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GOVERNMENT OF INDIA
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ESTIMATION OF METALLIC IMPURITIES IN URANIUM
BY CARRIER DISTILLATION METHOD

by

A. G. Page, S. V. Godbole, Kum. S. B. Deshkar
and B. D. Joshi
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BHABHA ATOMIC RESEARCH CENTRE
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ABSTRACT

An emission spectrographic method has been standardised for the estimation of twenty-two metallic impurities in uranium using carrier-distillation technique. Silver chloride with a concentration of 5% has been used as the carrier and palladium and gallium are used as internal standards. Precision and accuracy determinations of the synthetic samples indicate 6 - 15% deviation for most of the elements. Using the method described here, five uranium reference samples received from C.E.A. - France were analysed. The detection limits obtained for Cd, Co and W are lower than those reported in the literature while limits for the remaining elements are comparable to the values reported. The method is suitable for the chemical quality control analysis of uranium used for the Fast Breeder Test Reactor (FBTR) fuel.

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1. INTRODUCTION

Emission spectrographic analysis of common metallic impurities in uranium is usually carried out by using the 'carrier-distillation' technique originally developed by Scribner and Mullin⁽¹⁾. The main features of the methods reported in the literature are the conversion of various compounds of uranium to their refractory oxide form, U_3O_8 , use of a proper carrier with its suitable concentration in the sample and adoption of optimum exposure and current values in the d.c. arc. The principal function of the carrier is to selectively sweep out volatile impurities into the arc, leaving behind the more refractory uranium oxide; it also helps to stabilize the arc. The suitable choice of the carrier depends mainly on the volatilization rates in the arc, excitation potential and the sensitivity of the elements to be analysed. The choice of the optimum value for the concentration of the carrier is largely governed by the exposure time for which uranium-free spectrum is desired. A number of carriers and their combinations have been reported in the literature⁽²⁾; more common amongst them are silver-, alkali- and alkaline earth-halides, Ga_2O_3 , ZnO , Sb_2O_3 etc. The carrier distillation methods for the analysis of metallic impurities in uranium have been extensively reviewed in the literature^(3,4).

In the present work, a method has been standardised for the estimation of twenty-two metallic impurities viz. Al, B, Be, Ca, Cd, Co, Cr, Cu, Fe, In, Id, Mg, Mn, Mo, Ni, Pb, Si, Sn, Ti, V, W and Zn in uranium. Fifteen amongst these impurities are required to be analysed in the Fast Breeder Test Reactor (FBTR) fuel. The other impurities have been included here as their analysis was carried

out in uranium used in IMFBR/FFTF fuels⁽⁵⁾

Specpure silver chloride with 5% concentration in a charge of 100 mg. has been used as the carrier, while palladium and Ga_2O_3 each with 0.01% concentration serve as internal standards. Standards have been prepared with a view to cover adequately the maximum permissible levels of various impurities in FBTR fuel. Precision and accuracy of the method have been determined at an intermediate concentration by analysing ten replicate samples. Using the method developed here five uranium reference samples received from C.E.A. - France have been analysed. Comparatively low detection limits have been achieved in the present work.

2. EXPERIMENTAL

2.1 Preparation of Standards

High purity pre-analysed uranium metal, received from Uranium Metal Co. was converted to U_3O_8 by heating it in air in a silica muffle furnace for an hour at 850°C. The uranium oxide thus formed was ground to a fine powder, passed through a nylon sieve of 200 mesh (Sorex industries no. 3542) and then used in the preparation of standards. The 200 mesh sieve used at every stage in the preparation of standards, ensured the particle size to be less than 75 μm .

A mixture of all the impurity elements, taken mostly in the oxide form was thoroughly ground with a pestle and mortar and passed through the sieve to get a homogeneous impurity mixture. A fraction of this was mixed with U_3O_8 to make a 20 g. master standard (a). Silver chloride, palladium (in the form of $(NH_4)_2PdCl_4$) and Ga_2O_3 were ground together to make a homogeneous carrier-internal standard mixture (b).

A series of eight standards, each of 10 g. was then made by mixing graded amounts of master standard (a), fixed amount of mixture (b) and balance amounts of U_3O_8 . The composition of all the standards and the amounts of vari-

impurities in them are shown in Table I. The impurity concentrations between successive standards varied by a factor of 2 or 2.5.

2.2 Preparation of Sample

In the case of U metal samples about 1 g. of it was first cleaned using successively, carbon tetrachloride, water, dilute nitric acid and finally washed with quartz distilled water to remove any external contamination. The metal was then heated in a platinum crucible in the silica muffle furnace at 850°C for an hour. For UO_2 samples, known amounts of the powder samples were directly transferred to platinum crucibles and heated in the furnace. Part of the heated sample (U_3O_8) weighing 474.82 mg. was mixed with 25.18 mg. of the carrier mixture and ground for half an hour to form a homogeneous mixture.

In a systematic study of the percentage distribution of particle size as a function of grinding time, Martell⁽⁶⁾ observed that with a grinding time of 120 sec/100 mg., 100% of PuO_2 and carrier mixture had a particle size much less than 75 μm . He further found that the intensity ratios for the different elements depended on the particle size in the range 150 - 75 μm and that below 75 μm they were independent of particle size.

The grinding times of 360 sec/100 mg. in the preparation of samples used in these experiments suggest that particle size is less than 75 μm .

2.3 Spectrographic Procedure

The standards and the samples in duplicate, each weighing 100 mg. were loaded into the craters of 'carrier-distillation' (ASTM designation: E 130-66 type S-2) electrodes. Each electrode after heating under infra-red lamp to remove possible traces of moisture, was vigorously tapped so as to evenly spread the charge in the crater. A sharp, stainless steel venting tool was then used to make a vent hole in the charge and also to pack the charge to some extent. The vent hole facilitates smooth release of impurities in the gaseous form into the

arc, thus preventing violent ejection of the charge and subsequent appearance of uranium in the arc region. A d.c. arc with 12.5 amper. current was used to obtain the spectra of standards and samples. The detailed experimental conditions are shown below:

EXPERIMENTAL CONDITIONS

Spectrograph	Hilger E-546, 3.4 M. Ebert glass groove
Grating and blazed region	1200 grooves/mm; blazed at 3000 ⁰ in I order.
Reciprocal linear dispersion	2.5 Å/mm in I order
Wavelength range	2200-3400 Å
Slit	15 microns
Filter	None
Electrodes	Anode : Standard 'carrier distillation' type electrode. ASTM designation: E-130-66, type S-2 used on type S-1 pedestal Cathode: 0.120" dia. preformed pointed electrode. ASTM designation : E-130-66 type C-1.
Charge for analysis	100 mg. standard or sample
Venting tool	Standard size, stainless steel
Sieve	Nylon cloth, 200 mesh supplied by M/s. Spex industries, Inc. USA
Grinding	Agate mortar with pestle
Analytical gap	4 mm.
Exposure	25 secs.
Current (D.C.)	12.5 amperes.
Source Unit	Hilger source unit, P.S. 131
Photographic Emulsion	Kodak, Spectrum Analysis, No.1, 25.4 cm x 10.2.cm.

Plate development	Developed with Kodak D-19, developer at 18°C for 3 min. and fixed in Kodak acid fixing salt solution for three minutes
Plate calibration	Seven-step rotating sector with an iron arc.
Microrphotometer	Hilger non-recording micro-photometer
Calculator	Respektra

The intensity ratios for all the analysis lines were calculated and the estimations for the samples were made from the working curves. The precision and accuracy of estimation have been determined from ten replicate U_3O_8 synthetic samples with concentrations of impurities as in standard 5, with triplicate measurements for each. The estimations of various impurities in these ten samples were carried out in three separate experiments.

Five uranium reference samples obtained from French Atomic Energy Commission were analysed by taking each sample in duplicate. Four of these samples viz. An e'mons (A), Hortensia(H), Jonquille (J) and Kentia(K) were in the form of uranium metal turnings while the sample 'Mickey' (M) was in the form of U_3O_8 powder. Though initial calcination at 850°C might have been done while preparing M sample, it was again heated at 850°C for an hour prior to analysis. In the case of H and K samples, estimated values for Fe and Ni and for K sample, value for Cu also, exceeded the estimation range of the standards. Hence these samples were diluted by a factor of ten using pure U_3O_8 (from the same batch as that used for the preparation of standards) prior to analysis.

3. RESULTS AND DISCUSSION

The analysis lines used for various elements, internal standard lines and the estimation ranges covered by the analysis lines are shown in Table II. Two palladium lines viz. 2448 Å and 3027.9 Å could be effectively used as internal standard lines in the entire spectral region of interest. In the case of Ga_2O_3 , however, only one line at 2659.9 Å had the desired density at 0.01% concentration.

Hence this line was used only with the analysis lines in the wavelength region 2200-2750 Å. Some of the typical working curves obtained for different elements are shown in figures 1-7. The last column of Table II gives the maximum possible levels of the impurities in UO_2 used for FBTR fuel. From the data in the table that the estimation ranges obtained for all the elements, however, are within the FBTR fuel specification limits as also the limits specified for the impurities in IMFBR/FFTF fuel.

The precision was determined in terms of percentage standard deviation for all the elements. The percentage accuracy was determined from the data on results of the synthetic samples with three spectra for each. These results are shown in Table III. It is seen that most of the elements could be estimated with a precision ranging between 6-15%, excepting Cd, Mo and Ti, for which the precision ranged between 17 and 23%. As the estimation of the impurities in ten samples was carried out in three separate experiments over a period of two weeks, by three persons, the precision and accuracy obtained here, include the errors due to variations in the experimental parameters over the period and the experimental skill.

The results obtained from the analysis of each of the samples received from C.E.A. - France are given in the third column for the respective sample in Table IV. The second column represents the catalogue values⁽⁷⁾ given by the suppliers for the different elements. These values in most cases appear to be the probable values indicated in the report by Michele and Leclerc⁽⁸⁾. As reported therein, reference samples were analysed by different methods such as chemical analysis, spectrographic analysis with and without separation of uranium, atomic absorption, neutron activation analysis etc. The probable value for any element refers to the value of the median in a set of estimations by

various methods. The results obtained by these methods show large variations and they have been indicated graphically in their report. The same range of variation for each element and the sample has been computed in terms of numbers and is shown in the first column for every sample.

For the sample M, the probable value and the range of variation is not known as it is not included in the report, and hence the estimated values can only be compared with the catalogue values. While graphically giving the range of variation, authors have also indicated the analytical methods used for the estimation of impurities. It is seen that spectrographic estimation without separation of uranium (probably by carrier distillation method) was carried out for B, Be, Ca, Co, In, Pb, Sn, Ti and V impurities only; while other impurities have been estimated using either two or three other methods. Again, a few of the elements were not analysed in some of the samples. However, we have analysed all the five samples for the elements mentioned in the table. The authors in their report have indicated an anomaly in the determination of Al in all the samples. From the table it can be seen that the results obtained in the present work are in good agreement with the catalogue values except in the case of aluminium. However, a relatively closer agreement is observed between the estimates of elements made in this work and those reported using spectrographic method without chemical separation.

A comparison of the estimation limits obtained here for different elements and those reported in the literature^(1,4, 9-11) indicates that in the case of Cd, Co, and W, lowest limits have been achieved in the present work while Cr, In, Sn and V have comparable limits. In the case of other elements, however, the estimation limits obtained here are somewhat higher. As the development of an analytical method for the estimation of impurities in uranium was taken up as part of the program for the chemical analysis of FBTR fuel, the emphasis was more

on meeting the fuel specification limits rather than achieving low detection limits for various elements and hence no special effort was made to lower the detection limits.

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Table I

COMPOSITION OF STANDARDS

(Values are expressed in PPM based on U_3O_8)

Elements	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6	Std. 7	Std. 8
B, Be, Cd.	0.05	0.1	0.2	0.5	1.0	2.0	5.0	10.0
Li	0.25	0.5	1.0	2.5	5.0	10.0	25	50
Al, Ca, Co, Cr, Cu Fe, In, Mg, Mn, Ni, Pb, Si, Sn, Ti, V.	0.5	1	2	5	10	20	50	100
Mo	1	2	4	10	20	40	100	200
W	2.5	5	10	25	50	100	250	500
Zn	5	10	20	50	100	200	500	1000

Table II

ELEMENTS, ANALYSIS LINE, ESTIMATION RANGE AND SPECIFICATION
LIMITS FOR URANIUM USED IN FBTR AND IMPER/PPTF FUELS

Sr.No.	Element	Analysis Line	Internal Std.	Estimation Range	Maximum Permissible Level in UO ₂ (In PPM)
		A°	Line A°		
1	Al	3082.2	Pd.3027.9	2-100	150
2	B	2496.8	Pd.2448/Ga 2659.9	0.05-10	2
		2497.7	Pd.2448/Ga 2659.9	0.1 - 5	
3	Be	2348.6	Pd.2448/Ga 2659.9	0.05-1	20*
4	Ca	3158.9	Pd.3027.9	5 - 100	150
5	Cd	2288	Pd.2448/Ga 2659.9	0.05 - 10	20*
6	Co	2424.9	Pd.2448/Ga 2659.9	0.5 - 100	10*
7	Cr	2835.6	Pd.3027.9	0.5 - 100	40
		2843.3	Pd.3027.9	1.0 - 100	
8	Cu	2961.2	Pd.3027.9	5 - 100	50
9	Fe	2617.6	Pd.2448/Ga 2659.9	1 - 100	400*
		2788.1	Pd.3027.9	2 - 100	
10	In	2710.3	Pd.3027.9	2 - 100	**
		3256.1	Pd.3027.9	0.5 - 5	
		3258.6	Pd.3027.9	0.5 - 50	
11	Id	3232.6	Pd.3027.9	2.5 - 50	10*
12	Mg	2779.8	Pd.3027.9	0.5 - 100	20
13	Mn	2949.2	Pd.3027.9	1 - 100	
14	Mo	3158.2	Pd.3027.9	1 - 100	
15	Ni	2992.6	Pd.3027.9	1 - 100	400*

Str.No.	Element	Analysis Line A ^o	Internal Std. Line A ^o	Estimation Range	Maximum permissible level in UO ₂ (In PPM)
16.	Pb	2833	Pd 3027.9	0.5 - 10	
17	Si	2435.2	Pd 2448/Ga 2659.9	1 - 100	150
18	Sn	2421.7	Pd 2448/Ga 2659.9	1 - 100	5
		2840.0	Pd 3027.9	0.5 - 5	
19	Ti	3239	Pd 3027.9	1 - 100	
20	V	3125.3	Pd 3027.9	1 - 50	400*
		3184	Pd 3027.9	0.5 - 10	
21	W	2551.3	Pd 2448/Ga 2659.9	5 - 250	100*
		2831.4	Pd 3027.9	25 - 500	
22	Zn	3072.1	Pd 3027.9	10 - 1000	100
		3345.0	Pd 3027.9	5 - 20	
		3345.6	Pd 3027.9	20 - 200	
		3345.9	Pd 3027.9	20 - 1000	
	Sum of Cu, Si, Ti and Zn				800*
	Sum of Ag, Mn, Mo, Pb and Sn				200*

* Specification limits for IMFER/PPTF fuel materials

** Required to be analysed in some uranium samples

Table III

PRECISION AND ACCURACY

(Based on results of Ten replicate samples)

Sr.No.	Element	Amt.added (in ppm)	Amt. estimated (mean of 10 estimations in ppm)	Percentage Deviation (PRECISION)	Percentage Accuracy
1	Al	10	9.86	06.37	1.4
2	B	1	1.02	09.51	1.6
3	Be	1	1.02	14.37	1.9
4	Ca	10	10.34	06.22	3.4
5	Cd	1	1.06	17.05	5.7
6	Co	10	11.08	13.42	10.8
7	Cr	10	9.85	07.73	1.5
8	Cu	10	9.57	08.46	4.3
9	Fe	40	42.2	10.36	5.5
10	In	10	9.96	14.67	0.4
11	Li	5	4.89	13.08	2.1
12	Mg	10	9.55	13.15	4.5
13	Mn	10	9.8	07.93	2.0
14	Mo	20	17.06	23.20	11.7
15	Ni	10	10.54	06.06	5.4
16	Pb	10	8.18	10.54	18.2
17	Si	40	40.45	07.98	1.1
18	Sn	10	10.27	08.51	2.7
19	Ti	10	10.74	18.18	7.4
20	V	10	10.14	07.33	1.4
21	W	50	53.30	10.37	6.6
22	Zn	100	83.90	15.31	16.1

Table IV

ANALYSIS OF URANIUM REFERENCE SAMPLES

(Received from C.E.A - France)

Sample	Anemone			Hortensia		
	Element	Range	Catalogue Value	Present work	Range	Catalogue Value
Al	5-40	15	<5	44-86	60	5.7
B	<0.2-0.25	<0.2	<0.1	0.37-2.0	1	0.84
Be	-	-	<0.1	<0.1-1.25	<0.1	<0.1
Ca	-	-	7	<2-18	≤2	2.4
Co	-	≤1	<1	-	-	2.7
Cr	<3-14	3.5	2.2	130-157	140	130
Cu	2-4.8	2	3	40-120	80	83
Fe	10-63	25	<31	430-450	460	450
In	-	-	<1	1-1.5	1	0.6
Mn	<1-9	3.5	<1	12-16	15	19.5
Mo	<1-5	<1	<2	-	-	11.3
Ni	6-26.6	-	12	275-395	340	290
P	<1 - ≤1	≤1	<1	-	-	<1
Si	<5 - 15	10	<31	33.5-43.5	34	47.5
Sr	<2 - ≤2	2	<1	-	-	<2
Ti	-	-	<2	1-10	5	3.3
V	-	-	<1	2 - 5	4	2.7
Zn	-	-	12.5	-	<5	<10

Table IV (Contd.)

ANALYSIS OF URANIUM REFERENCE SAMPLES

(Received from C.E.A. - France)

Sample	Jonquille			Kentia			Mickey	
	Range	Catalogue value	Present work	Range	Catalogue value	Present work	Catalogue value	Present work
Al	82-98	85	<5	87-219	120	5.1	80	3.4
B	-	-	<0.1	0.25 -> 2	1.3	1.4	0.50	0.46
Be	0.2-4	0.25	0.155	-	-	<0.1	-	<0.1
Ca	<2-10	?	5.0	<2-3	-	6.9	-	2.9
Co	-	-	<1	-	-	2.7	-	4.9
Cr	8.5-16	12	5.8	4.5-18	9	12.2	3.0	2.5
Cu	14-16	15	6.0	120-147	130	119	4.0	7.0
Fe	80-102	85	77	80-151	110	102	85	64
In	2-25	5	4.9	1.2-16	-	2.2	-	<1
Mn	4-8	5	1.5	8 - 16	12	18.4	18	9.6
Mo	-	-	<2	-	-	2.7	14	16.4
Ni	30-60	40	48.5	376-560	480	480	13	11.1
Pb	-	-	<1	-	-	<1	-	<1
Si	28-54	37	<31	30 - 87	40	38	50	43
Sn	-	-	<2	-	-	<2	-	<2
Tl	5-33.5	22	4.0	26-115	40	13.3	-	3.1
V	4-19	10	9.5	2-3.5	3	2.4	-	<1
W	-	<5	20.1	-	5	28.5	-	13.2

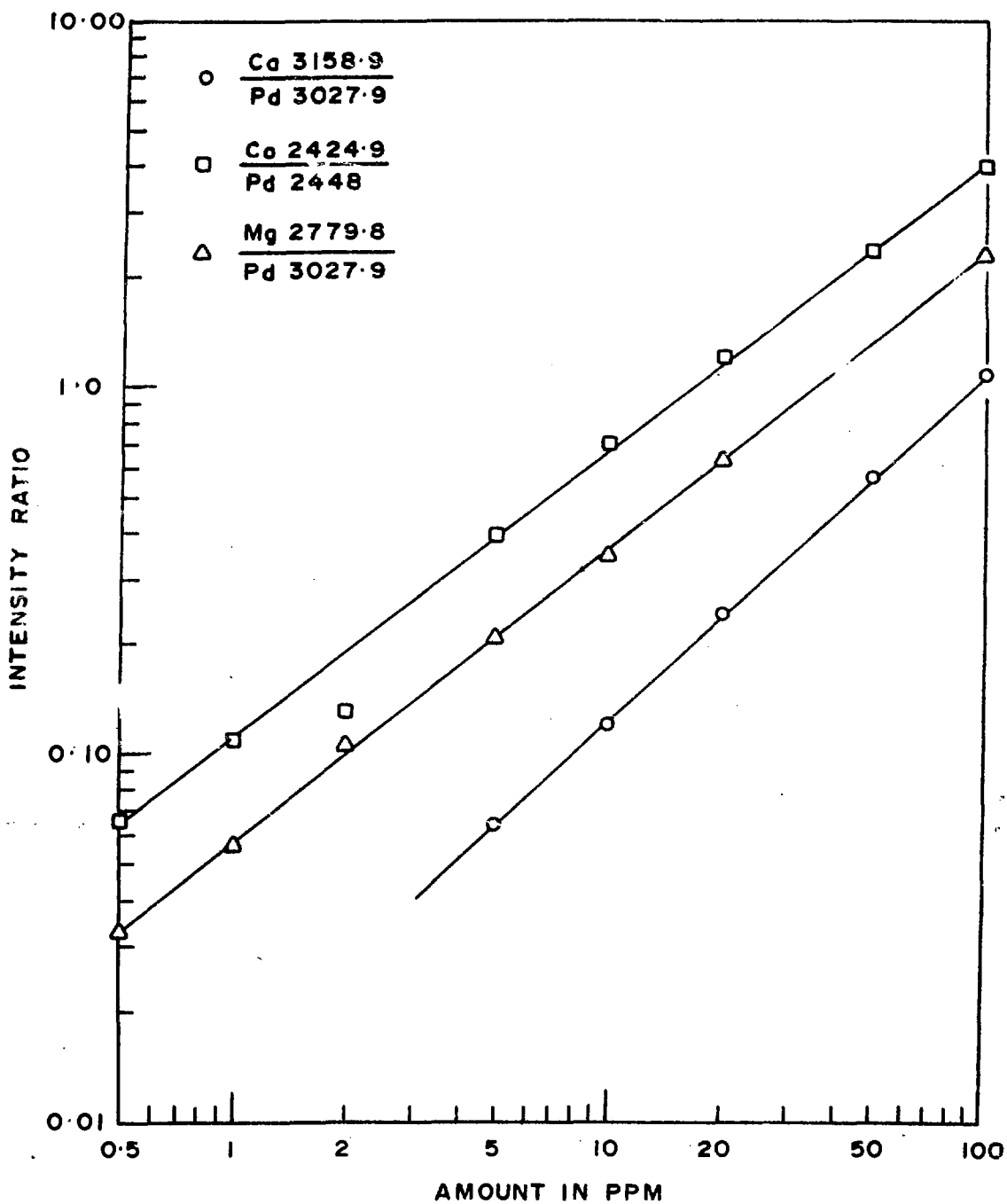


FIG.-1. WORKING CURVES FOR Ca, Co AND Mg.

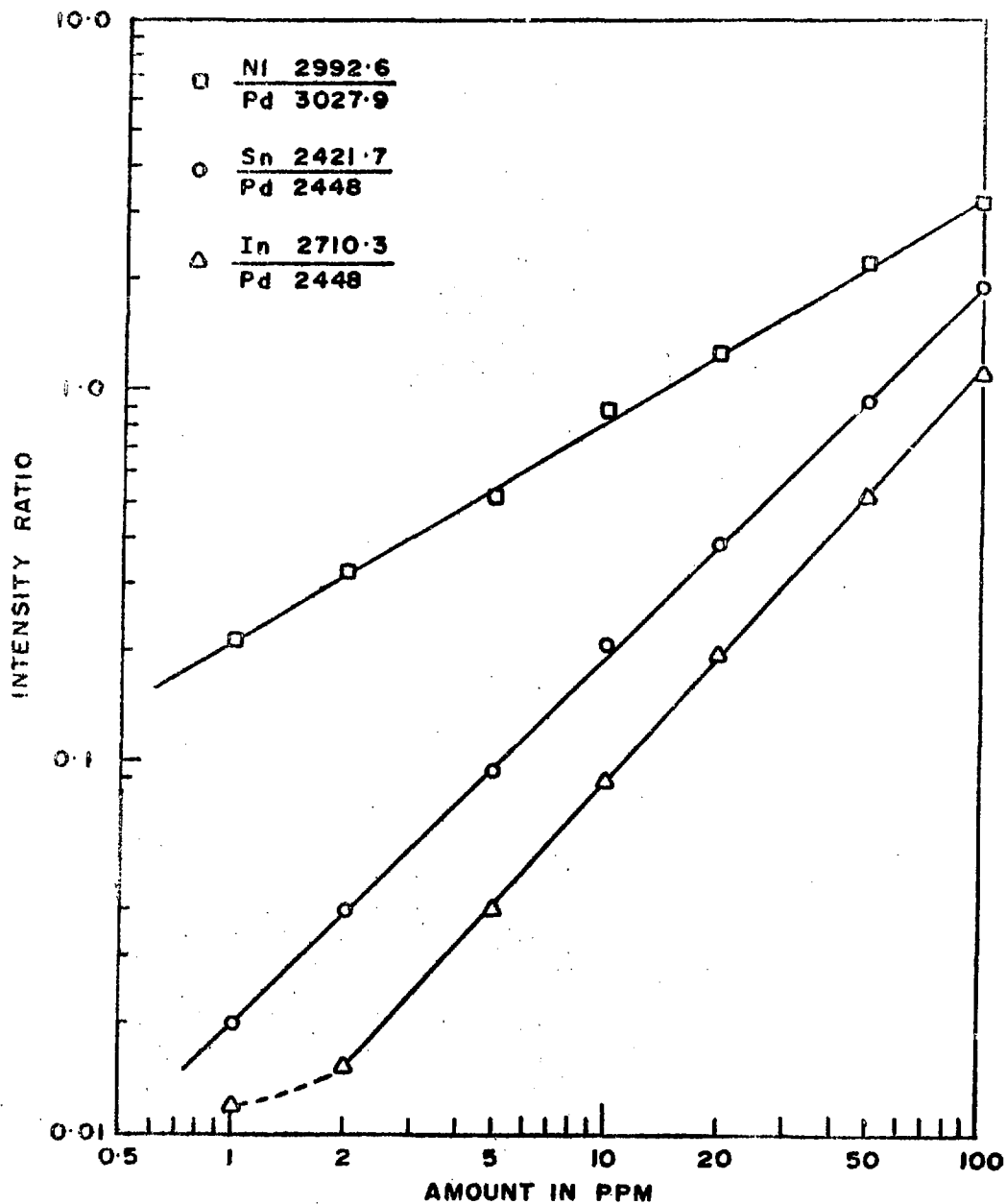


FIG.-2. WORKING CURVES FOR NI, Sn AND In.

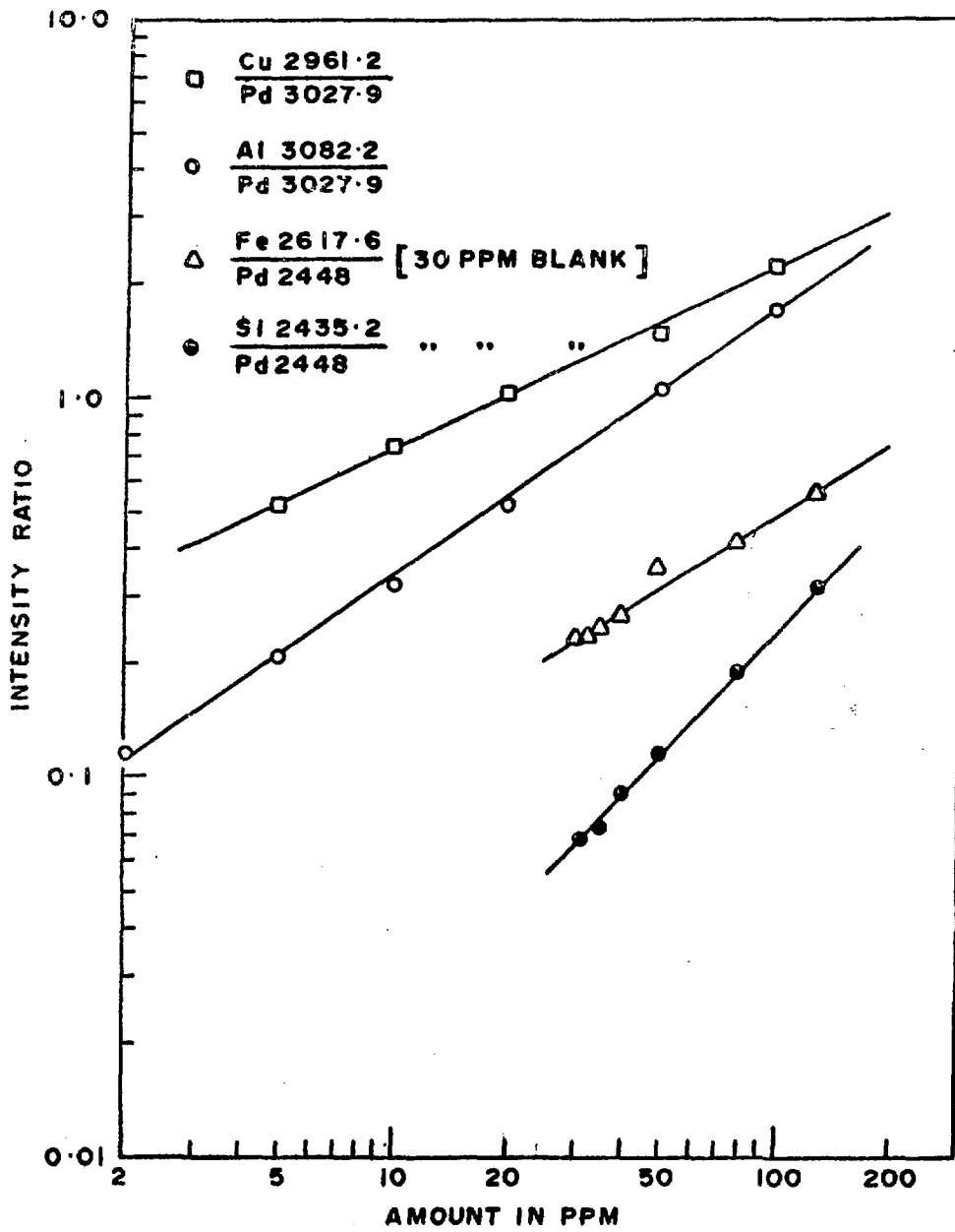


FIG.-3. WORKING CURVES FOR Cu, Al, Fe AND Si.

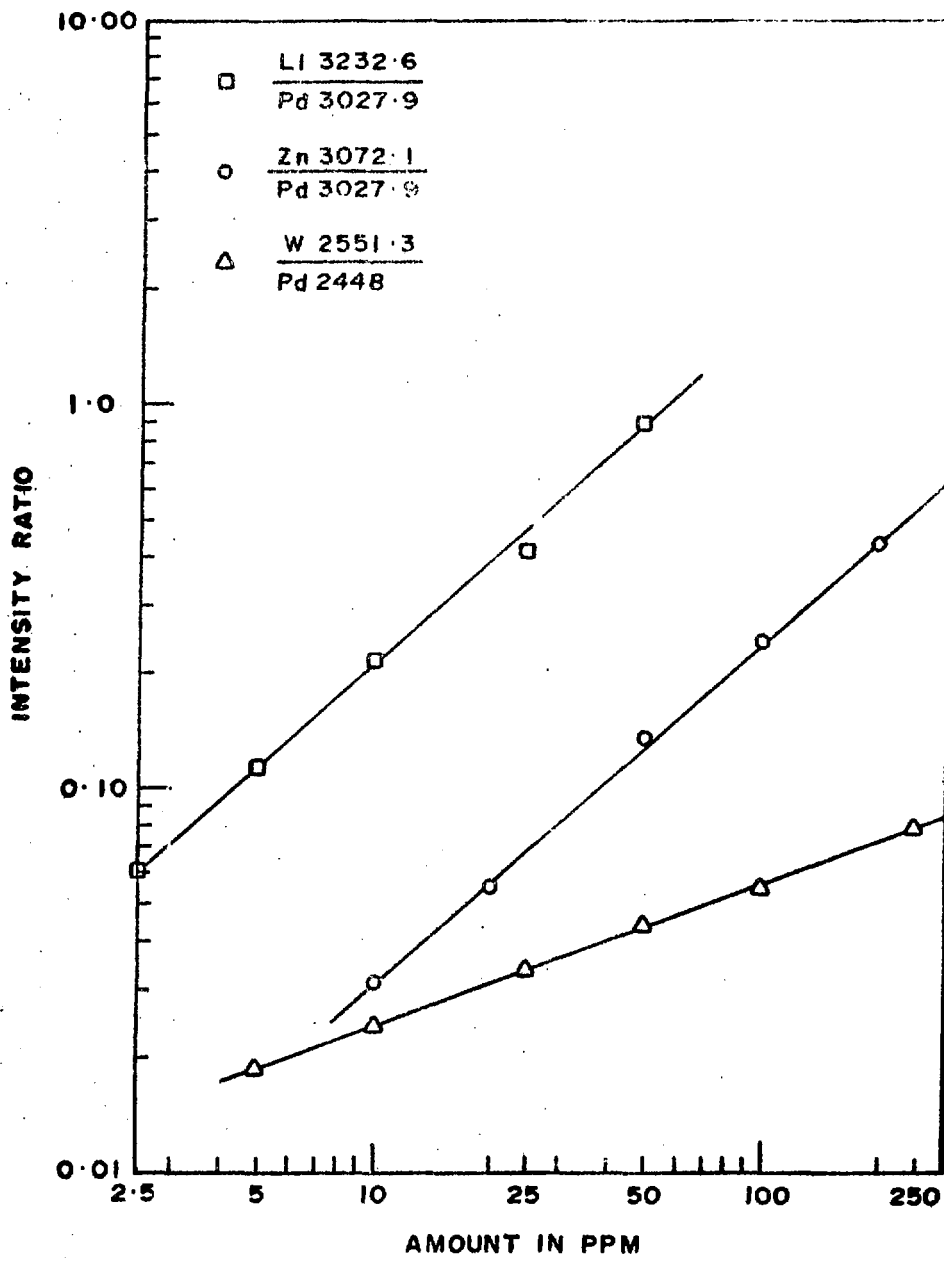


FIG.-4. WORKING CURVES FOR LI, ZN AND W.

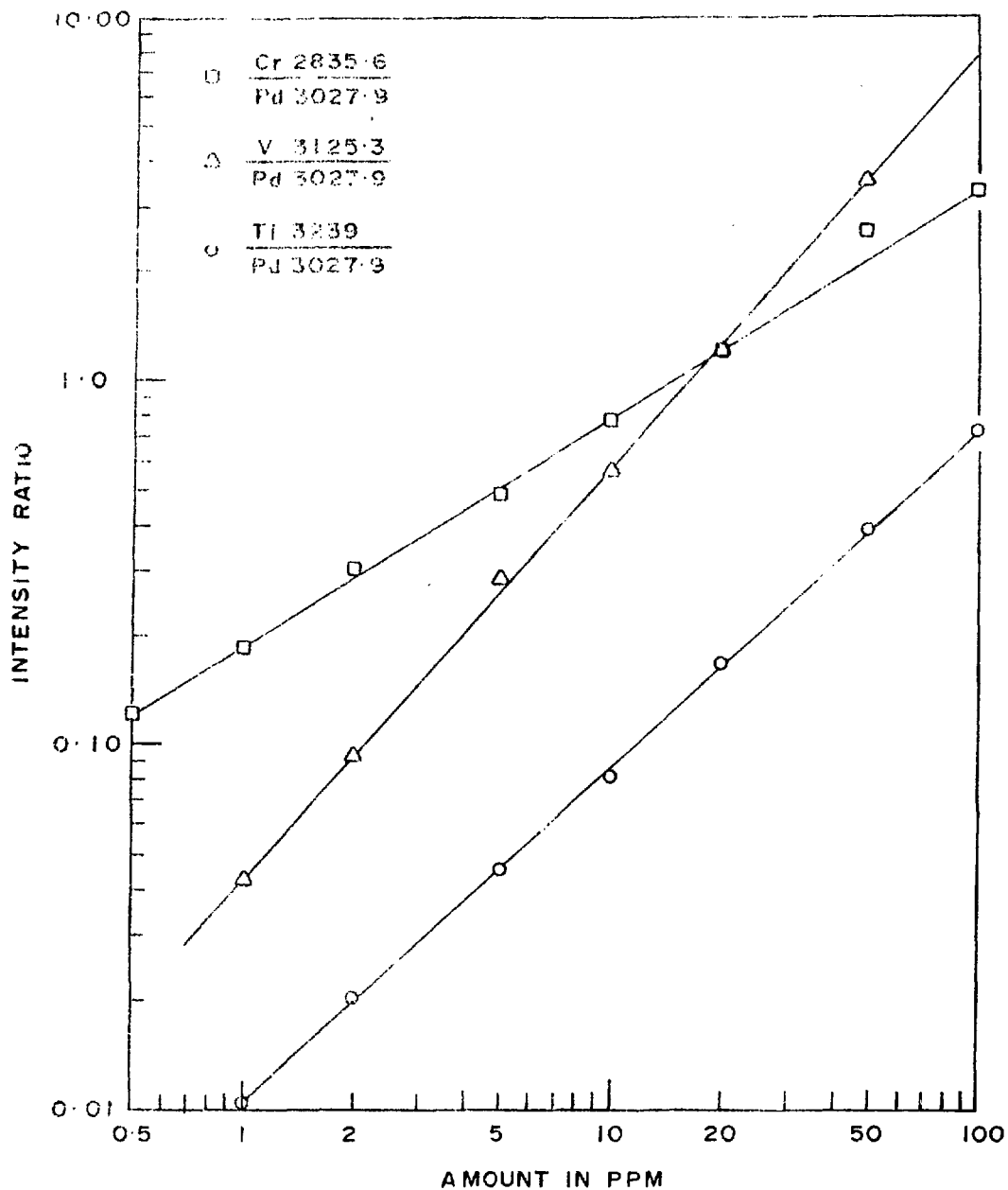


FIG.-5. WORKING CURVES FOR Cr, V AND Ti.

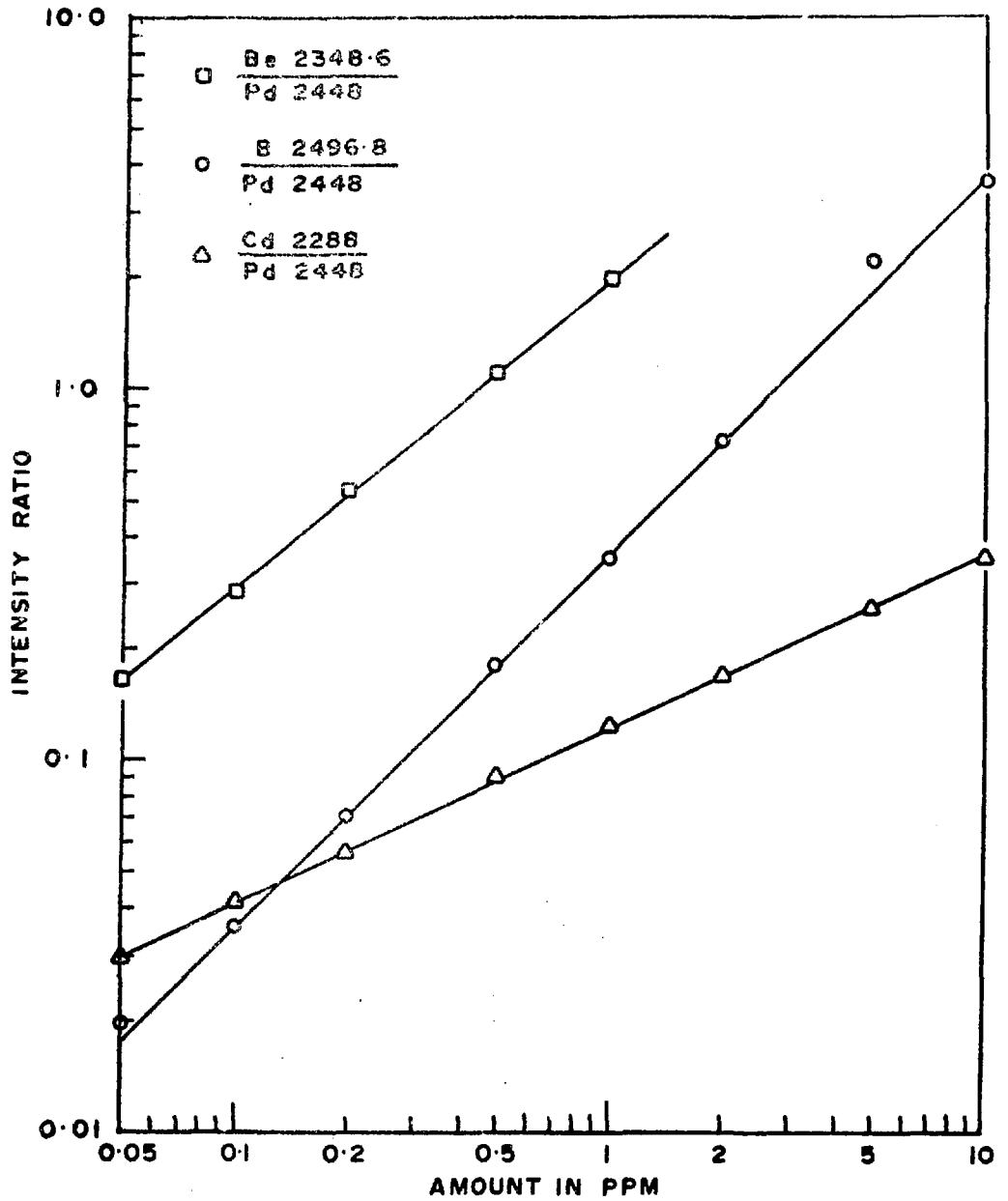


FIG.- 6. WORKING CURVES FOR Be, B AND Cd.

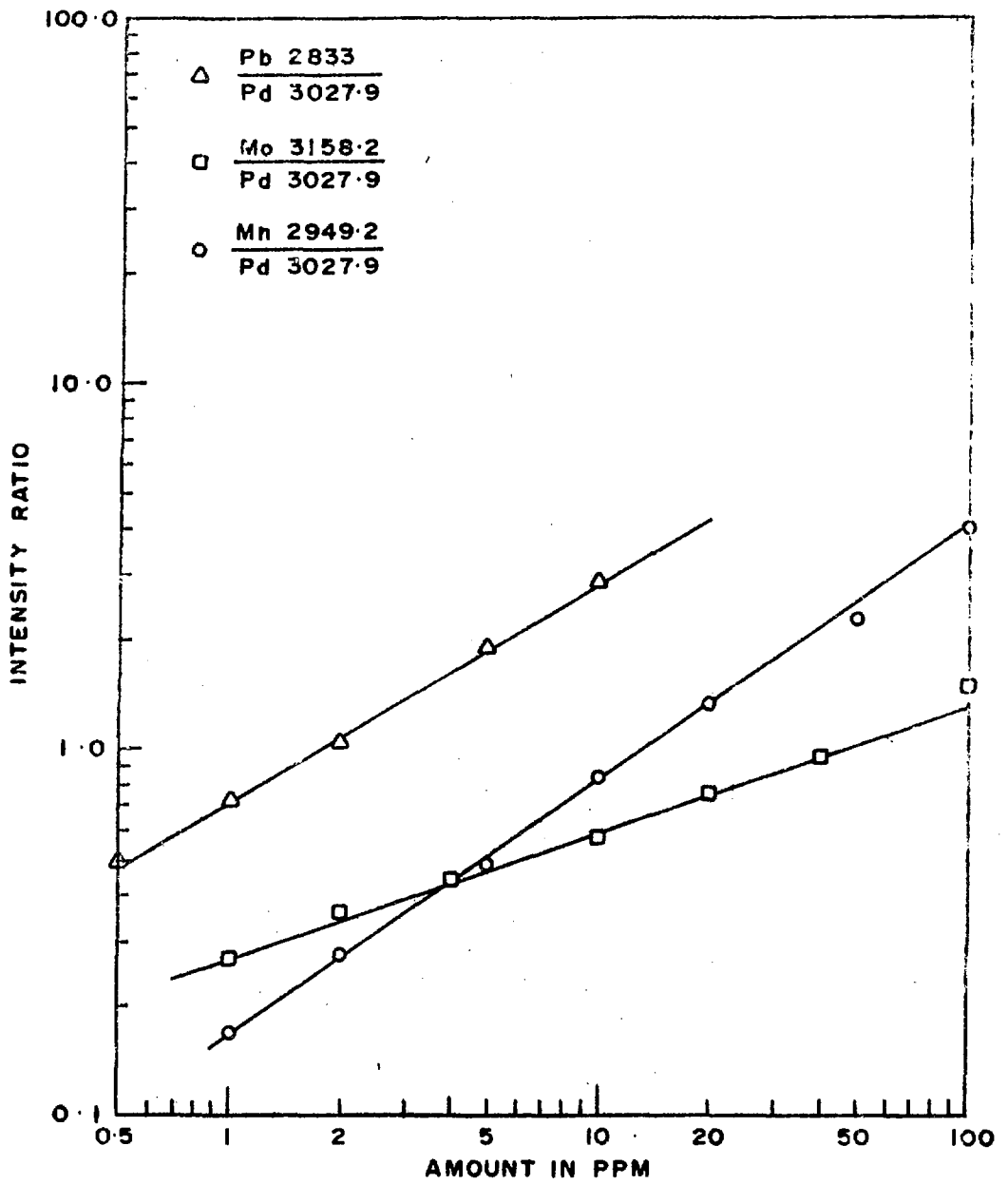


FIG.-7. WORKING CURVES FOR Pb, Mo AND Mn.

