lated wave-lengths of $2S-mD$ and $2S-mS$ transitions. Some of the values of $2S-mD$ are very close to observed lines but not with the $2S-mS$ values. Forbidden lines may be expected to appear when the alkali vapor density is high.

A spectrogram of potassium absorption spectrum was taken. Ny and Weng's data[2] are confirmed by the present measurements, except that one additional faint line is observed at λ3429 at temperature 710°C.

Finally the authors wish to thank Dr. Ny Tsi-ze for his interest in the experiment.

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Isotope Shifts in Uranium Spectra

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A study is made of the isotopic shift of U^{238}, U^{235}, and U^{233} in the emission spectrum of uranium. The shift is sufficient to allow quantitative determination of the concentration of the components of a mixture of the uranium isotopes by routine spectrographic analysis. Data show comparative values obtained by mass spectrometer and spectrograph.

INTRODUCTION

THE separation of the isotopes of uranium affords an excellent opportunity to study the isotope shifts in its spectrum. Shifts had been observed by D. D. Smith and D. R. Long in these laboratories in noting the difference in normal standards, chiefly the U^{238} isotopes and the enriched U^{235} samples on the same plate. This work extends the study to include U^{233}. The arc and the spark were used to produce the spectra of these isotopes, and a large number of shifts were observed at a dispersion of 2.47A per millimeter.

DISCUSSION

The explanation of the isotope effect is not simple, and no attempt is made to explain it here. The shifts in the uranium isotopes are so great that they were recognized in ordinary emission spectrographic analysis. An effort is made here to observe as many as can be obtained under the prescribed conditions and sample size. The difference of the nuclear radius, difference in the building up of the nucleus, or perhaps something peculiar to the uranium type elements, may contribute to this easily observed isotope shift.

The shifts observed in U^{235} and U^{233} by direct emission spectra were obtained on a 15,000-line Jarrell-Ash grating spectrograph. This Wood grating gives a strong second order spectrum with a dispersion of 2.47A per millimeter. One hundred micrograms of U_3O_8 were selected as sample size for obtaining the arc spectra, and this was mixed with 500 micrograms of powdered graphite. A uniform burning was obtained for a period of 45 seconds at 4 amperes direct current. However, currents up to 7 amperes may be used.

The spark spectrum was obtained by use of the Dietert Multisource with a spark produced with settings of 20 microfarads, 25 microhenries and 5.4 ohms. Five hundred micrograms of U_3O_8 mixed with a drop of cellulose acetate in acetone were placed in shallow copper electrodes and then dried. The sample was then sparked for 45 seconds using a 103-0 plate. A careful check was made throughout the 2500A–5000A region. The search did not disclose any appreciable differences between the spark and the arc spectra of uranium. The same lines shifted, and the amounts of shift were the same as for the arc spectra. The spectra obtained by the standard spark supply showed fewer lines but no greater shift than the arc spectra.

The region covered in the arc spectrum study

TABLE I. Frequency of recurrence of shifts.

Position in the spectrum	No. of lines
2500–2600A	18
2600–2700	57
2700–2800	109
2800–2900	140
2900–3000	174
3000–3100	94
3100–3200	56
3200–3300	35
3300–3400	75
3400–3500	61
3500–3600	28
3600–3700	18
3700–3800	14
3800–3900	7
3900–4000	16
4000–4100	6
4100–4200	9
4200–4300	11
4300–4400	10
4400–4500	7
4500–4600	4
4600–4700	7
4700–4800	16

was from 2500A to 8800A. Eastman S.A. No. 2 plates were used for second order plates in the region from 2500 to 4950A. Eastman 1F plates were used for the 4500 to 7300 setting, and a 1N plate for the 6000A to 8800A region, these observations being in the first order.

A large number of shifts were observed, and a total of more than 900 shifts were counted from 2500A to 8800A. A distribution of the occurrence is shown in steps of 100A in Table I. Only two lines, 6101.74 and 6465.0, were observed to exhibit a shift above 4800A. A sample size greater than 100 micrograms shows a larger number of lines and a larger number of shifts. The sample is small in order to compare the spectra of the three isotopes of uranium with a minimum amount of background.

The amount of shift was measured by calibrating the rate of sweep by the scanning motor on a densitometer by measuring the time interval between the minima of known lines. The speed of the sweep was determined to be 0.0179A per second for a second order spectrum. A number of the lines measured are shown in Table II. The largest single shift is in line 4244.37A.

It is of interest to note that in every case observed where there is a shift between the U^{238} and U^{235}, there is also a shift of the U^{233}. This shift is always in the same direction, i.e., toward the ultraviolet or shorter wave-length, in the progression of U^{238} to U^{233}. Even though there is some correlation between the mass difference and the direction of the shift, there does not seem to be any correlation between the mass difference and the amount of the shift. This is indicated on examination of Table II. As is apparent in lines 2, 3, 6, and 7, the shift is greater between U^{235} and U^{233} (mass difference of 2) than between U^{238} and U^{235} (mass difference of 3); while in the cases of the other lines listed in Table II, the greatest

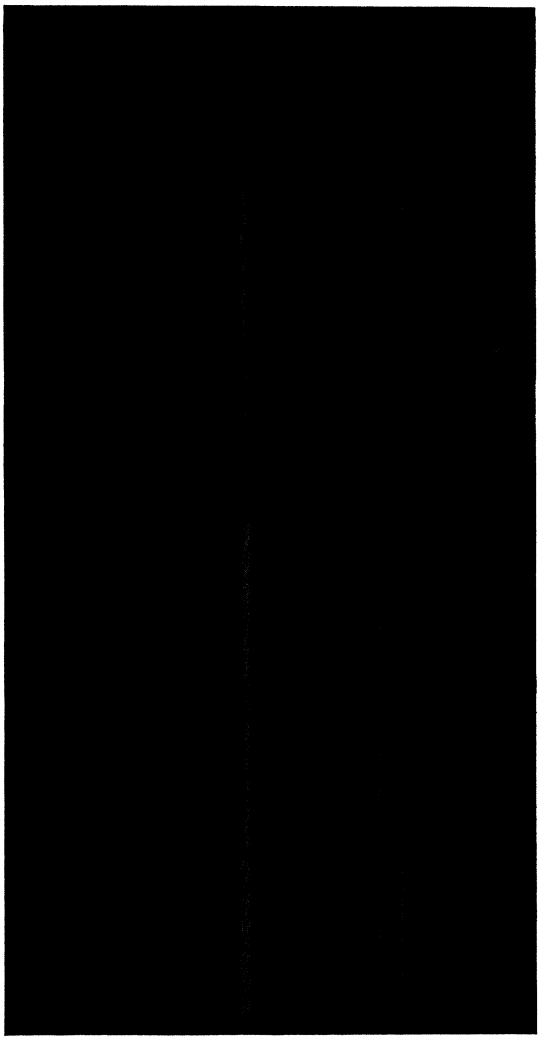

FIG. 1. Line *A* is the uranium 4241.67A line; line *B* is the uranium 4244.37A line. Reading from top to bottom, these spectra are of (1) U^{238}, (2) a mixture of U^{238} and U^{235}, (3) U^{235}, (4) a mixture of U^{235} and U^{233}, (5) U^{233}, and (6) a mixture of U^{238} and U^{233}.

TABLE II. Observed shifts in representative lines.

U^{238} line		$U^{238}-U^{235}$ shift		$U^{235}-U^{233}$ shift		$U^{238}-U^{233}$ shift	
A	cm^{-1}	A	cm^{-1}	A	cm^{-1}	A	cm^{-1}
2565.406	38980.18	0.075	1.14	0.070	1.06	0.145	2.20
2802.157	35686.79	0.018	0.23	0.020	0.25	0.038	0.48
3313.94	30121.02	0.016	0.14	0.036	0.33	0.052	0.47
3633.29	27523.26	0.104	0.79	0.064	0.48	0.168	1.27
3670.072	27247.42	0.009	0.06	0.009	0.07	0.018	0.13
3890.364	25704.53	0.036	0.24	0.055	0.36	0.091	0.60
3944.130	25354.13	0.057	0.37	0.091	0.58	0.148	0.95
4244.372	23560.61	0.248	1.37	0.125	0.70	0.373	2.07
4252.426	23515.98	0.168	0.93	0.089	0.49	0.257	1.42
4365.553	22906.60	0.208	1.09	0.073	0.38	0.281	1.47
4609.864	21692.61	0.077	0.36	0.054	0.26	0.131	0.62

shift is for the difference between U^{238} and U^{235}. Figure 1 is a photograph of a section of a plate which shows the shifts of the 4244.37A line and the reference line 4241.67A. The identities of the isotopes and mixtures are shown in the caption of Fig. 1.

On the basis of data obtained on mixtures of these isotopes, it becomes apparent that it is possible to assign quantitative values to the concentration of these components in mixtures of uranium isotopes. A sample of data of the spectrographic determination of the U^{235} content in a series of samples is given in Table III. These determinations were made by D. D. Smith. The values obtained by the conventional method of assay are listed in column 2, which shows how well the two methods agree.

TABLE III. Comparison of assay methods.

Sample No.	Spectrometer	Spectrograph	Deviation
1	30.5	30.2	+0.3
70	28.6	29.2	−0.6
83	28.3	29.5	−1.2
KJ-1	13.2	12.8	+0.4
2	13.2	12.0	+1.2
*Q*10	5.9	6.4	−0.5
*Q*5	0.61	1.0	—
		Average deviation	0.7

CONCLUSION

On examination of spectra taken, the following general observations may be made: (1) that any line showing a shift between U^{238} and U^{235} also shows a shift between U^{235} and U^{233}, (2) that the direction of shift of lighter isotopes is toward the shorter wave-length, (3) that there is no correlation between the amount of shift and atomic weight, and (4) that quantitative determination of the concentration of uranium isotopes may be made by emission spectrographic methods.

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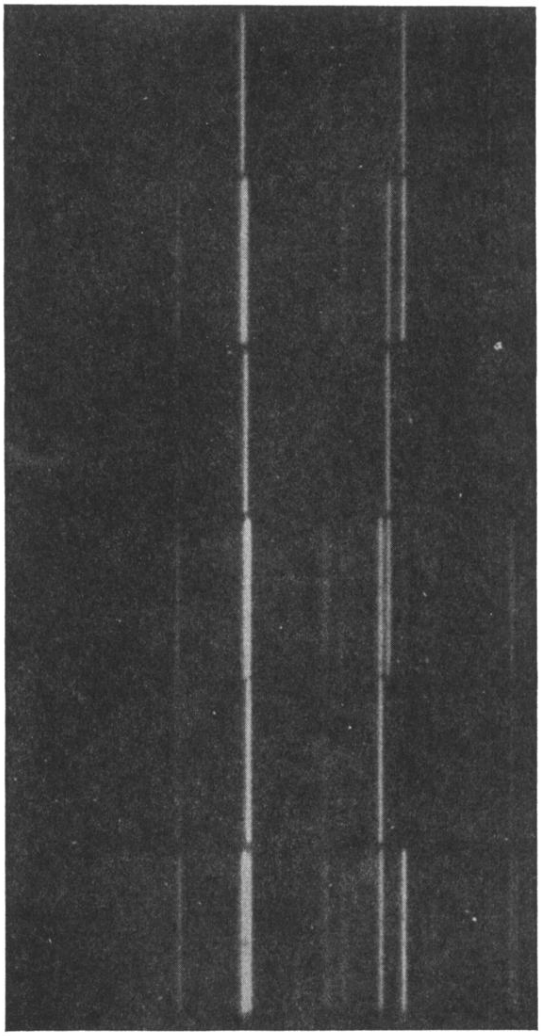

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