02 g/l plutonium(III), (IV), (VI), and (IV)-peroxy complex can be measured in the presence of each other, in mixtures containing a total of about 3 g/l plutonium, in a 10 mm cell. At these low concentrations precision is no better than a factor of two. However, at higher concentrations of the individual ions (up to 3 g/1), the precision is approximately ± 0.1, ± 0.05, and ± 0.1 g/l plutonium for the III, IV, and VI states. The presence of absorbing impurities decreases the precision. The DK-2 spectrophotometer itself has a duplication limit of ± 0.005 absorbance, or for typical peaks ± two per cent.

The maximum concentration which may be used for valence determination in 10 mm cells is 3-3.5 g/l. Concentrations below 0.3 g/l or above 3 g/l require longer or shorter cells, respectively.

Small temperature differences have little effect on the extinction coefficients or spectra of plutonium(III) or (VI) and cause only a slight change in two absorption peaks (702 mμ, 475 mμ) in the plutonium(IV) spectra. (A maximum error of plus four per cent in calculation results from a temperature change from 15 to 30 C).

As previously reported(1) variation in the nitric acid concentration causes shifting of absorption peaks, the appearance of a new peak for plutonium(VI) at high acidities, and some increase or decrease of the extinction coefficients. Tables II, III, and IV show the absorption coefficients for plutonium(III), (IV), and (VI) at various acidities. These values are only good to ± 5 per cent, although the precision within each valence state is probably better. Several discrepancies greater than five per cent are seen on comparison with Table I. No explanation is available, but it is proposed that absorption standards be checked frequently to assure that the machine response does not vary over particular absorption ranges, following periods of maintenance.

## Other Ions

The extinction coefficients of calcium, lanthanum, manganous and aluminum ions are so very low that up to ten grams per liter of these ions can be ignored in most valence determinations of plutonium.

Chromic ion has two strong absorption peaks in the region 390-1200 mμ at 405 and 575 mμ. Nickelous ion has absorption peaks at 394, 655, 670, 1180 mμ (Figure 3). No changes due to temperature, oxalic acid, sulfamic acid, nitrite, hydrogen peroxide, or nitric acid concentration in the region 0.5 to 6 M were observed with these ions.

Permanganate ion in 2 M nitric acid has very strong absorption at 450-600 mμ, with peaks at 506, 523, 542, and 562 mμ and possibly peaks at 467 and 490 mμ, as shown in Figure 10.

Ferrous iron has absorption peaks at 960 and 1100 mμ (Figure 4). Oxalic acid (0.1 M), nitric acid concentration (between 0.5 and 6.0 M $HNO_3$) and sulfamic acid have very little effect on either the absorption spectra or coefficients. Nitrite forms a complex with ferrous ion which absorbs strongly at wavelengths shorter than 800 mμ, but is too short-lived in 2 M nitric acid to obtain a spectrum.

Ferric iron has very low absorption in the range 450-1200 mμ. Below 450 mμ, absorption increases rapidly. Nitrite, hydrogen peroxide, and sulfamic acid have very little effect on the extinction coefficients. The extinction coefficients increase slightly with increasing acidity. Oxalic acid forms a complex with ferric iron, which absorbs strongly at wavelengths shorter than 500 mμ, as shown in Figure 5.

A summary of the extinction coefficients of the above ions is found in Table V. Chromic, nickelous, ferrous, and ferric ions follow the Beer-Lambert Law.

M N Myers

MNM:ag M. N. Myers

## REFERENCES

(1) Hindman, J. C., "Ionic and Molecular Species of Plutonium in Solution," National Nuclear Energy Series, Vol. IV-14A. *The Actinide Elements,* G. T. Seaborg and J. J. Katz, Ed. New York: McGraw-Hill, (1954) pp. 301-364.

## TABLE I

## MOLAR EXTINCTION COEFFICIENTS OF PLUTONIUM(III), (IV), (VI), AND (IV)-PEROXY COMPLEX

| Wavelength mμ | Molar Extinction Coefficients[a] | | | |
|---|---|---|---|---|
| | Plutonium(III) | Plutonium(IV) | Plutonium(VI) | Plutonium(IV)-Peroxy Complex |
| 421 | 18.4 | 33.0 | 18.6 | 247 |
| 457 | 7.6 | 26.5 | 22.0 | 197 |
| 475 | 7.6 | 81.7 | 21.3 | 193 |
| 502 | 6.4 | 15.3 | 17.4 | 304 |
| 541 | 21.7 | 23.2 | 10.8 | 176 |
| 565 | 45.4 | 9.8 | 7.7 | 89 |
| 598 | 44.7 | 7.7 | 6.5 | 40.6 |
| 656 | 17.0 | 39.0 | 6.7 | 31.5 |
| 702 | 3.6 | 19.8 | 5.0 | 22.9 |
| 795 | 18.2 | 26.0 | 6.5 | 25.1 |
| 829 | 10.0 | 14.3 | Graph[b] | 20.1 |
| 850 | 7.9 | 20.3 | 5.7 | 17.4 |
| 908 | 24.9 | 4.1 | 4.5 | 9.1 |
| 950 | 5.7 | 5.3 | 25.8 | 10.5 |
| 981 | 7.4 | 11.2 | 21.3 | 17.0 |
| 1017 | 18.4 | 17.4 | 4.5 | 22.7 |
| 1068 | 13.4 | 34.6 | 2.9 | 26.1 |
| 1101 | 25.3 | 19.1 | 2.5 | 15.5 |

NOTES:

(a) Determinations were made in 2 M $HNO_3$.

(b) Figure 1 shows the molar extinction coefficient variation with absorbance.

## TABLE II

## EFFECT OF ACIDITY ON ABSORPTION SPECTRA AND COEFFICIENTS OF PLUTONIUM(III)

| Wavelength mμ | Molar Extinction Coefficients in 0.52 $\underline{M}$ $HNO_3$ | 2.12 $\underline{M}$ $HNO_3$ | 3.92 $\underline{M}$ $HNO_3$ | 5.79 $\underline{M}$ $HNO_3$ |
|---|---|---|---|---|
| 565 (a) | 48 | 47 | 49 | 49 |
| 598 | 45 | 47 | 48 | 48 |
| 662 | 19 | 17 | 16 | 16 |
| 808 | 20 | 18 | 17 | 16 |
| 908 (b) | 25 | 24 | 23 | 23 |
| 1017 | 19 | 18 | 16 | 16 |
| 1101 | 27 | 25 | 23 | 22 |

NOTES:

(a) This peak shifted from 568 mμ at 0.52 $\underline{M}$ $HNO_3$ to 563 mμ at 5.79 $\underline{M}$ $HNO_3$.

(b) This peak shifted from 908 mμ at 0.52 $\underline{M}$ $HNO_3$ to 916 mμ at 5.79 $\underline{M}$ $HNO_3$.

## TABLE III

## EFFECT OF ACIDITY ON ABSORPTION SPECTRA AND COEFFICIENTS OF PLUTONIUM(IV)

| Wavelength mμ | Molar Extinction Coefficients in 0.52 $\underline{M}$ $HNO_3$ | 2.0 $\underline{M}$ $HNO_3$ | 3.93 $\underline{M}$ $HNO_3$ | 5.96 $\underline{M}$ $HNO_3$ |
|---|---|---|---|---|
| 421 (a) | 26 | 32 | 39 | 38 |
| 475 | 81 | 91 | 94 | 79 |
| 541 (b) | 21 | 22 | 24 | 24 |
| 656 | 40 | 40 | 43 | 40 |
| 702 | 20 | 19 | 21 | 21 |
| 795 (c) | 27 | 26 | 27 | 26 |
| 850 | 17 | 19 | 21 | 19 |
| 1068 | 34 | 35 | 38 | 38 |

NOTES:

(a) This peak shifted from 425 mμ at 0.52 $\underline{M}$ $HNO_3$ to 421 mμ at 5.96 $\underline{M}$ $HNO_3$.

(b) This peak shifted from 546 mμ at 0.52 $\underline{M}$ $HNO_3$ to 538 mμ at 5.96 $\underline{M}$ $HNO_3$.

(c) This peak shifted from 802 mμ at 0.52 $\underline{M}$ $HNO_3$ to 785 mμ at 5.96 $\underline{M}$ $HNO_3$.

## TABLE IV

## EFFECT OF ACIDITY ON ABSORPTION SPECTRA AND COEFFICIENTS OF PLUTONIUM(VI)

| Wavelength mμ | Molar Extinction Coefficients in 0.62 $\underline{M}$ $HNO_3$ | 2.06 $\underline{M}$ $HNO_3$ | 3.95 $\underline{M}$ $HNO_3$ | 5.55 $\underline{M}$ $HNO_3$ |
|---|---|---|---|---|
| 457 | 17 | 18 | 21 | 23 |
| 785 | 4.7 | 4.7 | 4.8 | 5.5 |
| 815 | 5.8 | 5.8 | 8.3 | 21 (a) |
| 829 (b) | 117 | 114 | 118 | 118 |
| 950 | 27 | 26 | 25 | 22 |
| 980 | 21 | 21 | 20 | 18 |

**NOTES:**

(a) This was a new peak.

(b) These values hold only for the concentration used for this particular run.

## TABLE V

## MOLAR EXTINCTION COEFFICIENTS OF VARIOUS IONS IN 2 M $HNO_3$

| Wavelength mμ | $Ni^{+2}$(a) | $Cr^{+3}$(b) | $Fe^{+2}$(c) | $Fe^{+3}$ | $Fe^{+3}$ + 0.1 M Oxalic Acid | $MnO_4^-$(d) | $Mn^{+2}$ | $Al^{+3}$ | $La^{+3}$ |
|---|---|---|---|---|---|---|---|---|---|
| 421 | 2.1 | 4.6 | 0.20 | 0.35 | | 120 | | | |
| 457 | 0.32 | 2.9 | 0.13 | 0.05 | 20 | 210 | | | |
| 475 | 0.20 | 3.5 | 0.11 | 0.05 | 9.2 | 640 | | 0.027(f) | 0.38(f) |
| 502 | 0.16 | 9.1 | 0.10 | 0.0 | 2.6 | 1600 | | | |
| 541 | 0.25 | 11.6 | 0.10 | 0.0 | 0.65 | 2090 | .027(e) | | |
| 565 | 0.32 | 10.7 | 0.10 | 0.0 | 0.36 | 1180 | | | |
| 598 | 0.60 | 3.0 | 0.10 | 0.0 | 0.22 | 250 | | | |
| 656 | 1.7 | 0.6 | 0.15 | 0.0 | 0.19 | 140 | | | |
| 702 | 2.0 | 0.0 | 0.22 | 0.01 | 0.15 | 70 | | | |
| 795 | 1.0 | 0.0 | 0.53 | 0.04 | 0.18 | 40 | | | |
| 829 | 0.55 | 0.0 | 0.81 | 0.03 | 0.22 | | | | |
| 850 | 0.36 | 0.0 | 1.0 | 0.02 | 0.25 | | | | |
| 908 | 0.33 | 0.0 | 1.4 | 0.01 | 0.28 | | | | |
| 950 | 0.50 | 0.0 | 1.5 | 0.01 | 0.27 | | | | |
| 981 | 0.75 | 0.0 | 1.3 | 0.01 | 0.26 | | | | |
| 1017 | 1.0 | 0.0 | 0.90 | 0.0 | 0.25 | | | | |
| 1068 | 1.5 | 0.0 | 1.2 | 0.0 | 0.25 | | | | |
| 1101 | 1.7 | 0.0 | 1.2 | 0.0 | 0.25 | | | | |

NOTES:

(a) Absorption peaks for nickelous ion are at 394, 655, 670, 1180 mμ with extinction coefficients of 4.5, 1.7, 1.7, and 2.0, respectively.

(b) Absorption peaks for chromic ion are at 405, and 575 mμ, with extinction coefficients of 14.0 and 11.8, respectively.

(c) Ferrous ion has absorption peaks at 960 and 1100 mμ, with extinction coefficients of 1.5 and 1.3, respectively.

(d) Absorption peaks for permanganate ion are at 506, 523, 542, and 562 mμ with extinction coefficients of 1650, 2175, 2090, and 1220, respectively. At wavelengths longer than 702 mμ, the extinction coefficients drop sharply.

## TABLE V (contd.)

NOTES (contd.)

(e) Maximum absorption for manganous ion occurs at 400 and 538 mμ with extinction coefficients of 0.092 and 0.027, respectively. Extinction coefficients are nearly zero at other wavelengths between 400-1200 mμ.

(f) This is the maximum extinction coefficient for this ion. Extinction coefficients at other wavelengths between 400-1200 mμ are slightly smaller.

(g) Absorption coefficients for calcium ion are zero in the wavelength range 400-1200 mμ.

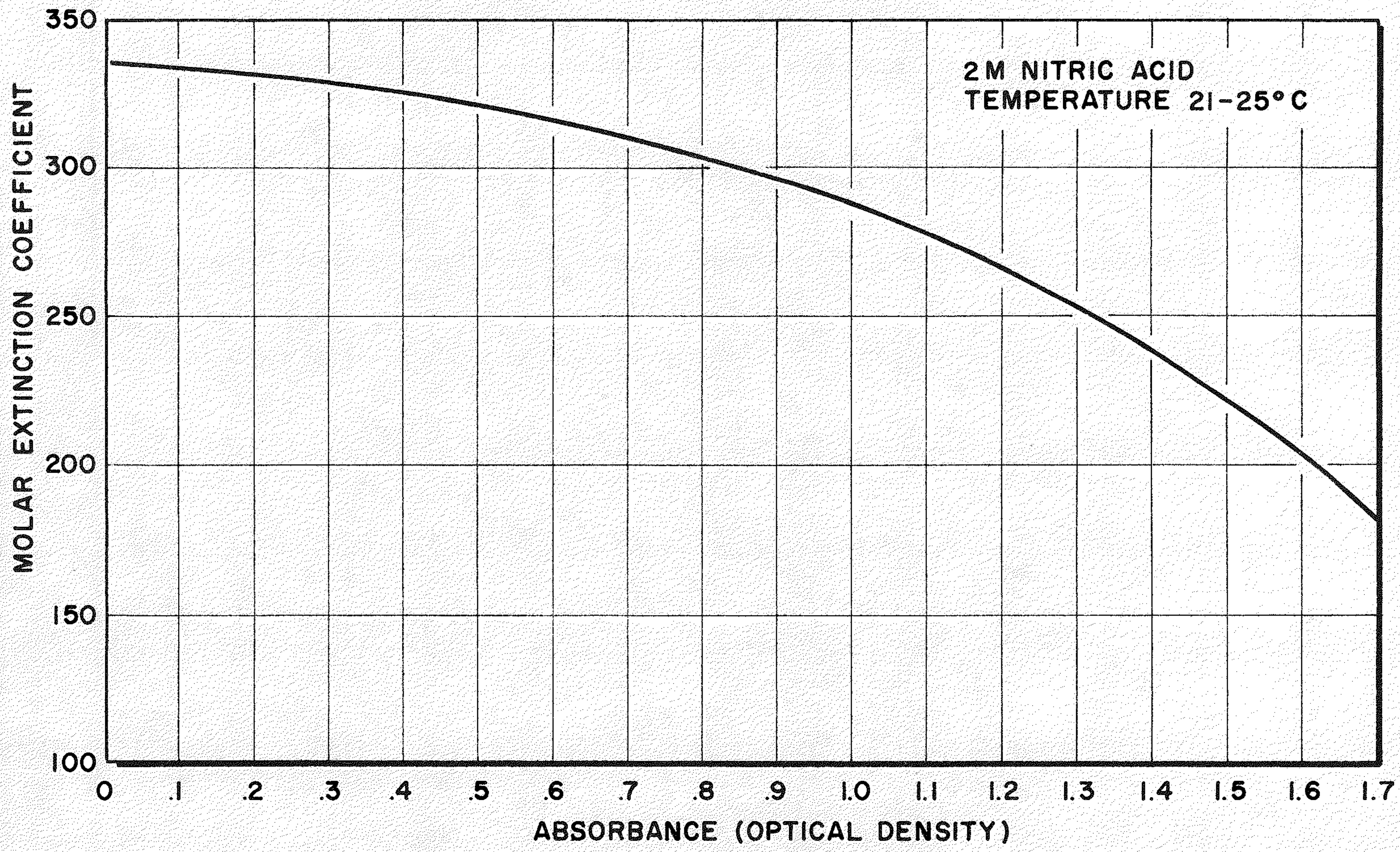

FIGURE 1

ABSORPTION OF PLUTONIUM(VI) AT 829 mμ 2 M $HNO_3$

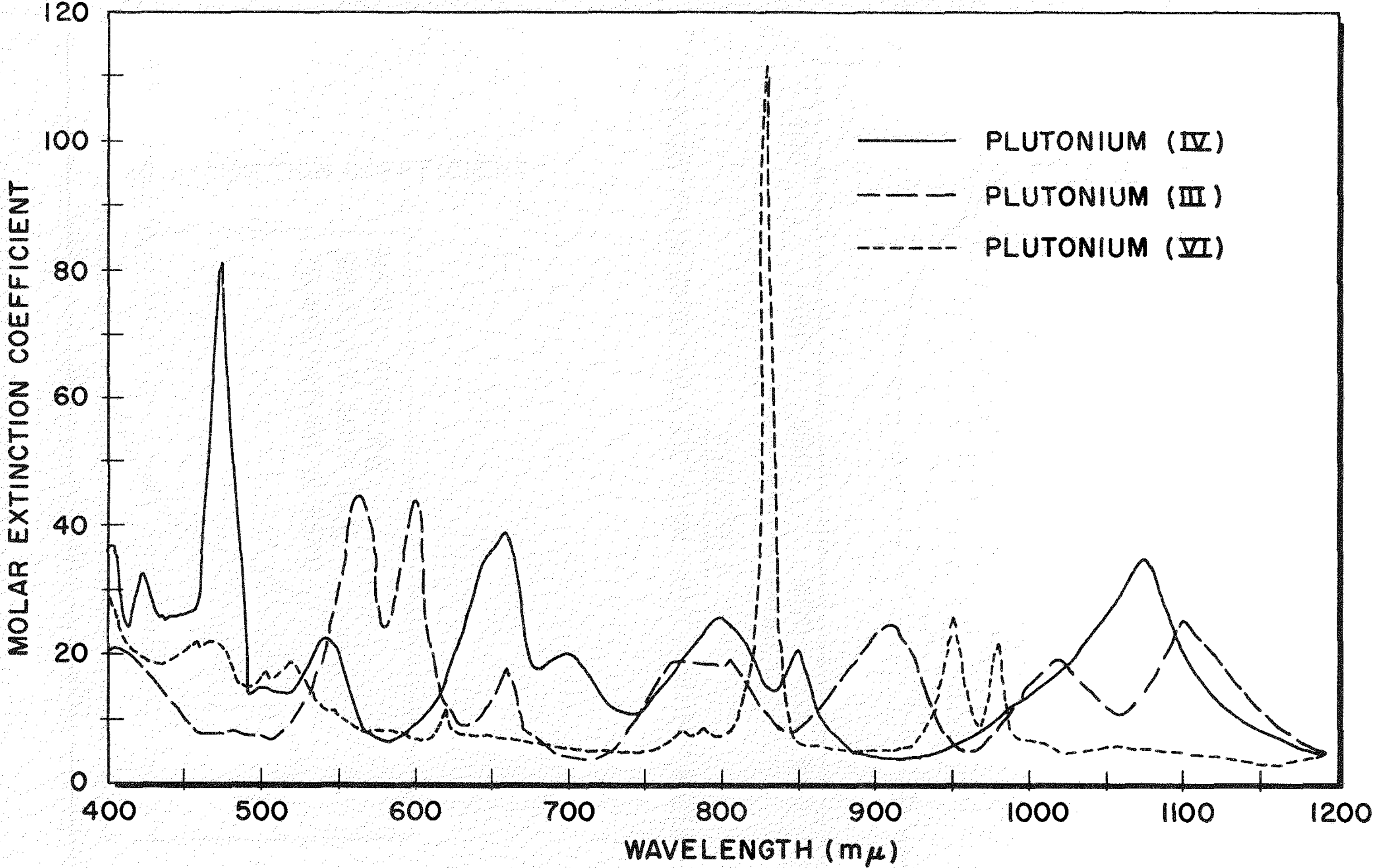

FIGURE 2

ABSORPTION SPECTRA OF PLUTONIUM(III), (IV), AND (VI) IN 2 M $HNO_3$ AT 21-25 C

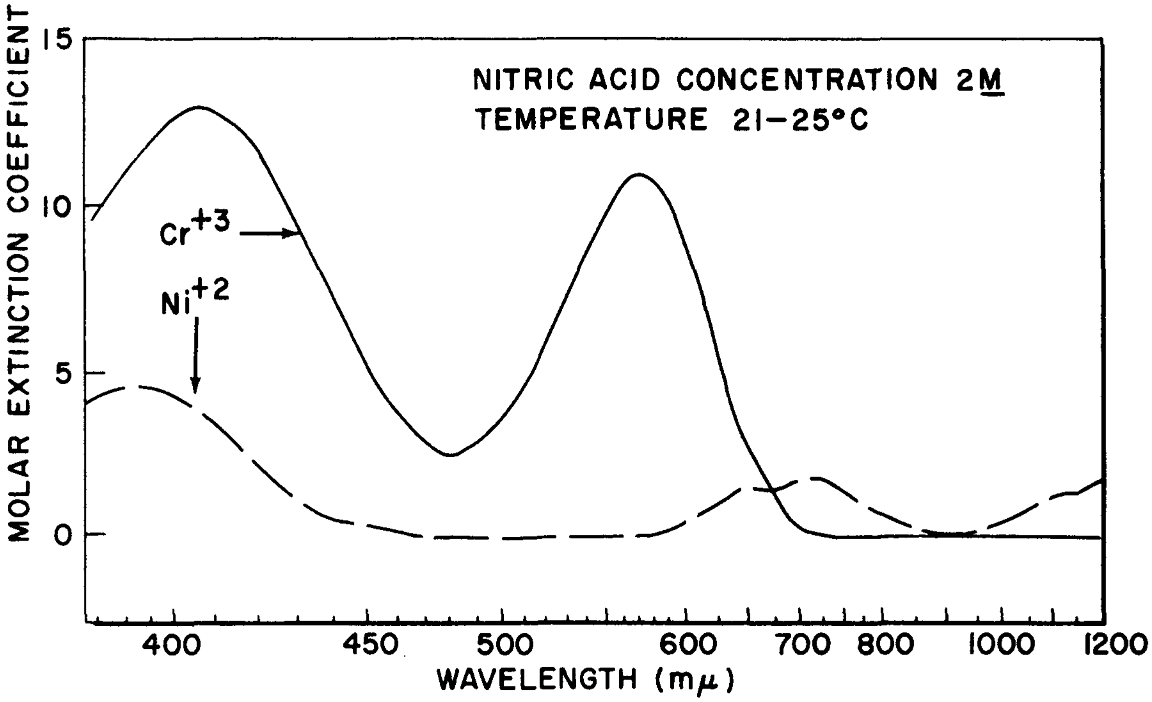

FIGURE 3

ABSORPTION SPECTRA OF CHROMIC AND NICKELOUS IONS

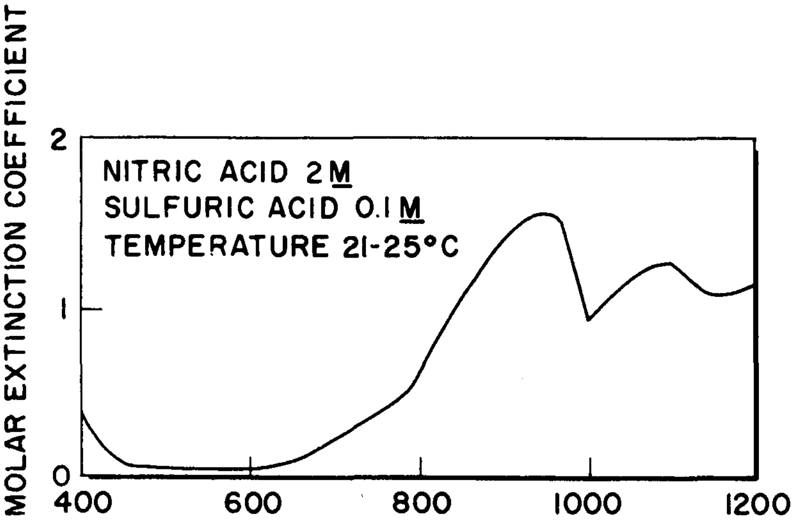

FIGURE 4

ABSORPTION SPECTRA OF FERROUS ION

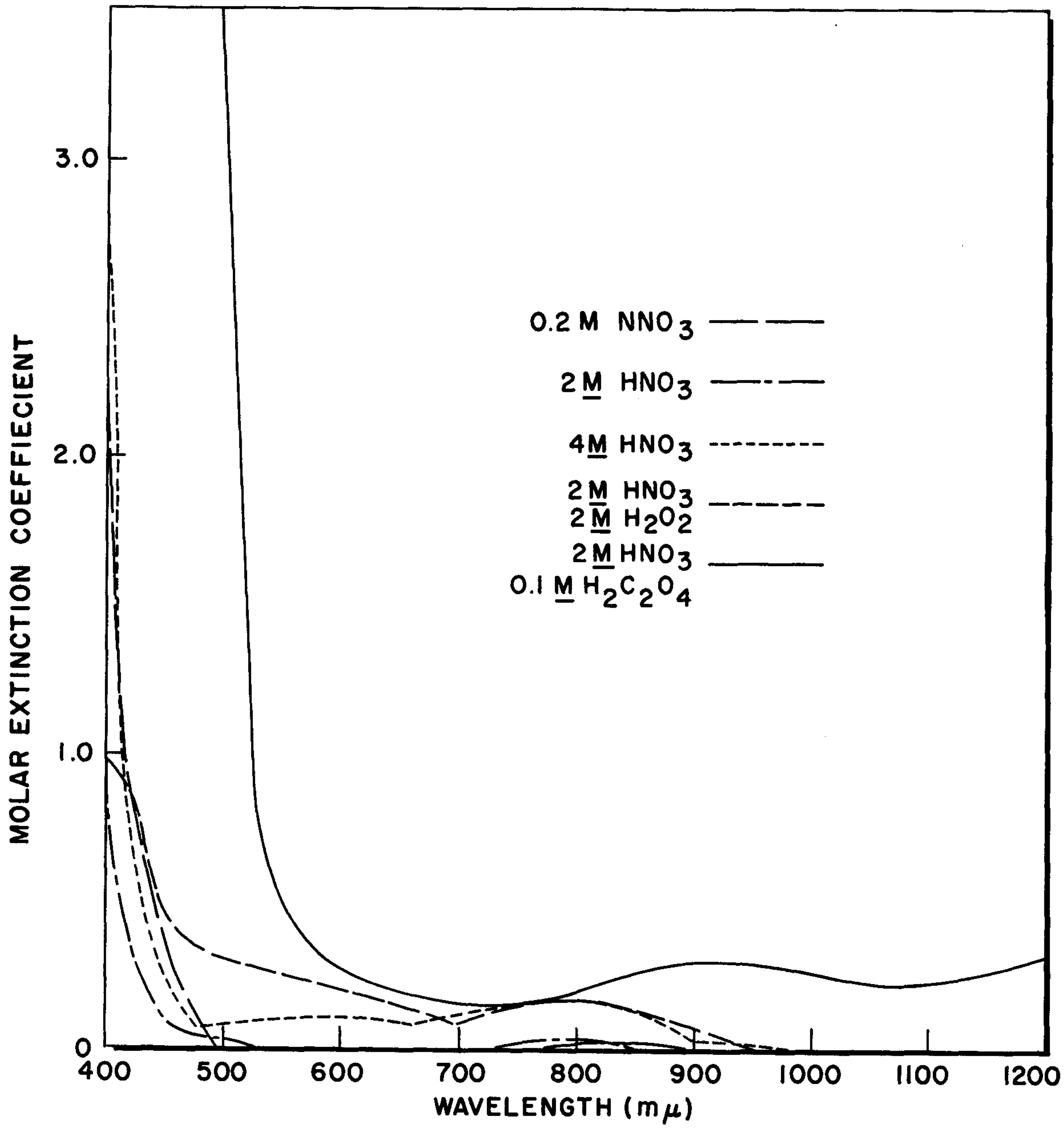

FIGURE 5

ABSORPTION SPECTRA OF FERRIC IRON

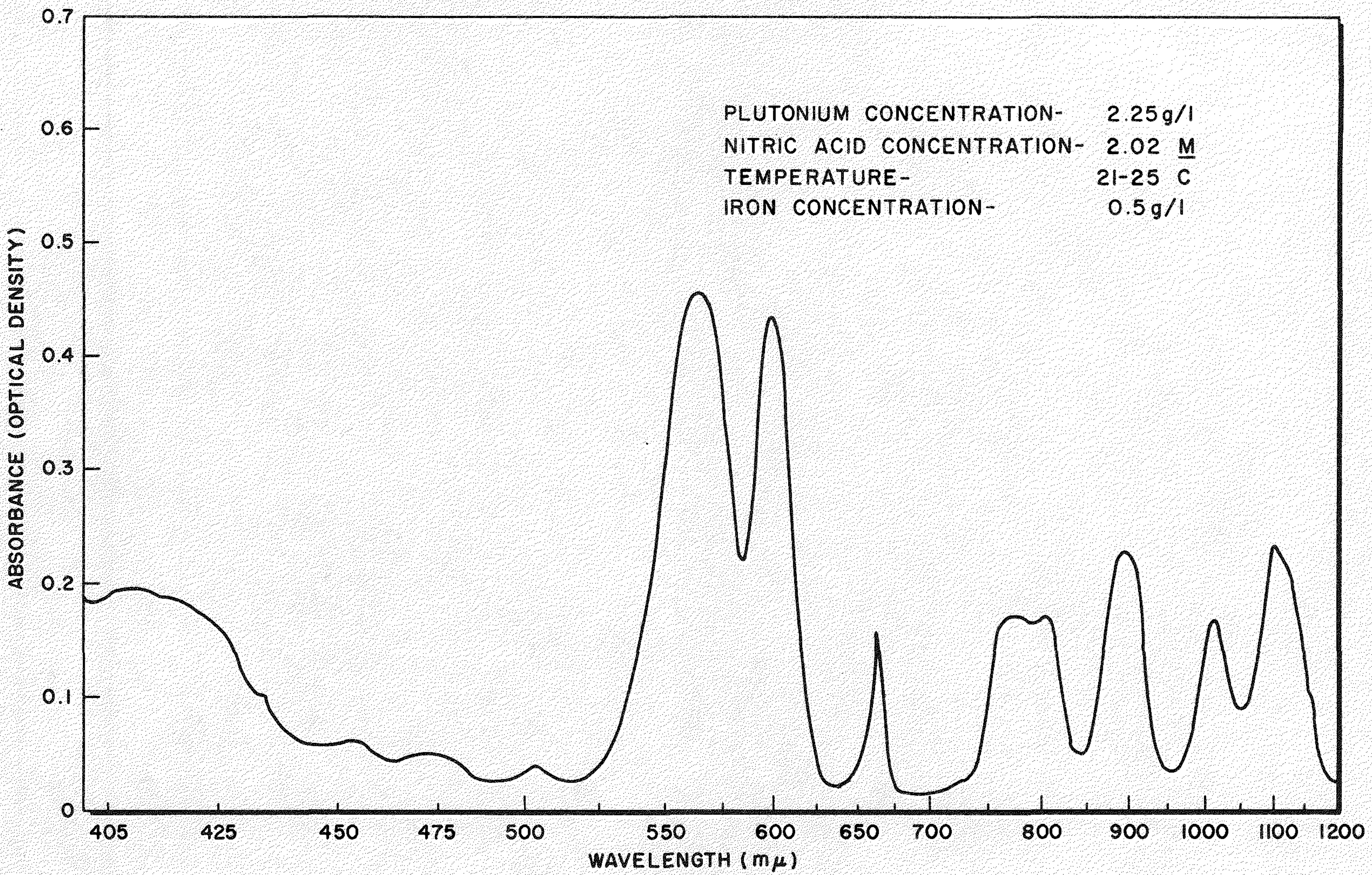

FIGURE 6

ABSORPTION SPECTRUM OF PLUTONIUM(III), DK-2 PLOT

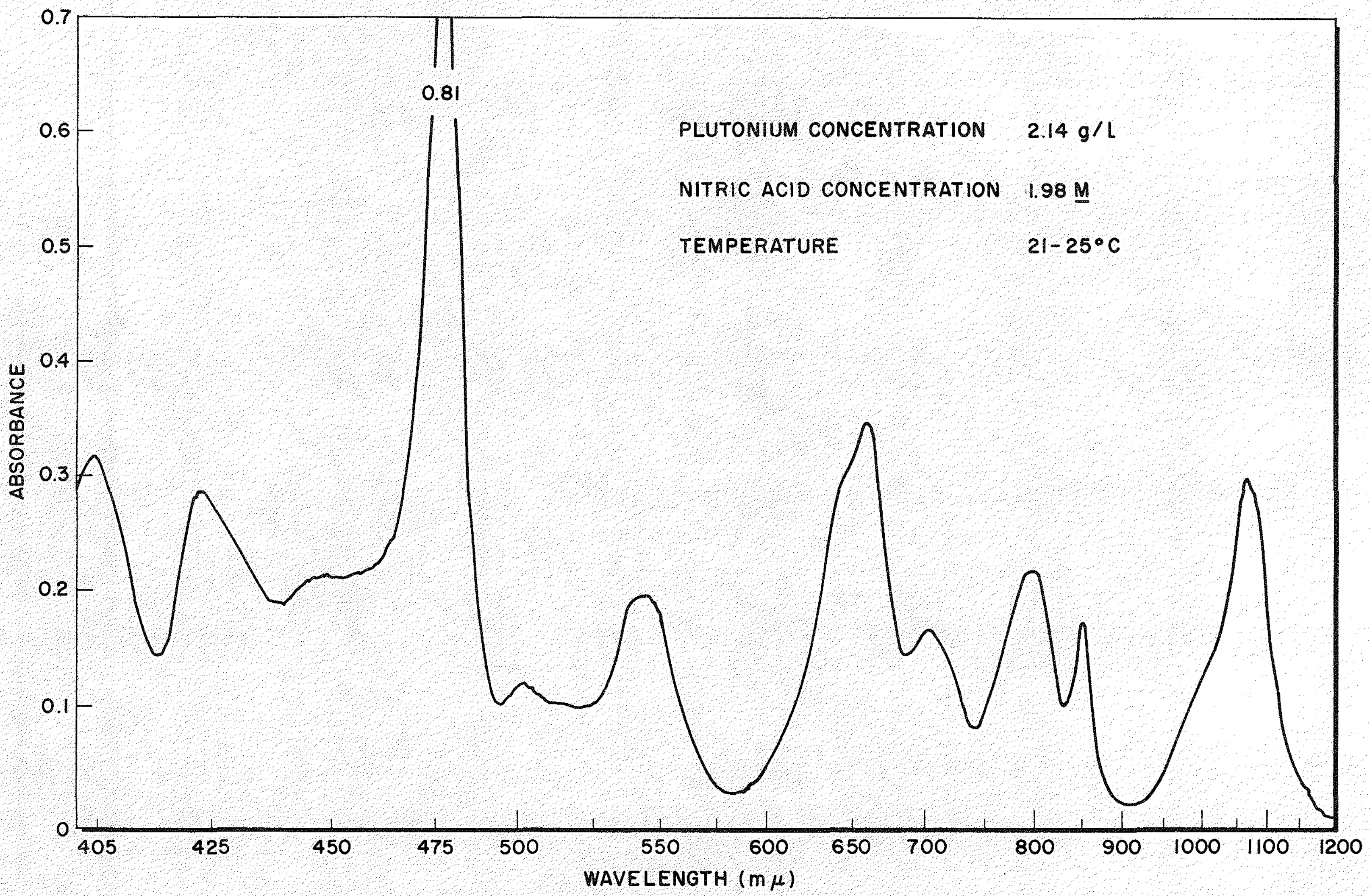

FIGURE 7

ABSORPTION SPECTRUM OF PLUTONIUM(IV), DK-2 PLOT

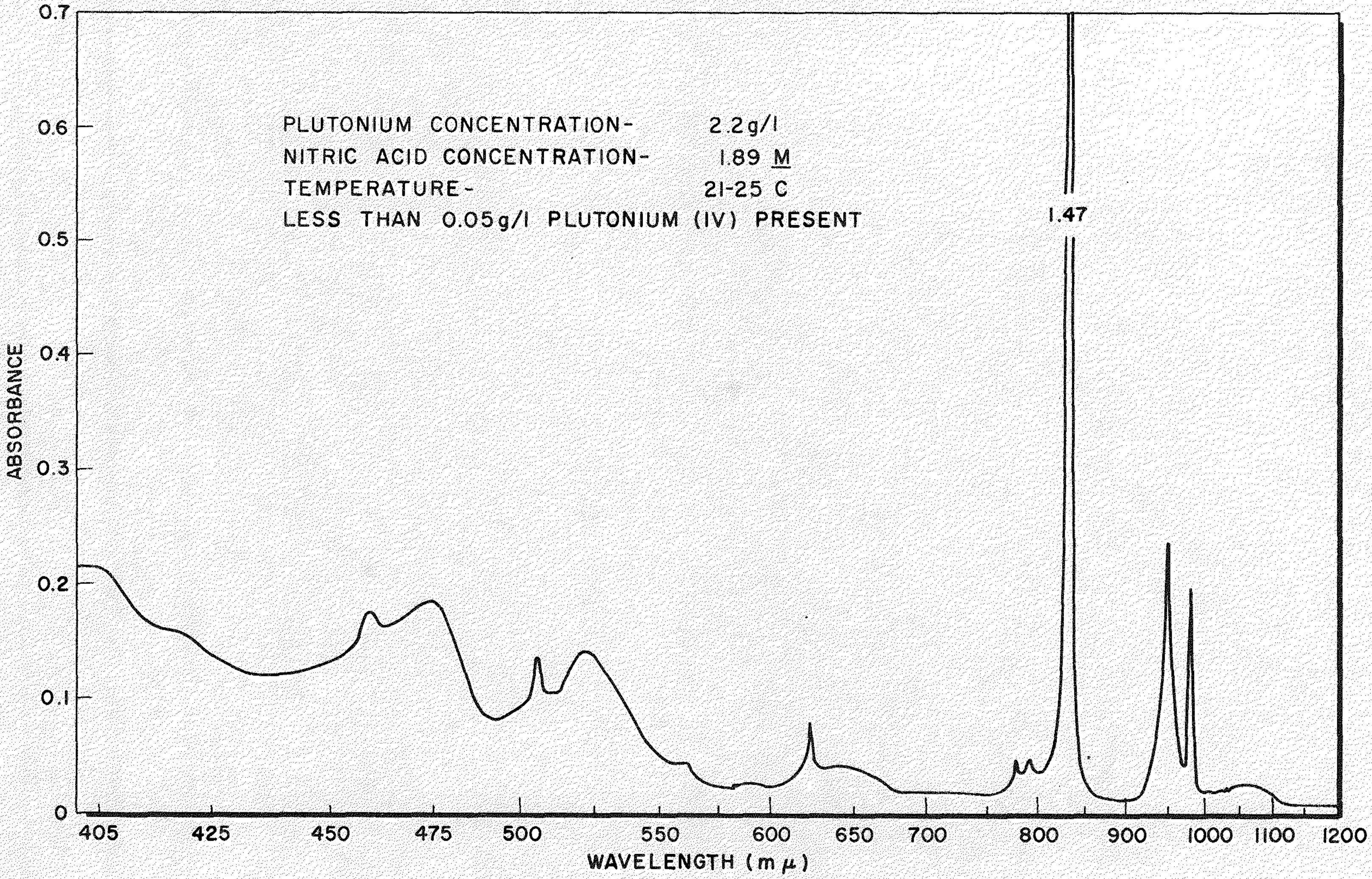

FIGURE 8

ABSORPTION SPECTRUM OF PLUTONIUM(VI), DK-2 PLOT

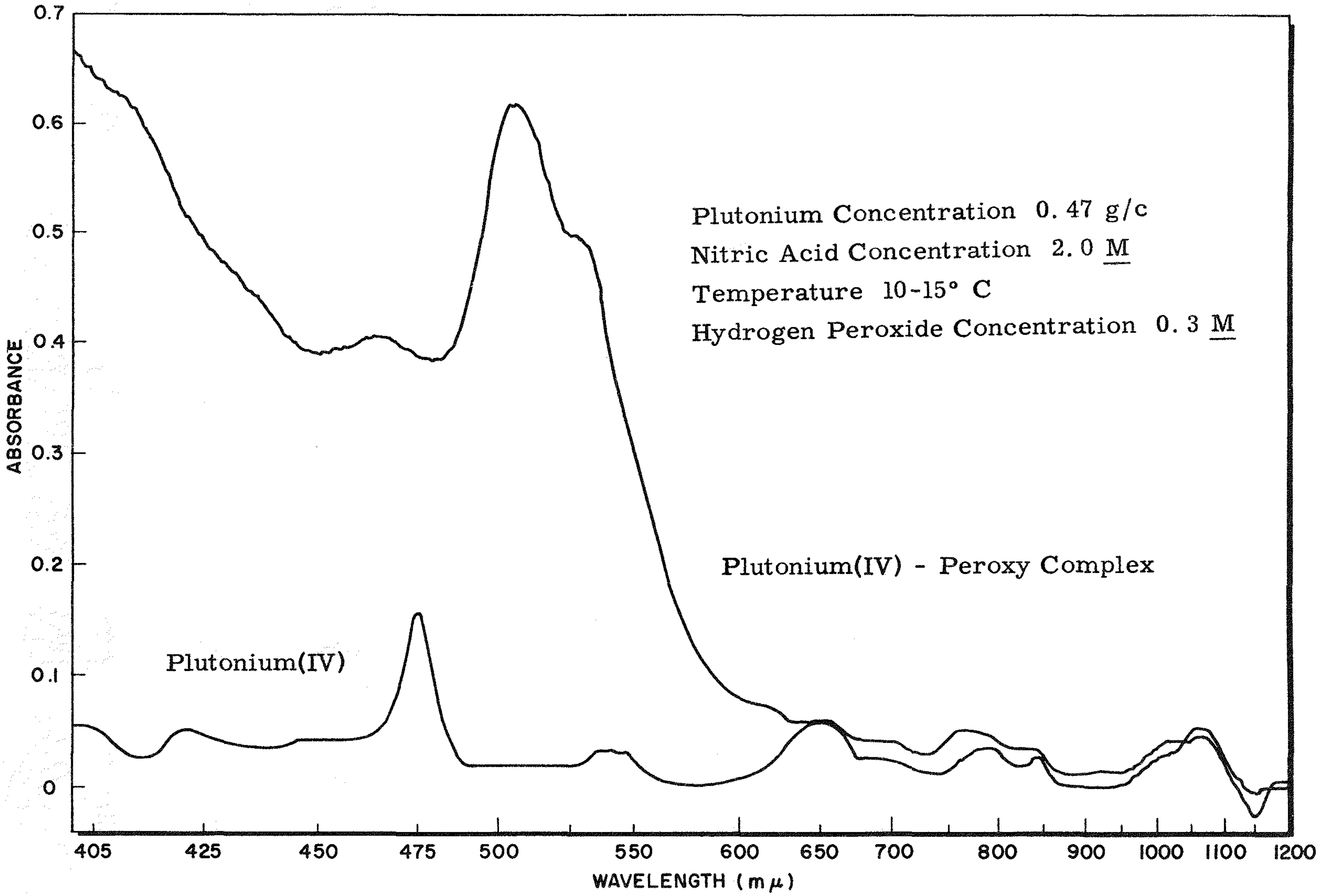

FIGURE 9

ABSORPTION SPECTRUM OF PLUTONIUM(IV)-PEROXY COMPLEX DK-2 PLOT

22

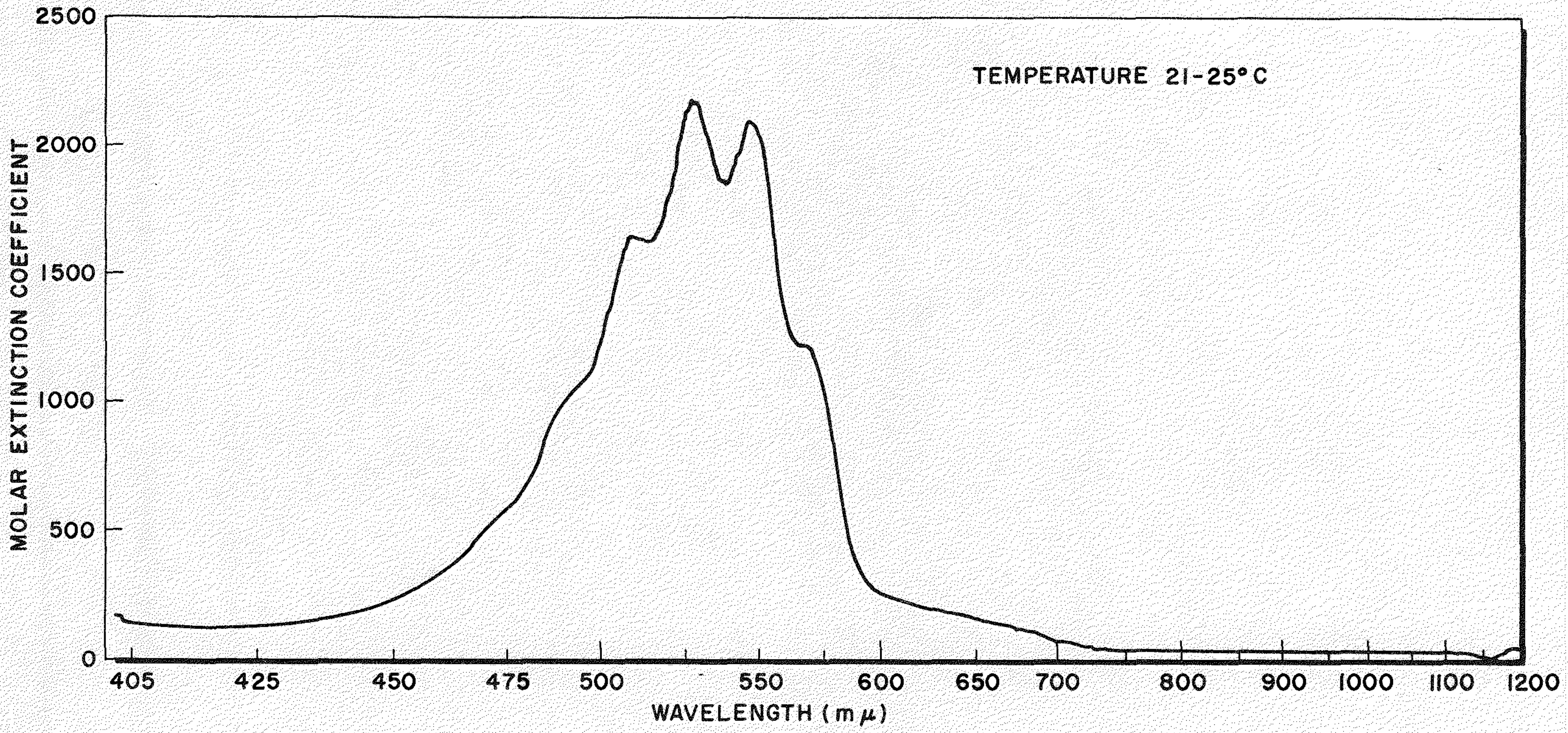

FIGURE 10

ABSORPTION SPECTRUM OF POTASSIUM PERMANGANATE IN 2 M $HNO_3$