AN INVESTIGATION INTO THE DETERMINATION OF SOME VOLATILE ELEMENTS IN SILICATE ROCKS EMPLOYING D.C. ARC EMISSION SPECTROSCOPY IN ARTIFICIAL ATMOSPHERES

by

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APPENDIX - A

Tables 1 - 16

TABLE 1

COMPARISON OF GEOLOGICAL ABUNDANCE LEVELS WITH DETECTION LIMITS OF SELECTED INSTRUMENTAL TECHNIQUES OF ANALYSIS

Element	(1) Ultrabasic rocks ppm	(1) Basalts ppm	(1) Granite Low Ca ppm	(1) Shale ppm	(1) Igneous Average ppm	(2) Optical Spectrography ppm	X-ray Fluorescence ppm	(6) Atomic Absorption ug/ml	(5) Nuclear Activation ug	(6) I.C.P. ug/ml
Ag	1	0.11	0.037	0.07	0.08	0.5	3 (8)	0.0004	0.001	0.02
As	0.06	2	1.5	13	2	100	2.4 (7)	0.1	0.01	0.01
Bi	-	0.007	0.01	-	0.2	20	4.5 (7)	0.05	-	0.05
Cd	-	0.22	0.13	0.3	0.15	10	3 (8)	0.01	0.001	0.03
Cu	10	87	10	45	55	0.5	1.2 (3)	0.005	0.01	
Ga	1.5	17	17	19	19	3	1.4 (3)	0.07	0.001	
Ge	1.5	1.3	1.3	1.6	1.1	5	0.9 (7)	1	0.01	
Hg	-	0.09	0.08	0.4	0.08	100	-	0.5	0.01	0.2
In	0.01	0.22	0.26	0.1	0.11	1	3 (8)	0.05	0.0001	
Pb	1	6	19	20	15	5	3.3 (3)	0.01	0.1	0.008
Sb	0.1	0.2	0.2	1.5	0.1	20	3 (8)	0.1	0.01	0.2
Sn	0.5	1.5	3	6	2	10	1.1 (3)	0.03	0.001	0.3
Tl	0.06	0.21	2.3	1.4	1.3	1	3 (8)	0.03	-	0.2
Zn	50	105	39	95	40	100	0.9 (3)	0.002	0.01	0.009

Compiled from the following sources:-

(1) Turekian and Wedepohl (1961)
(2) Ahrens and Taylor (1961)
(3) Willis (1968)
(4) Fassel (1972)
(5) Fite et al (1971)
(6) Fassel (1972)
(7) Willis and Crank (1980). Detection limits quoted are calculated as 3 times the detection limit for a coal matrix.
(8) Willis J.P. Personal Communication.

TABLE 2

COMPARISON OF IGNEOUS ROCK ABUNDANCE LEVEL, DETECTION LIMIT USING A.A.S. AND MASS OF SAMPLE REQUIRED FOR THE VOLATILE ELEMENT TO BE DETECTED IF A.A.S. IS EMPLOYED AS THE ANALYTICAL TECHNIQUE

Element	Abundance in igneous rocks ug/gm (a)	Detection limit in ug/ml (b)	ug present in a 50ml solution at the detection limit	Mass in grams of igneous rock required to achieve detectable cone in 50ml of solution (c)
Ag	0.08	0.0004	0.02	0.25
As	2.0	0.1	5	2.5
Bi	0.2	0.05	2.5	12.5
Cd	0.15	0.01	0.50	3.5
Cu	55	0.005	0.25	0.005
Ga	19	0.07	3.5	0.18
Ge	1.1	1	50	50
Hg	0.08	0.5	25	312
In	0.11	0.05	2.5	25
Pb	15	0.01	0.50	0.3
Sb	0.1	0.10	5	50
Sn	2	0.03	1.50	1
Tl	1	0.03	1.50	2
Zn	40	0.002	0.10	0.0025

(a) Turekian and Wedepohl (1961)

(b) Fassel (1972).

(c) The mass of igneous rock required is calculated. The calculation assumes that the concentration level of the volatile element present in the igneous rock is equal to the average igneous rock abundance level. The mass calculated is the minimum required to ensure that the element is detected. This calculated mass can also be regarded as an enrichment factor assuming that the mass of sample usually taken is 1gm.

TABLE 3

THE DETECTION LIMITS, LOWER LIMITS OF DETERMINATION AND RELATIVE STANDARD DEVIATIONS OBTAINED WITH VARIOUS X.R.F. CONFIGURATIONS.

The average igneous abundance levels are included for comparative purposes.

Element	Instrumental Conditions Tube, kV/mA, Crystal		L.L.D. ppm	L.L. Dt. ppm	R.S.D. %	Abundance Level ppm
Ag	W 48/20	Topaz	3	9	2.84	0.08
Bi	Mo 48/20	Topaz	6	18	3.11	0.20
Cd	W 48/20	Topaz	10	30	4.53	0.15
Cu	Au 60/32	LiF (200)	1	3	0.83	55
Cu	Mo 48/20	LiF (200)	2	6	1.16	55
Cu	W 48/20	Topaz	3	9	1.38	55
Zn	Au 60/32	LiF (200)	1	3	0.79	40
Zn	Au 60/32	Topaz	2	6	1.31	40
Zn	W 48/20	Topaz	3	6	1.63	40
Ga	Mo 50/20	LiF (200)	1	3	0.89	19
Ga	Mo 48/20	Topaz	3	9	1.85	19
Ga	W 48/20	Topaz	5	15	3.40	19

L.L.D. = Lower limit of detection

L.L. Dt. = Lower limit of determination (Jenkins 1974).

R.S.D. = Relative Standard Deviation calculated for 100ppm artificial standard

Abundance level is the Igneous average taken from Turekian et al (1961).

TABLE 4

INSTRUMENTAL PARAMETERS USED FOR THE DETERMINATION OF THE VOLATILE ELEMENTS

Spectrograph	Jarrell 3.4 meter Ebert mount plane grating 15 000 line/inch Dispersion 5.2A/mm.
Slit width	10 microns
Lens system	Three lens system to give maximum intensity with uniform illumination.
Step sector	Rotating 7 step.
Excitation	anode d.c. arc supplied by a Jarrell Ash custom d.c. source unit.
Electrodes	Cut as required from carbon or graphite rods of preferred quality using a watchmakers lathe.
Photographic plates	Ilford ordinary N 30. Kodak 103-0.
Developer	Kodak D-19b
Fixer	Amfix rapid.
Photoprocessing	A.R.L. rocking bath. 4½ minutes developer 10 seconds acetic acid stop bath 5 minutes fixer Water washed, air dried.
Plate calibration	Self calibration method. Modified self-calibration method for single step intensity readings. Ahrens and Taylor (1961).

TABLE 5

WAVELENGTH IN NANOMETERS OF THE MOST SENSITIVE SPECTRAL LINES OF THE VOLATILE ELEMENTS. RELATIVE INTENSITIES APPEAR ALONGSIDE IN BRACKETS.

Elements	Spectral lines and respective relative intensities			
As	234.98 (250)	278.02 (75)	286.05 (50)	
Ag	328.07 (2 000)	338.29 (1 000)		
Bi	306.77 (3 000)	472.26 (1 000)	289.79 (500)	
Cd	228.8 (1 500)	346.62 (1 000)	326.11 (300)	
Cu	324.75 (5 000)	327.39 (3 000)		
Ga	417.21 (2 000)	403.29 (1 000)	294.36 (100)	
Ge	303.91 (1 000)	265.12 (400)	326.95 (300)	
Hg	435.84 (3 000)	253.65 (2 000)		
In	451.13 (5 000)	325.61 (1 500)	303.94 (1 000)	
Pb	405.78 (2 000)	283.31 (500)	368.35 (300)	
Sb	252.85 (300)	287.79 (250)	259.81 (200)	
Sn	317.50 (500)	326.23 (400)	283.99 (300)	
Tl	377.57 (3 000)	351.92 (2 000)		
Zn	213.86 (800)	334.50 (800)	334.56 (500)	481.05 (400)

Reference: Ahrens and Taylor (1961)

TABLE 6

WAVELENGTHS IN NANOMETERS OF VOLATILE ELEMENT SPECTRAL LINES CHOSEN FOR THIS INVESTIGATION.
RELATIVE INTENSITIES APPEAR IN BRACKETS

Element	Spectral line in nm and Relative intensities	
Ag	328.07 (2 000)	338.29 (1 000)
Bi	306.77 (3 000)	289.79 (500)
Cd	346.62 (1 000)	326.11 (300)
Cu	324.75 (5 000)	327.39 (3 000)
Ga	294.36 (100)	
Ge	303.91 (1 000)	326.95 (300)
In	325.61 (1 500)	303.94 (1 000)
Pb	283.31 (500)	
Sn	317.50 (500)	326.23 (400)
Tl	377.5 (3 000)	
Zn	334.50 (800)	334.56 (500)

Reference: Ahrens and Taylor (1961)

TABLE 7

COMPARISON OF VOLATILIZATION TIMES OBTAINED FOR THE LESS VOLATILE ELEMENTS EMPLOYING VARIOUS ADDITIVES AND DEMONSTRATING THE ABSENCE OF OVERALL IMPROVEMENT IN VOLATILIZATION TIMES

ADDITIVE CONCENTRATION USED	VOLATILIZATION TIMES IN MINUTES						TOTAL EXPOSURE TIME
	Zn 334.5	Ag 328.0	Cu 327.4	Sn 317.5	Ga 294.3	Pb 283.3	
25% Li_2CO_3	3.5	1	2	4	2	1	4
25% LiF	5	4	5	5	5	4.5	5
10% WANG MIX (a)	1	1	4	4	1	1	4
20/2/3 (b)	6	2	6	6	3	1.5	6
10% CaF_2	2.5	3	4.5	4.5	3.5	2.5	4.5
25% CaF_2	5	1.5	5	5	3.5	3	5
25% NaF	5	1.5	5	5	3	3.5	5

(a) WANG MIX 1 part Li_2CO_3 and 1 part graphite

(b) 20/2/3 80% sample, 8% K_2SO_4, 12% graphite.

General Conditions

Sample	Bushveld granite
Electrode	D-5 carrier
Atmosphere	Argon
Excitation	20 amps.

TABLE 8

VOLATILIZATION TIME IN MINUTES DISPLAYED BY THE LESS VOLATILE ELEMENTS DISTILLING FROM SAMPLES EMPLOYING A CARRIER ELECTRODE FITTED WITH ANODE CAP AND EXCITATION AT 30 AMPS.

ADDITIVE CONCENTRATION USED	VOLATILIZATION TIMES IN MINUTES						TOTAL EXPOSURE TIME
	Zn 334.5	Ag 328.0	Cu 327.4	Sn 317.5	Ga 294.3	Pb 283.3	
20/2/3(a)	1	1	3	2	1.5	1.5	3
Schroll 1(b)	1.5	1.5	3	1.5	1	1	3
Schroll 2(c)	1.5	1.5	3	1	1	1.5	3

(a) 20/2/3 80% sample, 8% K_2SO_4, 12% graphite.

(b) Schroll 1 46.25% sample, 46.25% graphite, 7.5% $BaSO_4$

(c) Schroll 2 43.75% sample, 43.75% graphite, 7.5% $BaSO_4$, 5% sulphur.

General Conditions

Sample	Bushveld granite
Electrode	I.S-4 carrier with anode cap.
Atmosphere	Argon.

TABLE 9

VOLATILIZATION TIME IN MINUTES DISPLAYED BY THE LESS VOLATILE ELEMENTS DISTILLING FROM A SAMPLE CONTAINED IN A SMALL CARRIER ELECTRODE

ADDITIVE USED	VOLATILIZATION TIME IN MINUTES						TOTAL EXPOSURE TIME
	Zn 334.5	Ag 328.0	Cu 327.4	Sn 317.5	Ga 294.3	Pb 283.3	
GRAPHITE 1:1	3	1	3	3	1	1	3

General Conditions

Sample	Bushveld granite
Electrode	C-6 carrier
Atmosphere	Argon
Excitation	17 amps.

TABLE 10

COMPARISON OF THE VOLATILIZATION TIMES OBTAINED FOR THE LESS VOLATILE ELEMENTS EMPLOYING VARIOUS ADDITIVE MIXTURES WHICH ENHANCE VOLATILIZATION BY THERMOCHEMICAL REACTIONS IN THE ELECTRODE CRATER

ADDITIVE CONCENTRATION USED	VOLATILIZATION TIMES IN MINUTES						TOTAL EXPOSURE TIME
	Zn 334.5	Ag 328.0	Cu 327.4	Sn 317.5	Ga 294.3	Pb 283.3	
25% mixed (a)	4	4	4	3	4	4	4
25% Joensuu (b)	1	1	4	3	1	1	4
Schroll 1 (c)	4	2	4	2	2	1	4
Schroll 2 (d)	4	1	4	2	2	1	4

(a)	Mixed	1 part NH_4CL + 3 parts Li_2CO_3
(b)	Joensuu	1 part K_2SO_4 + 1 part $CaCO_3$ + 3 parts graphite
(c)	Schroll 1	46.25% sample, 46.25% graphite, 7.5% $BASO_4$
(d)	Schroll 2	43.75% sample, 43.75% graphite, 7.5% $BaSO_4$ + 5% sulphur.

General Conditions

Sample	Bushveld Granite
Electrode	I.S-4 carrier with anode cap.
Atmosphere	Argon
Excitation	25 amps.

TABLE 11

COMPARISON OF THE COEFFICIENTS OF VARIATION (C.O.V.) OF THE SPECTRAL LINE INTENSITIES OBTAINED FOR THE VOLATILE ELEMENTS DURING REPLICATE ARCINGS IN ARGON, ARGON-OXYGEN AND NITROGEN. THE C.O.V.'S OBTAINED EMPLOYING In AS POSSIBLE INTERNAL STANDARD ARE INCLUDED

Element	Spectral line wavelength in nm	ARGON		ARGON-OXYGEN		NITROGEN	
		No. int. std.	In int. std.	No. int. std.	In int. std.	No. int. std.	In int. std.
Ag	338,2	26,3	13,9	25,1	15,4	5,7	20,2
Ag	328,0	21,8	15,5	19,3	17,8	6,0	21,5
Bi	306,7	20,8	26,5	11,5	20,4	10,7	20,9
Cd	326,1	9,4	17,3	12,8	37,6	19,5	30,1
Cu	324,7	50,4	38,9	31,5	32,0	24,8	25,5
Cu	327,4	48,9	37,0	29,2	26,2	24,0	25,6
Ga	294,3	26,3	20,5	33,3	22,5	11,8	14,7
Ge	303,9	10,7	21,5	15,5	19,6	16,2	20,4
In	325,6	27,4	-	23,6	-	17,6	-
In	303,9	19,5	-	26,7	-	14,7	-
Pb	283,3	14,1	13,5	18,2	15,8	12,0	15,4
Sn	326,2	17,1	14,0	27,4	18,5	6,5	21,7
Sn	317,5	16,8	14,1	27,4	24,1	8,1	14,6
Zn	334,5	20,3	27,5	19,3	29,3	-	-

General Conditions

Sample	10ppm artificial standard buffered 20/2/3
Electrode	D-5 carrier
Excitation	15 amps.
Exposure	Argon - 90 secs., Argon-oxygen - 40 secs., Nitrogen - 30 secs.

TABLE 13

VISUAL ESTIMATES OF THE STRENGTH OF SOME VOLATILE ELEMENT SPECTRAL LINES IN GEOLOGICAL REFERENCE MATERIALS

	Ag 328,0nm	Bi 306,7nm	Cd 326,1nm	Cu 327,4nm	Ga 294,4nm	Ge 303,9nm	In 303,9nm	Pb 283,3nm	Sn 317,nm	Zn 334,5nm
In Argon										
T-1	W	a	a	S	W	a	a	S	M	S
GR	a	W	W	VS	M	W	a	S	M	S
G-1	W	W	W	S	M	VW	a	S	W	S
Sy-1	S	VW	VW	S	M	a	a	VS	M	VS
Sulphide ore	S	W	VW	VS	W	a	a	S	W	VS
In Argon/oxygen										
T-1	W	a	a	S	M	a	a	S	S	S
GR	a	W	W	VS	M	W	a	S	M	S
G-1	W	W	VW	S	M	W	a	S	M	S
Sy-1	M	W	VW	S	W	W	a	VS	M	VS
Sulphide ore	S	S	VW	VS	M	a	a	S	M	VS
In Nitrogen										
T-1	W	a	-	S	S	-	a	S	S	S
GR	a	W	-	VS	S	-	a	S	S	S
G-1	W	W	-	S	S	-	a	S	M	M
Sy-1	M	W	-	S	S	-	a	VS	S	S
Sulphide ores	S	W	-	VS	M	-	a	S	M	S
Concentration levels										
T-1	< 1	< 10	< 20	47	21	< 10	< 10	37	43	190
GR				270-1000	15-22			30-250	9	57
G-1	0.04	0.20	0.06	13	18	1.0	0.03	49	2-3	40
Sy-1	1.6	?	1.0	25	18	< 10	< 10	516	12	200
Sulphide ore	3.5	5	1-50	8291	13	< 10	< 10	248	11	298
Normal O.E.S. Detection Limit	0.5	20	10	0.5	3	5	1	5	10	100

EXPLANATARY NOTES

Visual estimates of spectral line intensities appear in the table above. These estimates are for the volatile elements present in a few selected International Reference Materials, and are intended to give some idea of the detectability of these elements during excitation in atmospheres of argon, argon-oxygen and nitrogen.

The strength of the spectral lines recorded has been graded using the no of steps of the step sectored spectra visible as a guide.

LEGEND

VS = very strong > 7 steps
S = strong 7 steps
M = moderate 5 steps
W = weak 3 steps
VW = very weak 2 steps
a = absent
- = background too high

GENERAL CONDITIONS

Excitation	15 amps
Electrode	D-5 carrier
Additive	8% K_2SO_4, 12% Graphite
Photographic Plate	Kodak 103-0.

TABLE 14

REPLICATE DETERMINATION OF THE INTENSITY RATIO CU 324.7/CU 327.4NM AND AG 328.0/AG 338.2NM EMPLOYING VARIOUS ATMOSPHERES

	ARGON		ARGON-OXYGEN		NITROGEN	
	90 seconds exposure		40 seconds exposure		30 seconds exposure	
	Cu 324.7/Cu 327.4	Ag 328.0/Ag 338.2	Cu 324.7/Cu 327.4	Ag 328.0/Ag 338.2	Cu 324.7/Cu 327.4	Ag 328.0/Ag 338.2
	2.03	1.65	1.82	1.88	1.59	1.43
	1.66	1.53	1.81	1.54	1.54	1.41
	1.63	1.84	1.84	1.96	1.48	1.46
	1.75	1.53	1.85	1.58	1.54	1.47
	1.76	1.85	1.82	1.54	1.49	1.47
	1.94	1.73	1.64	1.45	1.45	1.51
	1.61	1.37	1.84	1.61	1.40	1.46
	1.75	1.88	2.03	1.57	1.59	1.47
	1.68	1.77	2.18	1.55	1.62	1.48
	1.68	1.71	1.93	1.50	1.55	1.48
	1.59	1.82	1.96	1.54	1.53	1.47
	1.81	1.67	2.08	1.53	1.45	1.47
	2.13	1.80	1.85	1.40	1.57	1.41
	1.35	1.82	2.00	1.59	1.50	1.36
MEAN	1.74	1.71	1.90	1.59	1.52	1.45

General conditions

Sample 10ppm artificial standard buffered 20/2/3.

Electrode	D-5 carrier
Excitation	15 amps.

TABLE 15

INTENSITY RATIOS FOR CU 324.7/CU 327.4NM AND AG 328.0/AG338.2NM SPECTRAL LINES VARYING ELEMENTAL CONCENTRATION AND GAS COMPOSITION (ADELSTEIN AND VALLEE 1954)

$\frac{\text{Cu } 324.7\text{nm}}{\text{Cu } 327.4\text{nm}}$

Concentration ppm	100% A/0% He	50% A/50% He	0% A/100% He
67	5.68	5.00	4.20
13	3.88	2.50	2.34
6.7	3.16	1.93	4.50
1.3	3.15	2.06	2.34

$\frac{\text{Ag } 328.0\text{nm}}{\text{Ag } 338.2\text{nm}}$

Concentration ppm	100% A/0% He	50% A/50% He	0% A/100% He
67	7.03	5.28	5.23
13	3.00	2.94	2.62
6.7	2.66	2.30	1.41
1.3	1.43	2.30	0.94

Ratios calculated from relative intensities reported by (Adelstein and Vallee 1954 pp 137).

TABLE 16

INTENSITY RATIOS OBTAINED DURING THIS INVESTIGATION FOR CU 324,7/CU 327,4NM AND AG 328,0/AG 338,2NM SPECTRAL LINES VARYING ELEMENTAL CONCENTRATION AND GAS COMPOSITION

$\frac{\text{Cu } 324{,}7\text{nm}}{\text{Cu } 327{,}4\text{nm}}$

Concentration ppm	100% A	90%A/10%O_2	100% N_2
3	1.70	1.83	1.90
10	1.70	1.80	1.70
31.6	1.85	1.65	1.85

$\frac{\text{Ag } 328.0\text{nm}}{\text{Ag } 338.2\text{nm}}$

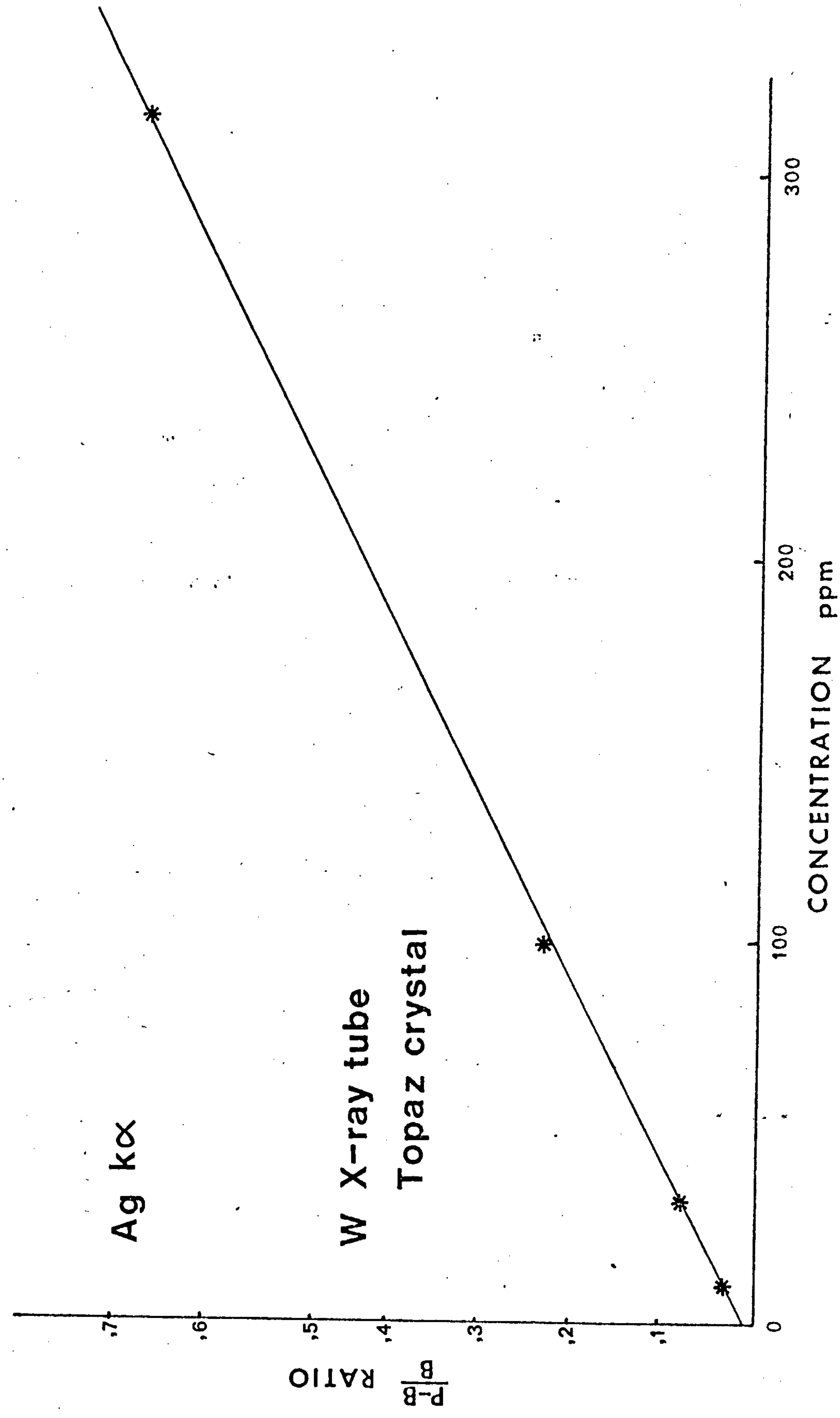
Concentration ppm	100% A	90%A/10%O_2	100% N_2
3	1.87	1.65	1.56
10	1.75	1.63	1.52
31.6	1.65	1.25	1.31

General Conditions

Sample	Artificial standards buffered 20/2/3.
Electrode	D-5 carrier.
Excitation	15 amps.

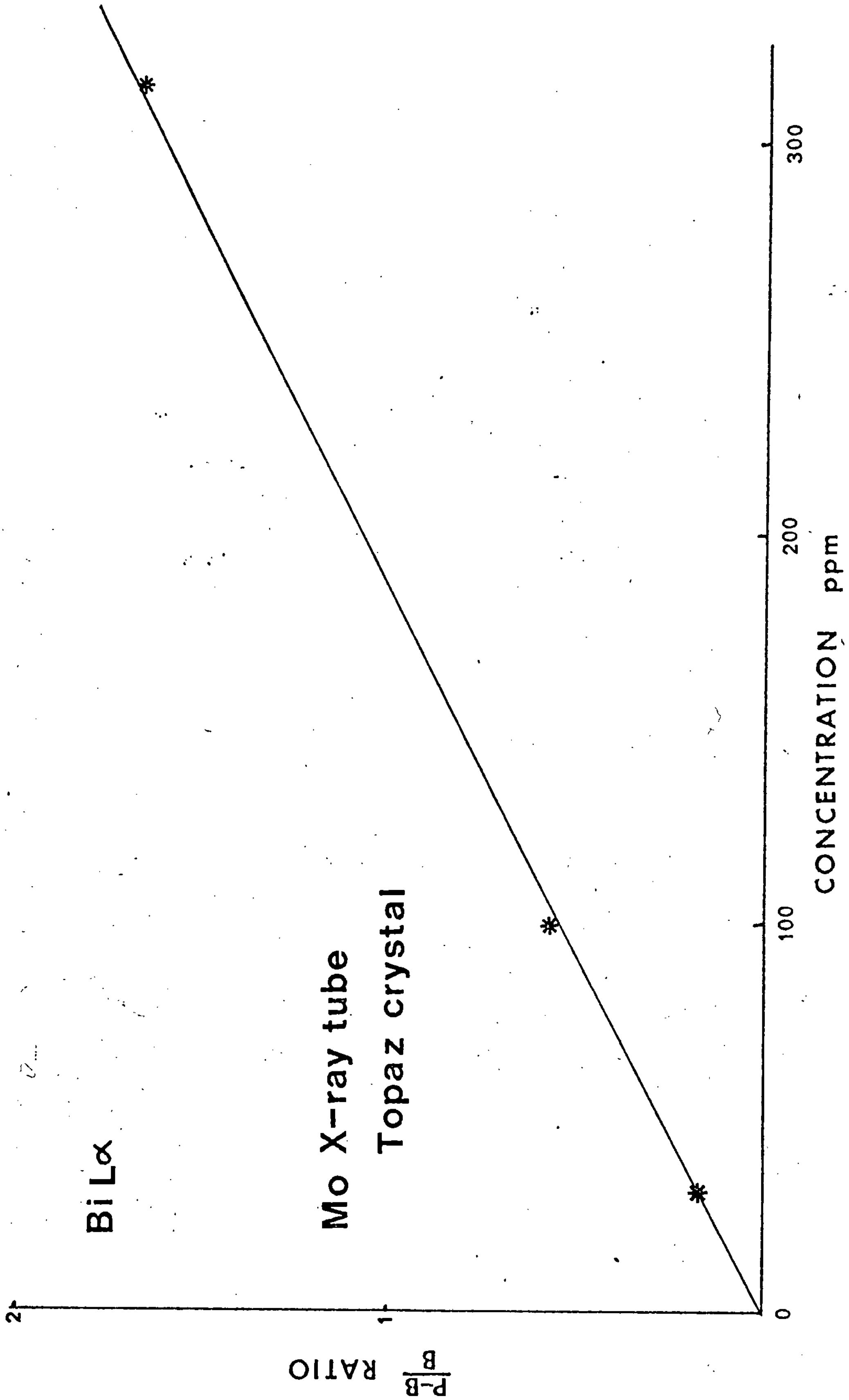
APPENDIX - B

Figures 1 - 55
Plates 1 - 3



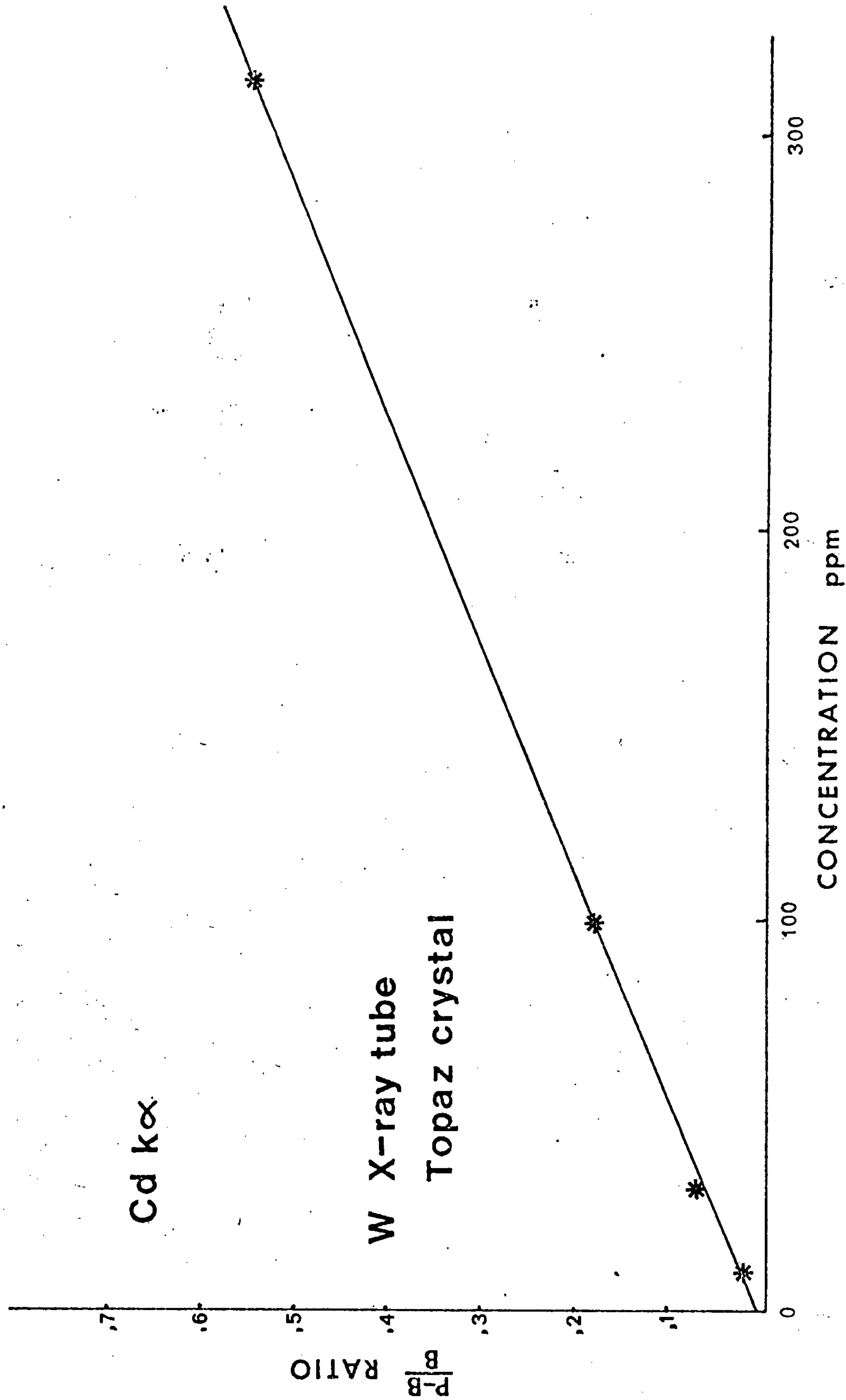
RELATIONSHIP BETWEEN $\frac{P-B}{B}$ RATIO & CONCENTRATION CONFIRMING DILUTIONS

FIGURE 1



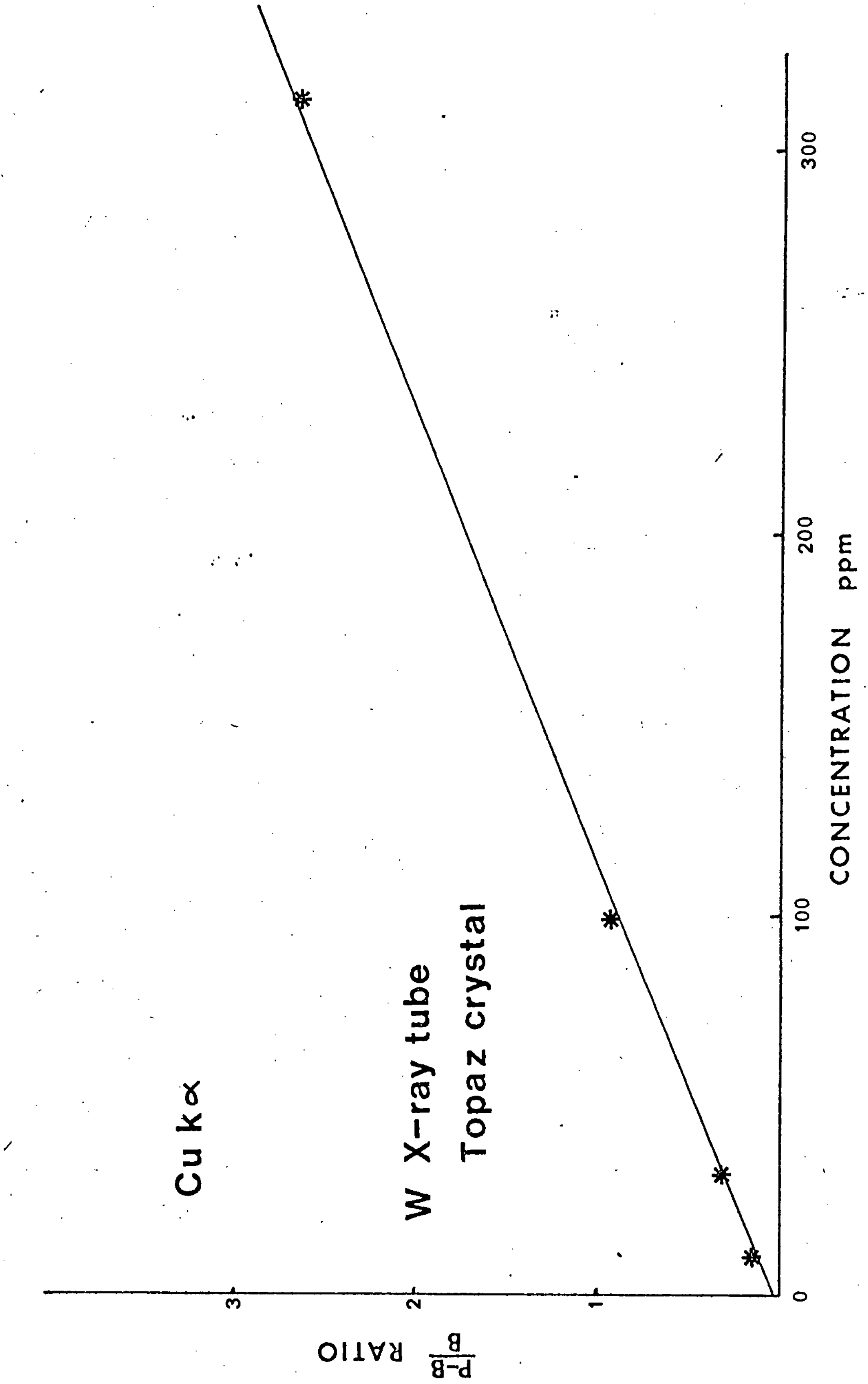
RELATIONSHIP BETWEEN $\frac{P-B}{B}$ RATIO & CONCENTRATION CONFIRMING DILUTIONS

FIGURE 2



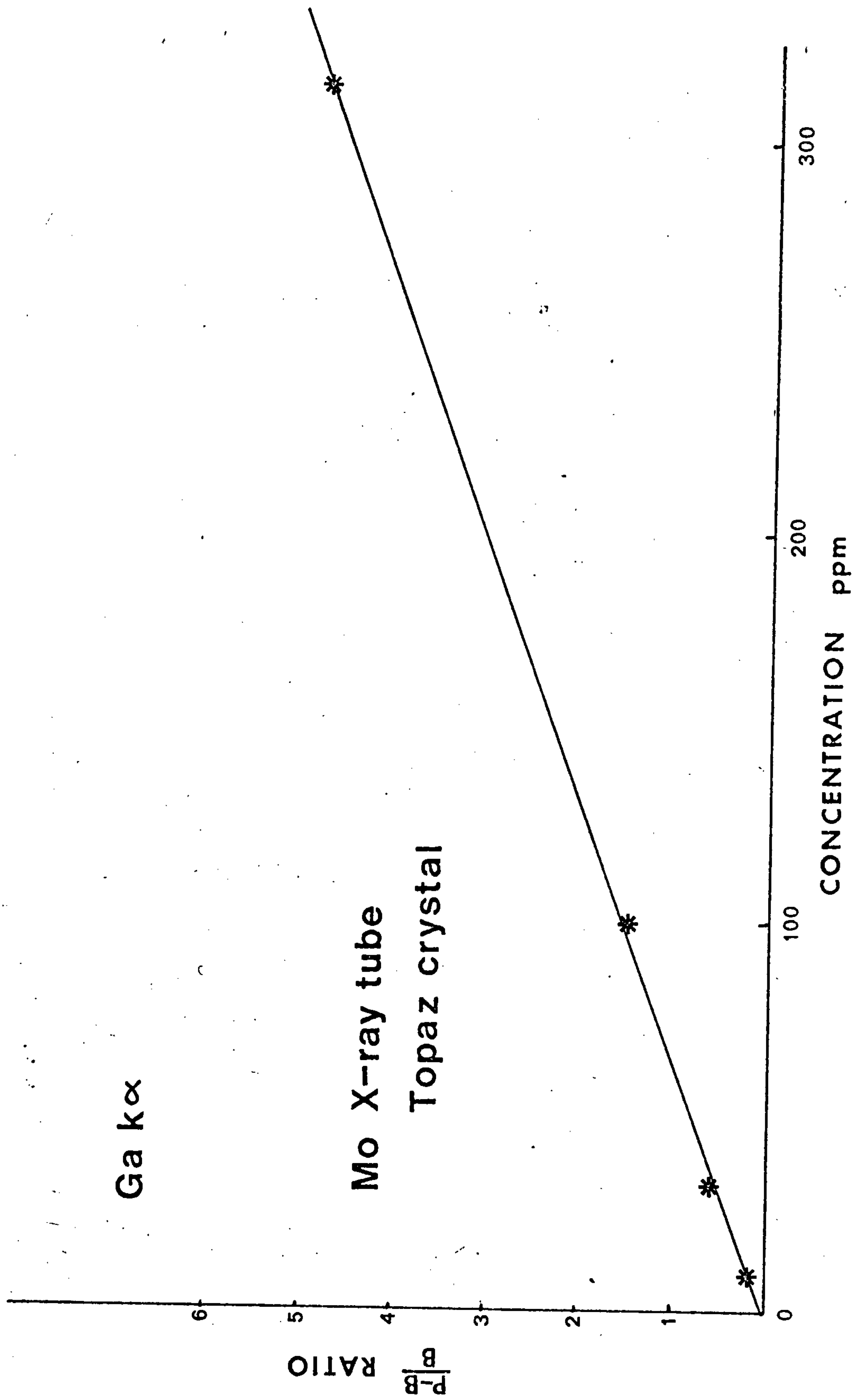
RELATIONSHIP BETWEEN $\frac{P-B}{B}$ RATIO & CONCENTRATION CONFIRMING DILUTIONS

FIGURE 3



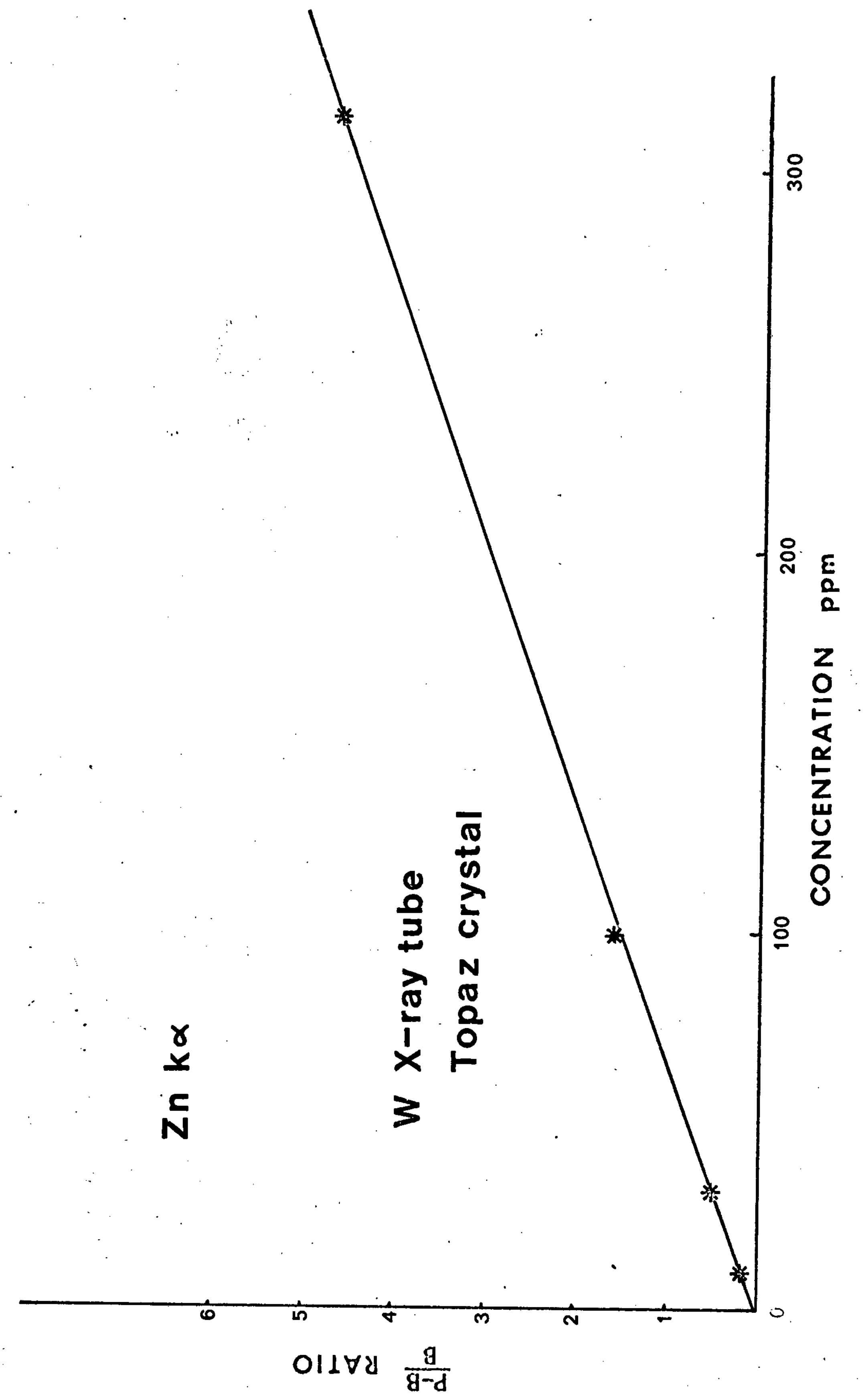
RELATIONSHIP BETWEEN $\frac{P-B}{B}$ RATIO & CONCENTRATION CONFIRMING DILUTIONS

FIGURE 4



RELATIONSHIP BETWEEN $\frac{P-B}{B}$ RATIO & CONCENTRATION CONFIRMING DILUTIONS

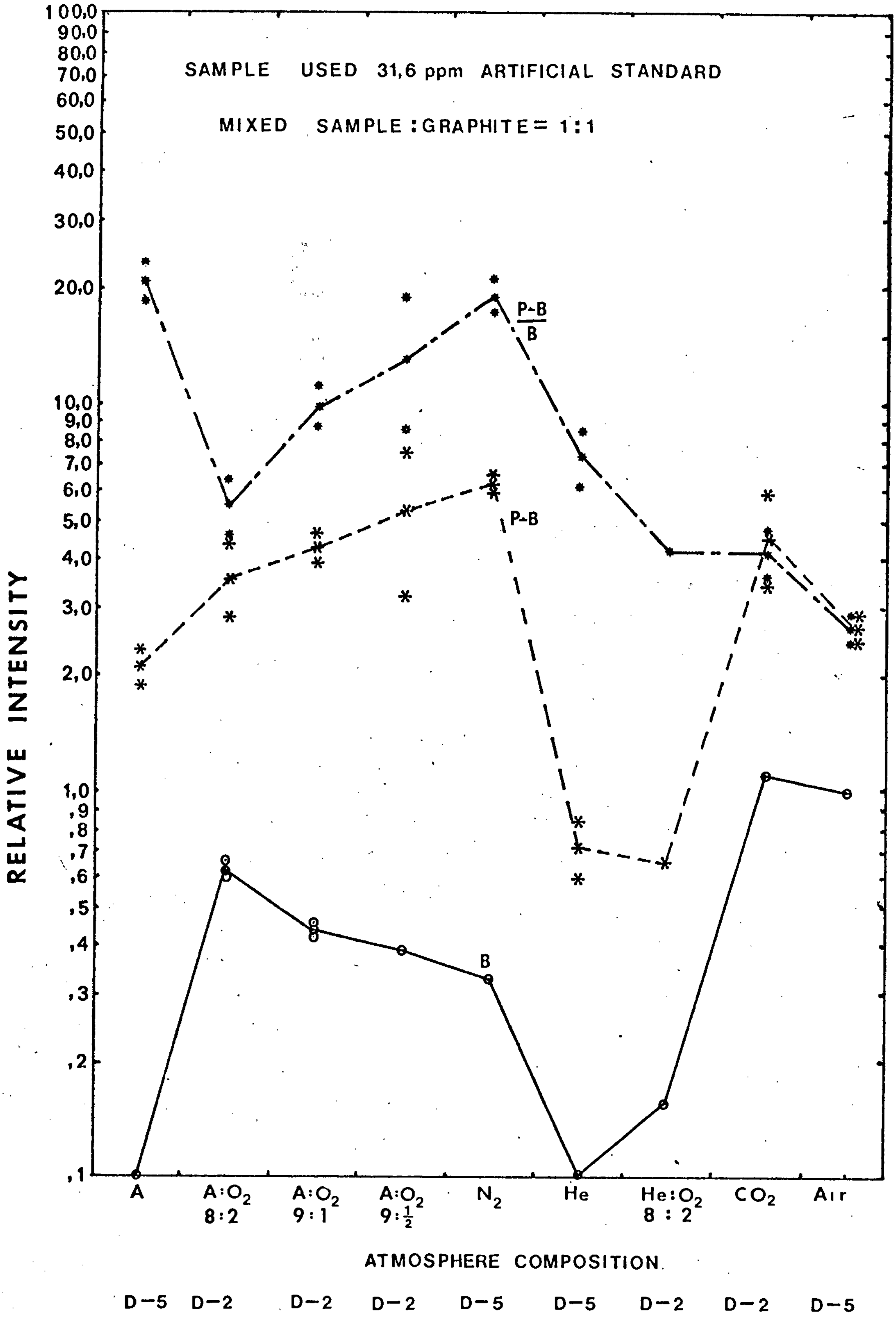
FIGURE 5



RELATIONSHIP BETWEEN $\frac{P-B}{B}$ RATIO & CONCENTRATION CONFIRMING DILUTIONS

FIGURE 6

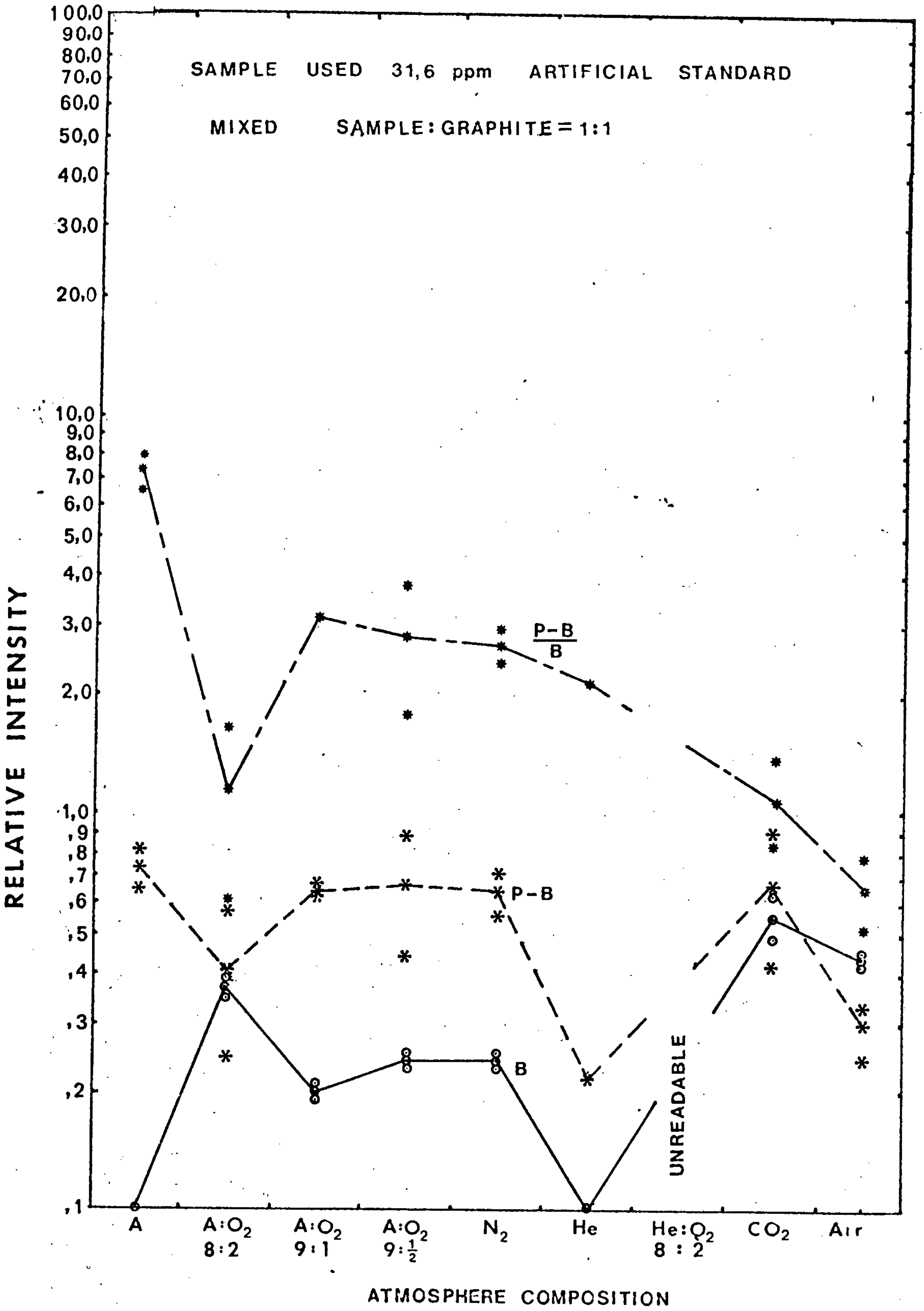
Bi 306,77 nm



COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ATMOSPHERES

FIGURE 7

Cd 326,11 nm

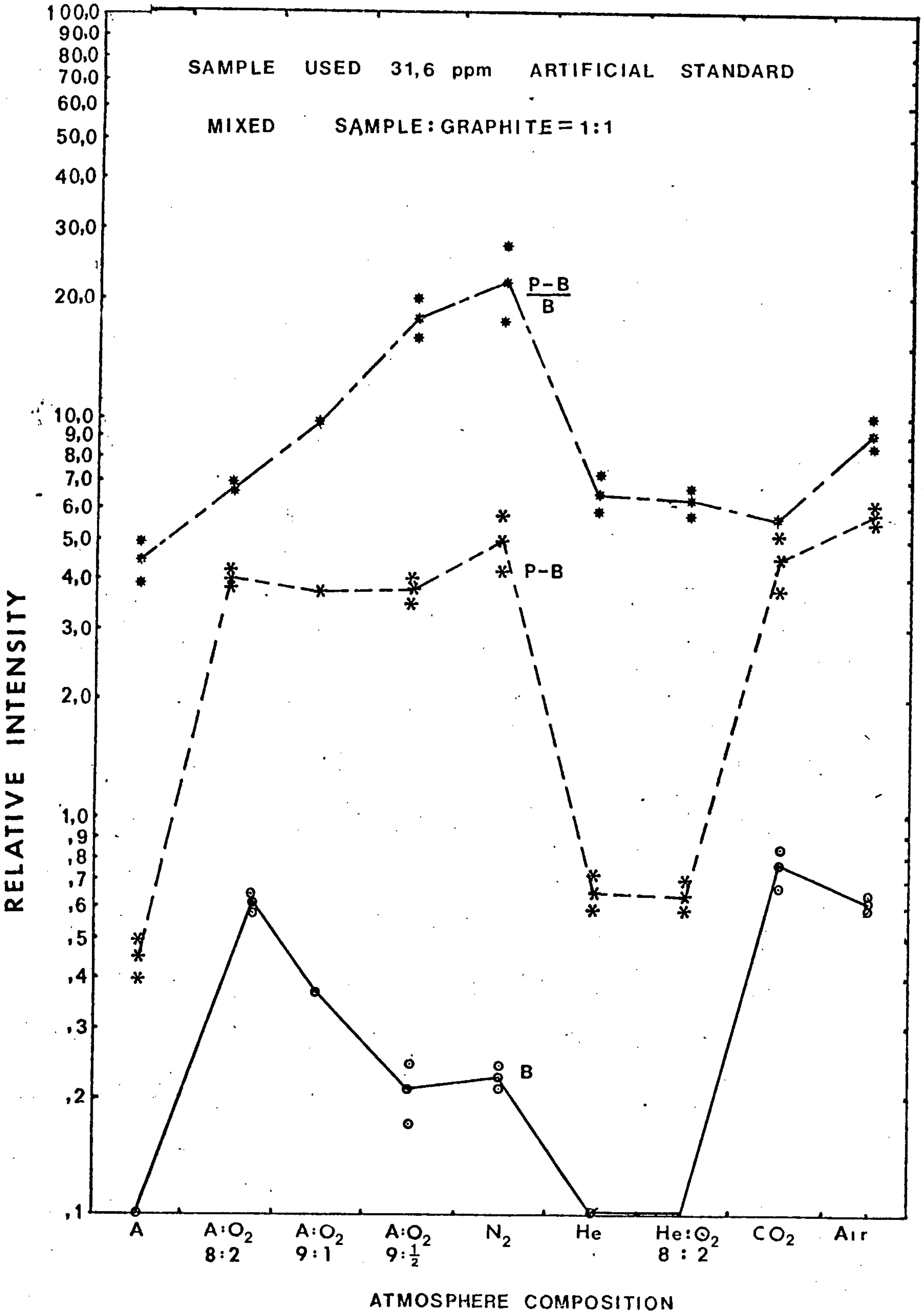


ELECTRODES AS DESIGNATED IN FIGURE 7

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ATMOSPHERES

FIGURE 8

Ga 294,36 nm

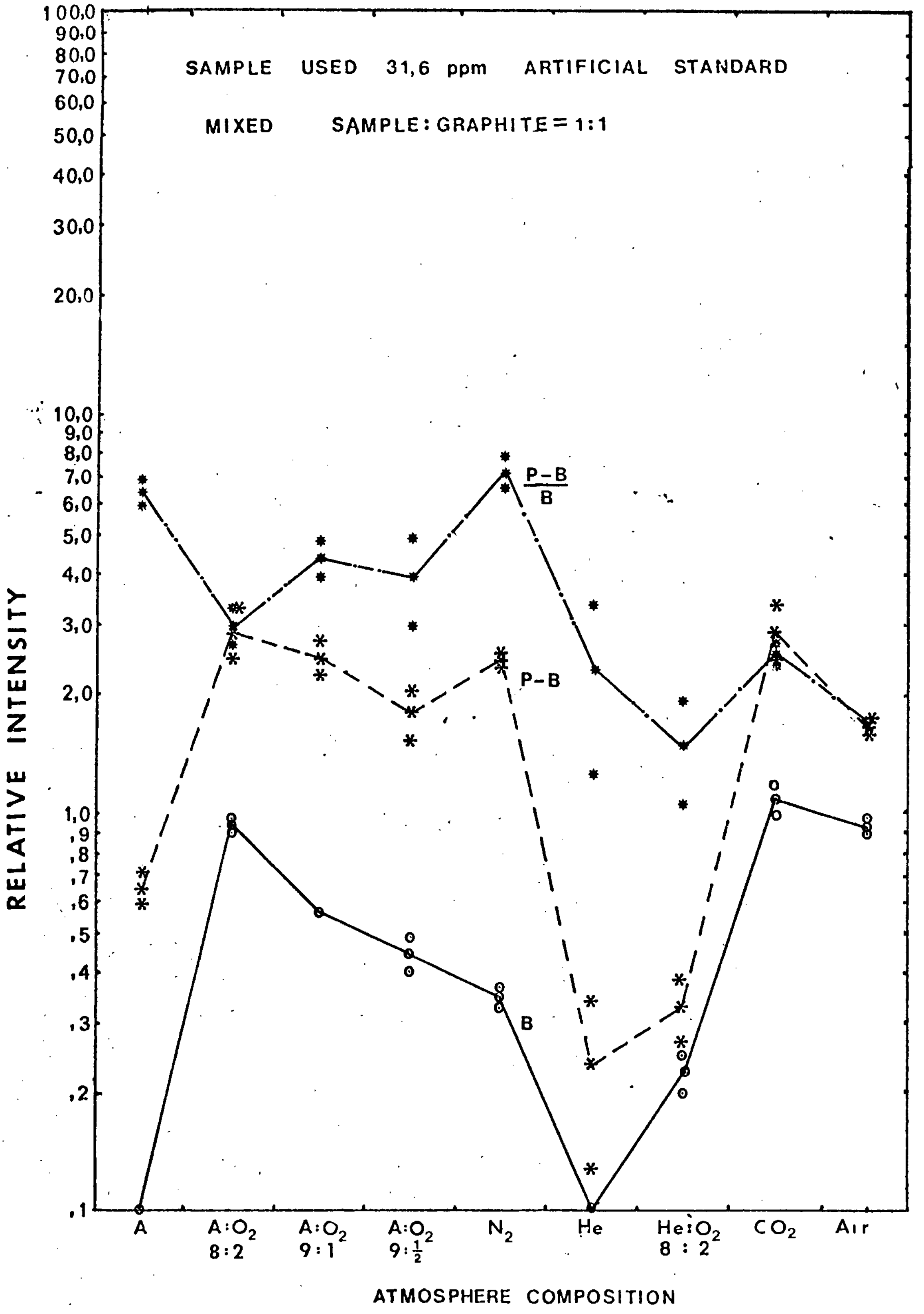


ELECTRODES AS DESIGNATED IN FIGURE 7

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ATMOSPHERES

FIGURE 9

Ge 303,91 nm

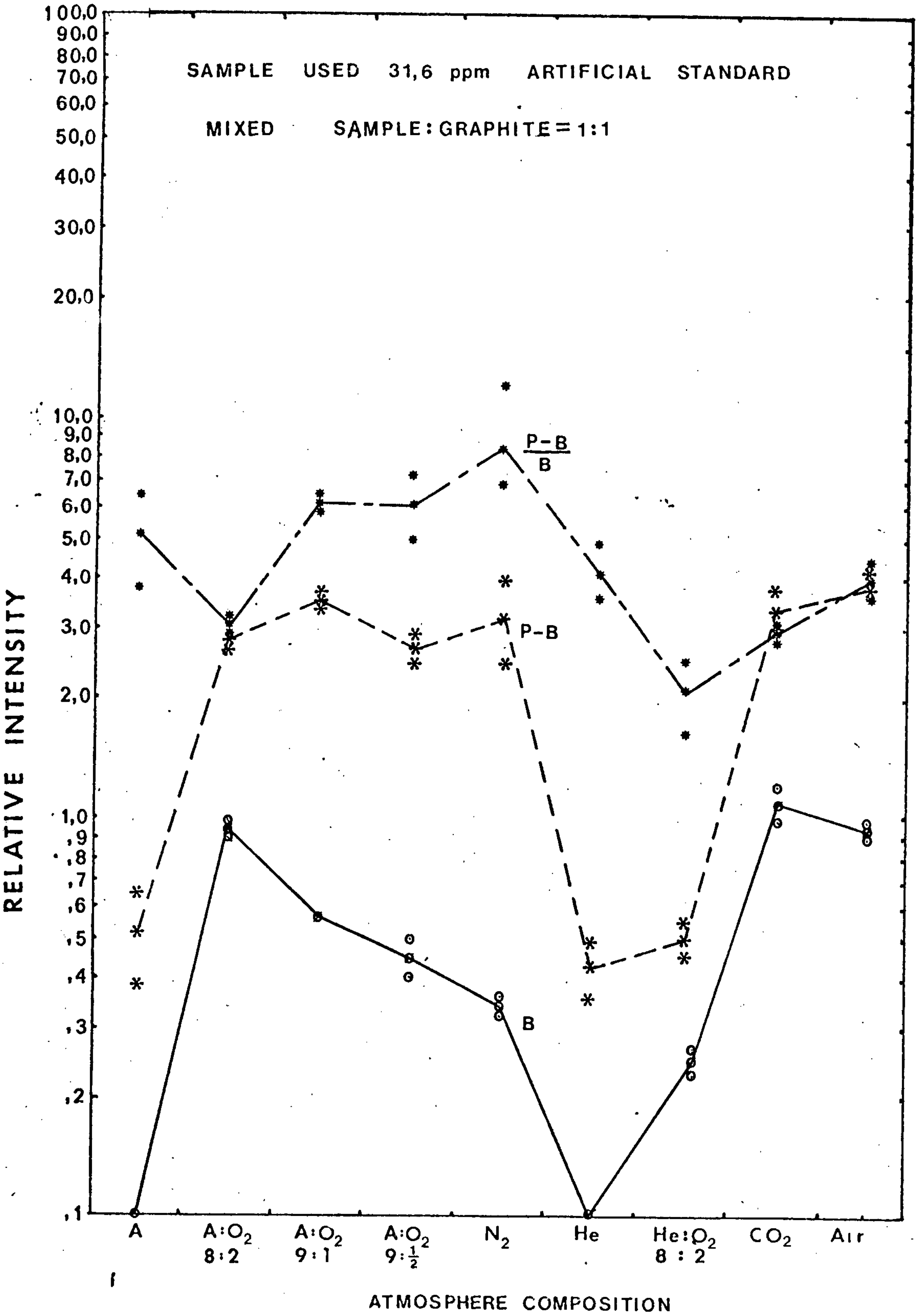


ELECTRODES AS DESIGNATED IN FIGURE 7

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ATMOSPHERES

FIGURE 10

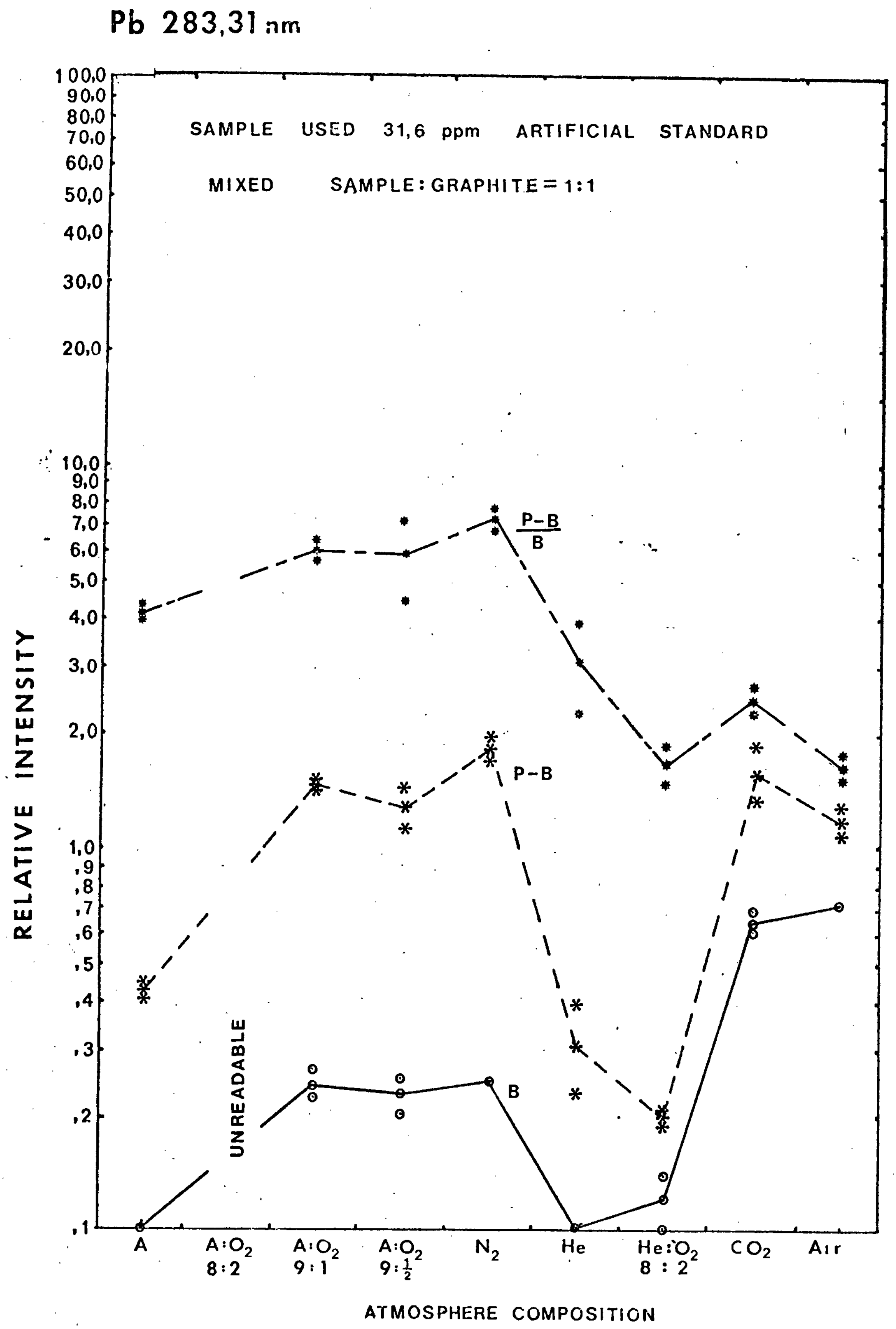
In 303,94 nm



ELECTRODES AS DESIGNATED IN FIGURE7

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ATMOSPHERES

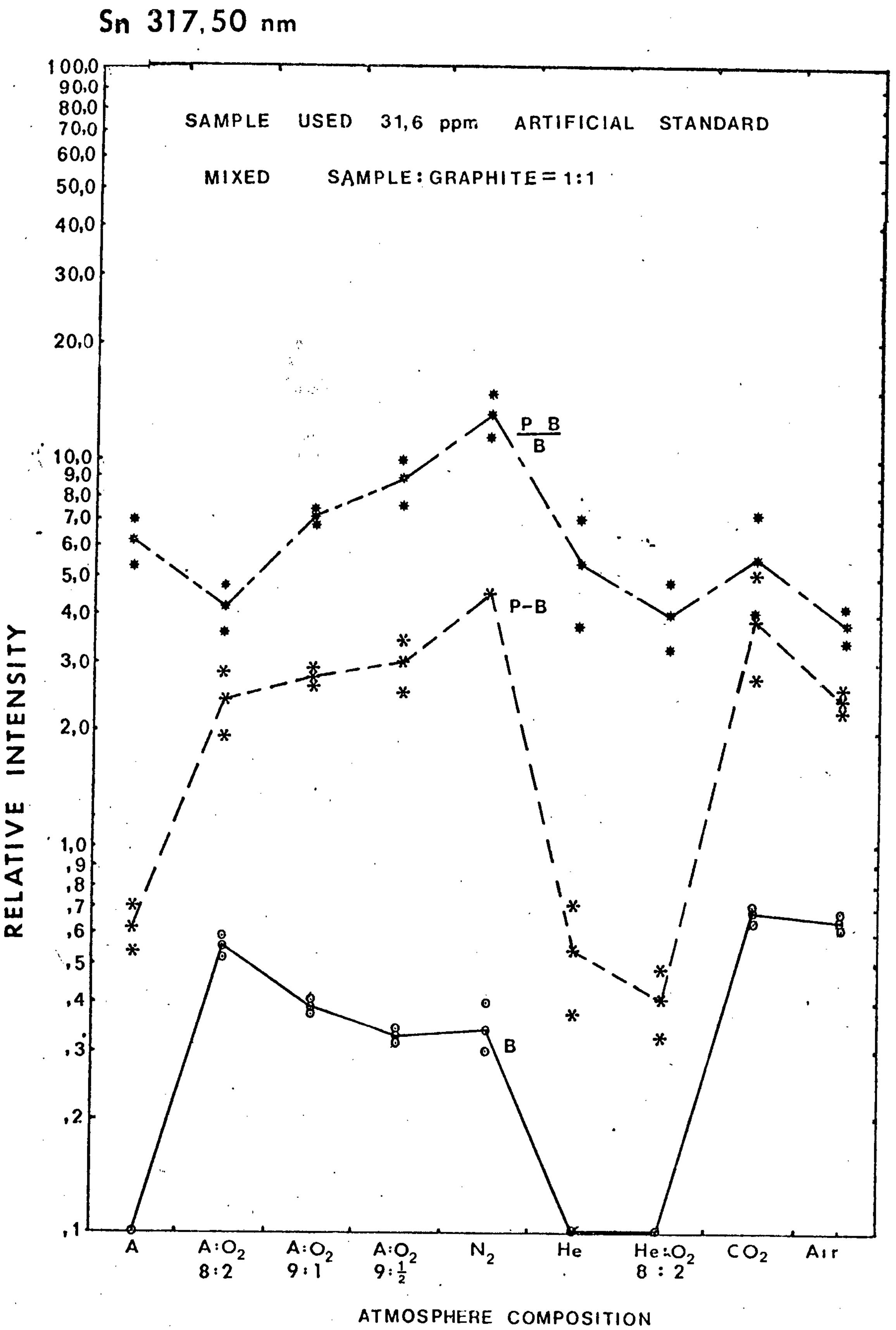
FIGURE 11



ELECTRODES AS DESIGNATED IN FIGURE 7

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ATMOSPHERES

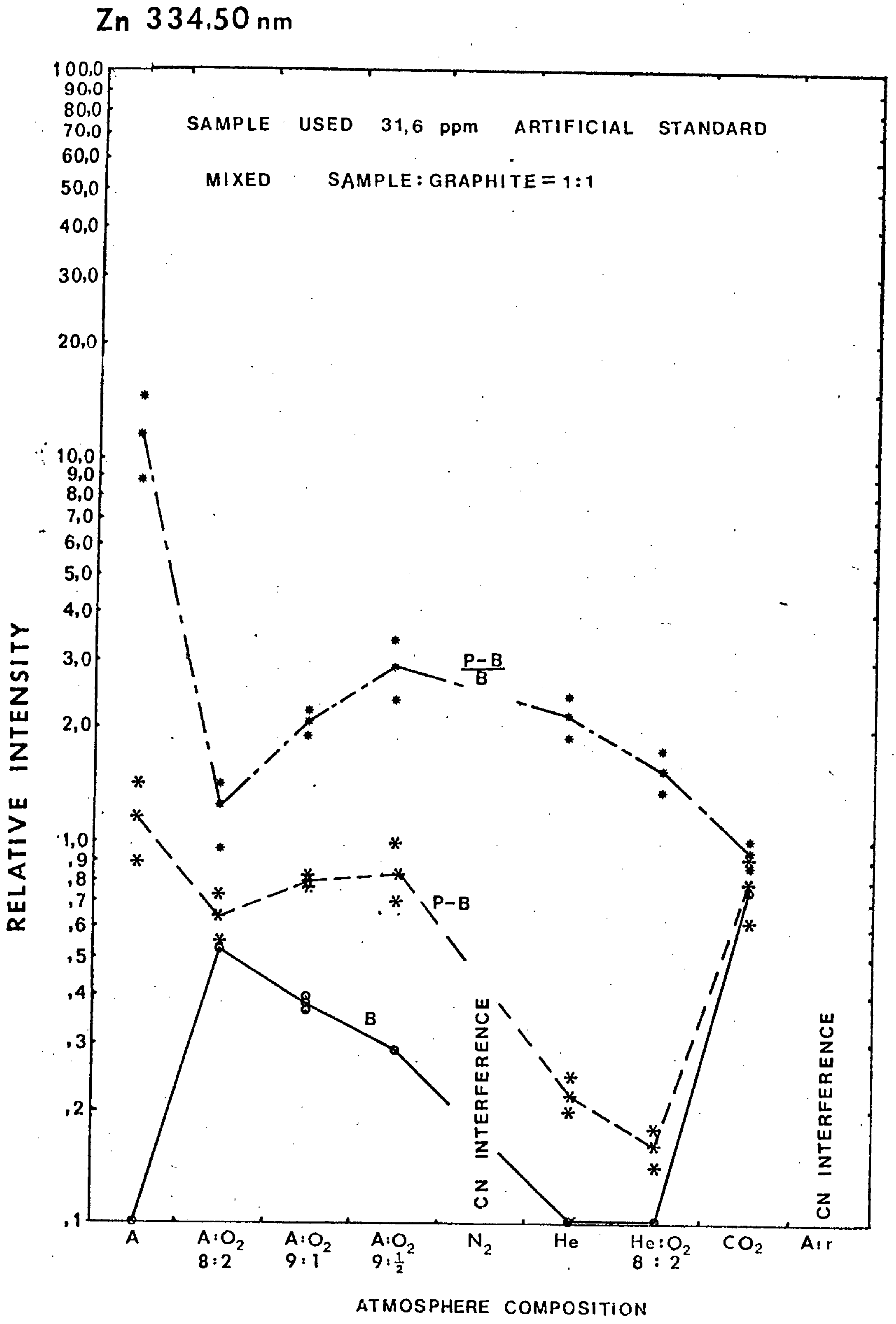
FIGURE 12



ELECTRODES AS DESIGNATED IN FIGURE 7

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ATMOSPHERES

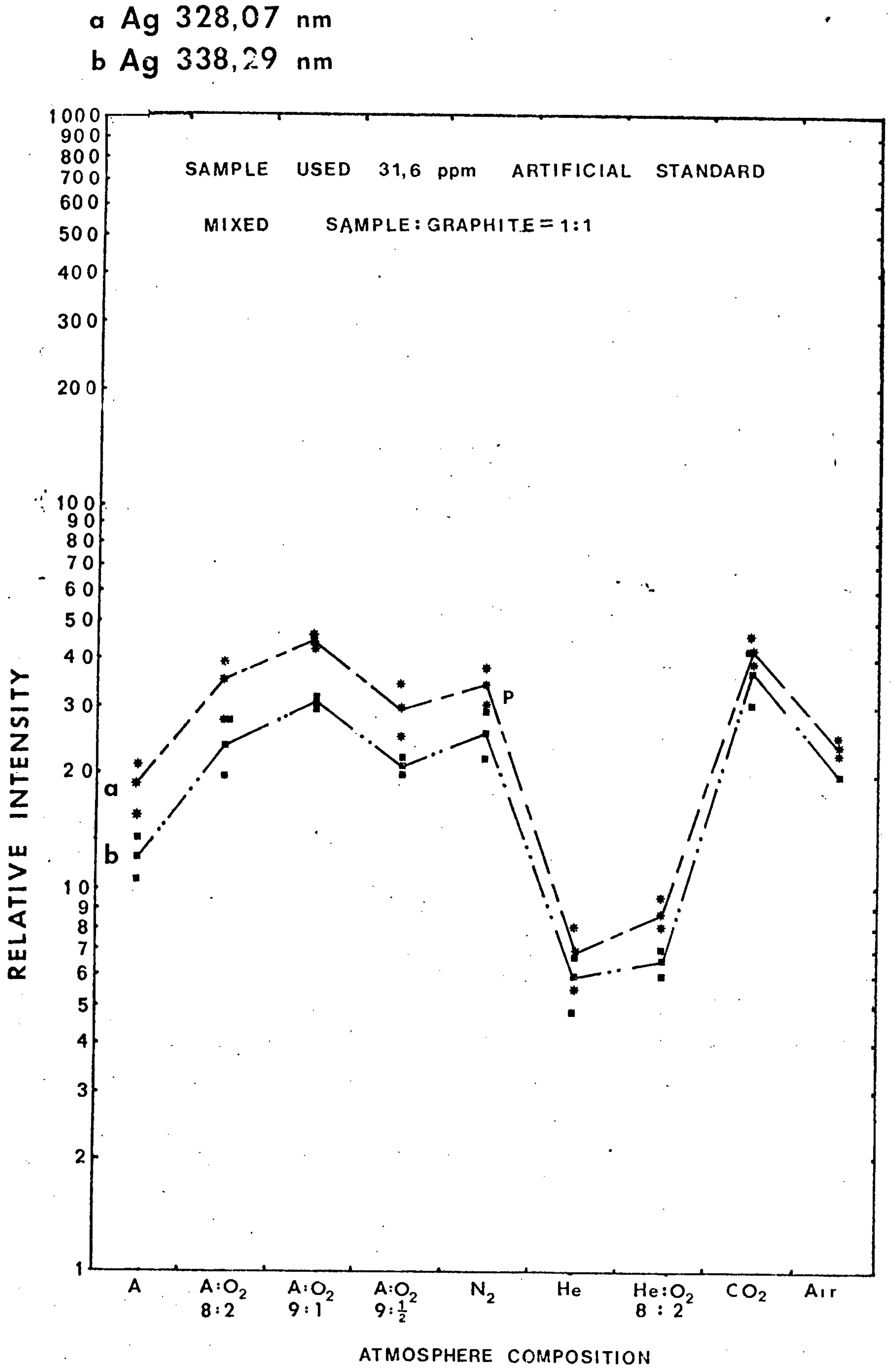
FIGURE 13



ELECTRODES AS DESIGNATED IN FIGURE 7

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ATMOSPHERES

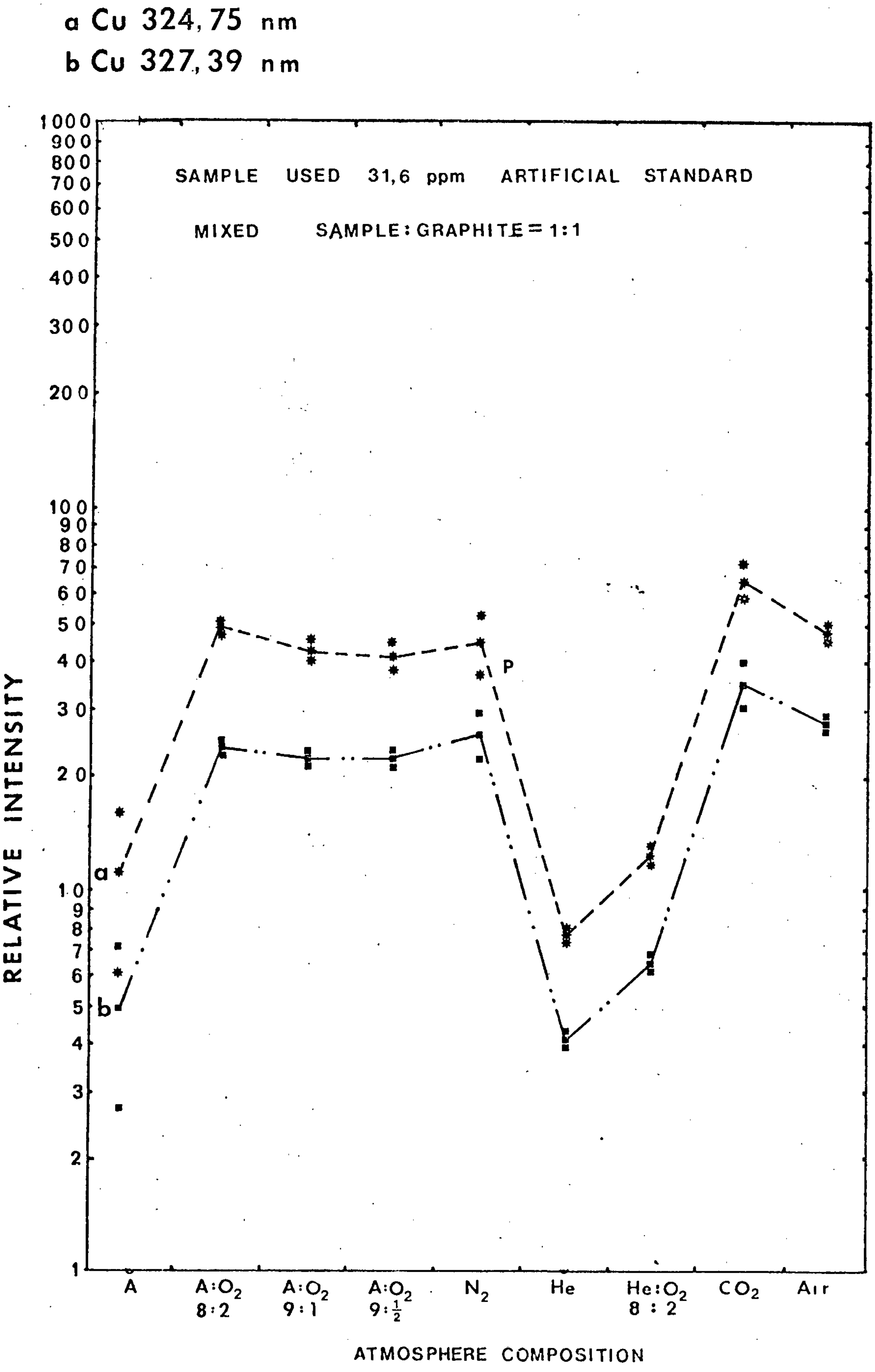
FIGURE 14



ELECTRODES AS DESIGNATED IN FIGURE 7

COMPARISON OF GROSS PEAKS (P) OBTAINED USING VARIOUS ATMOSPHERES

FIGURE 15

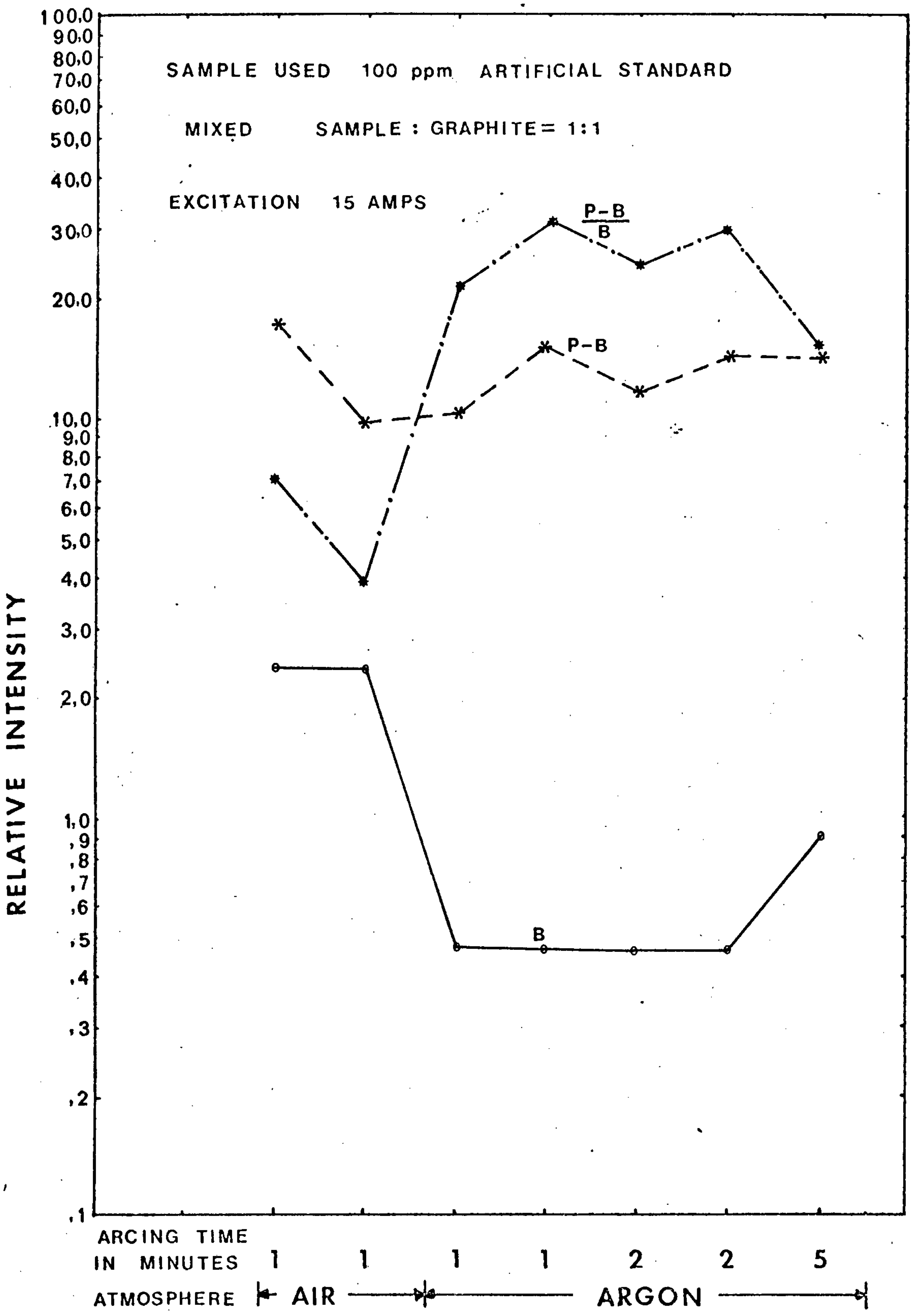


ELECTRODES AS DESIGNATED IN FIGURE 7

COMPARISON OF GROSS PEAKS (P) OBTAINED USING VARIOUS ATMOSPHERES

FIGURE 16

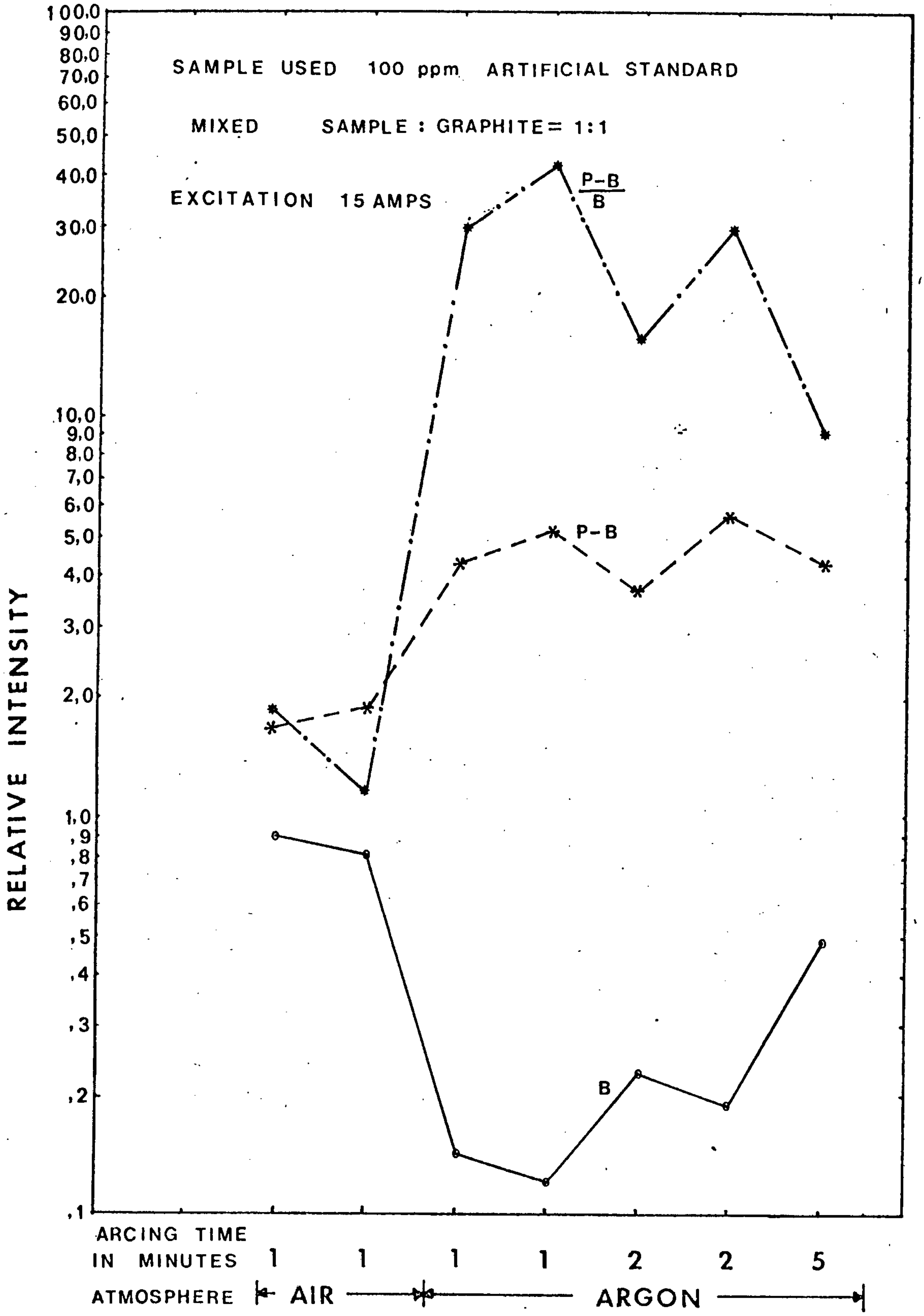
Bi 306,77 nm



COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ARCING TIMES IN ARGON

FIGURE 17

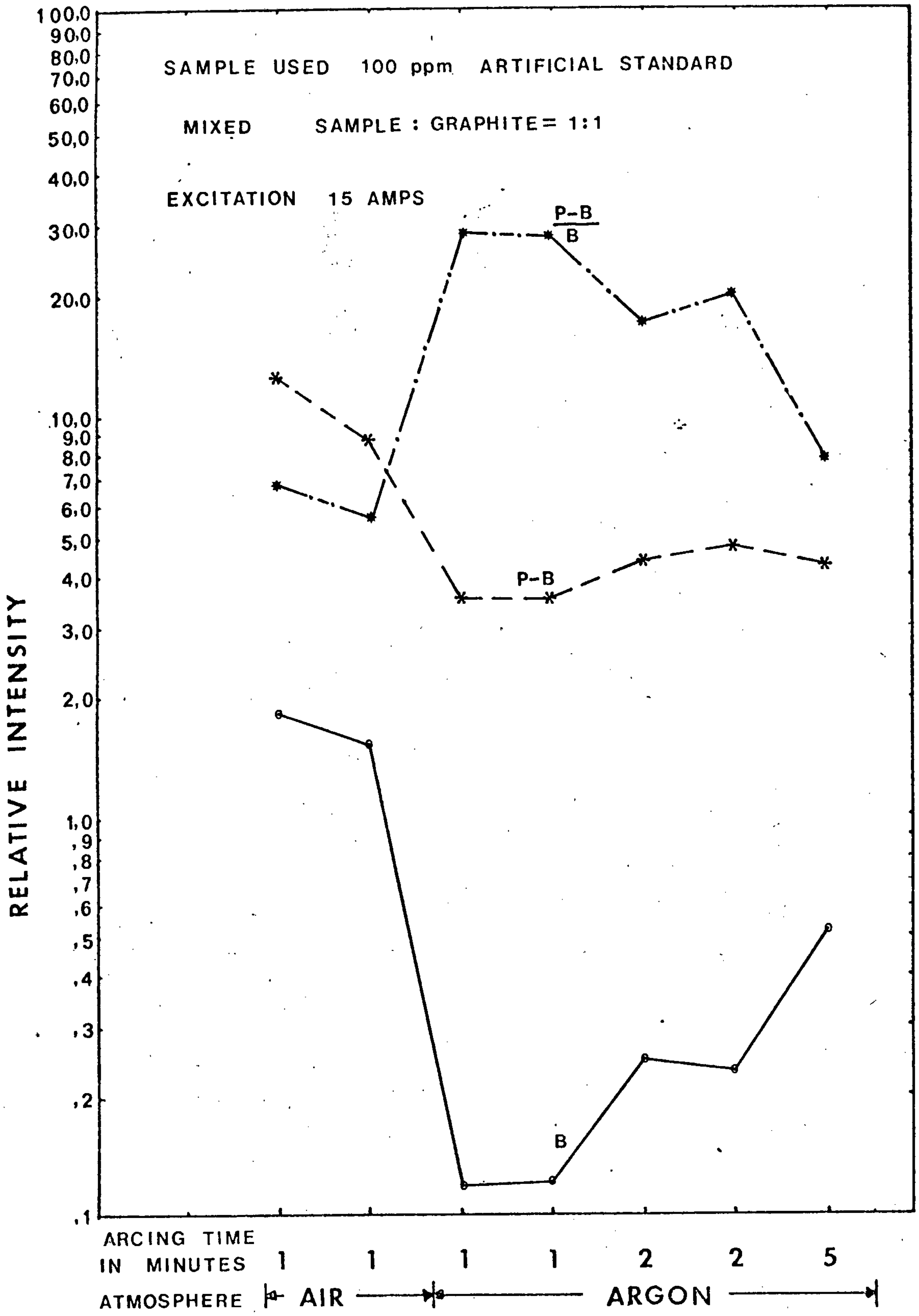
Cd 326,11 nm



COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ARCING TIMES IN ARGON

FIGURE 18

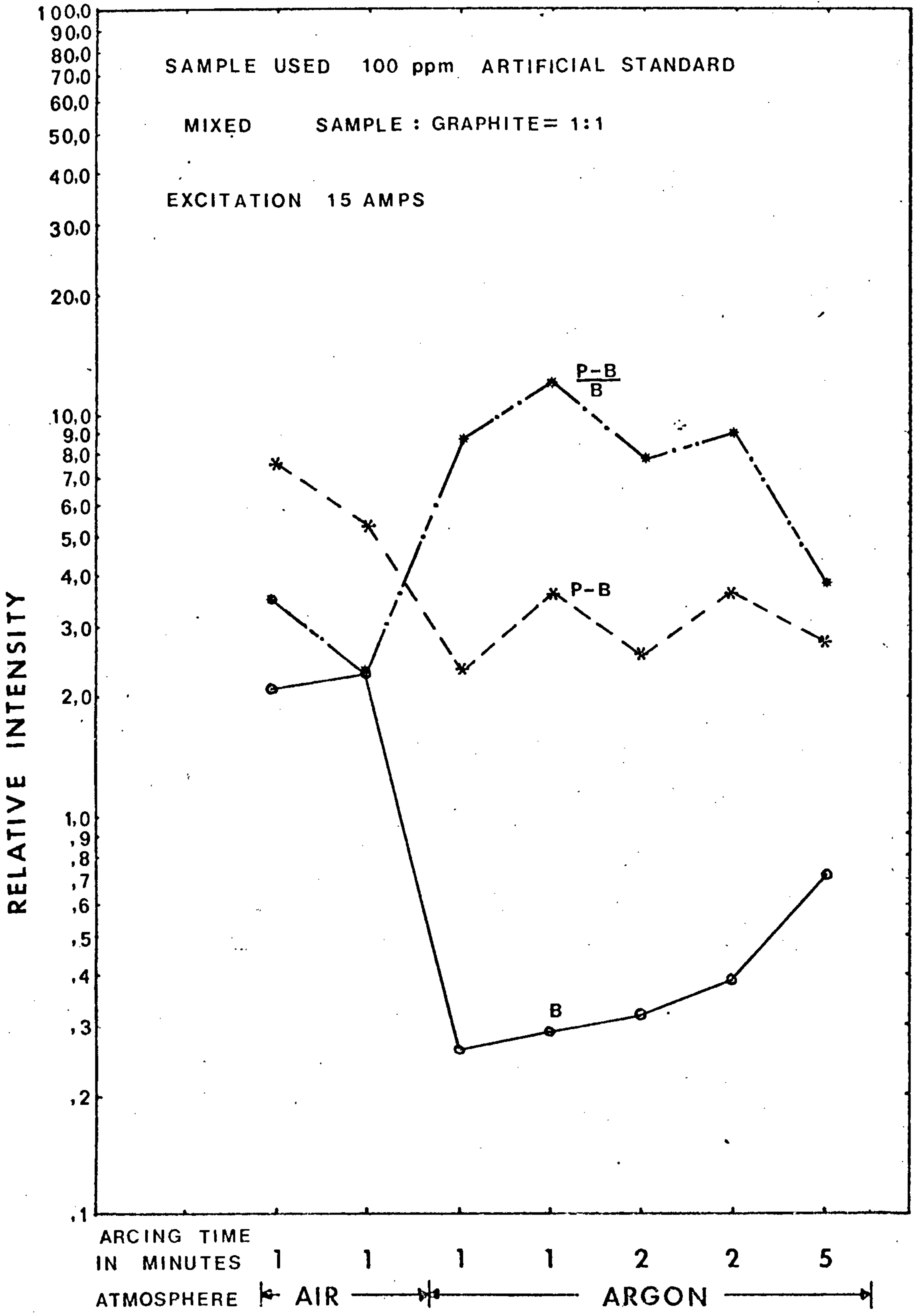
Ge 303,91 nm



COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ARCING TIMES IN ARGON

FIGURE 19

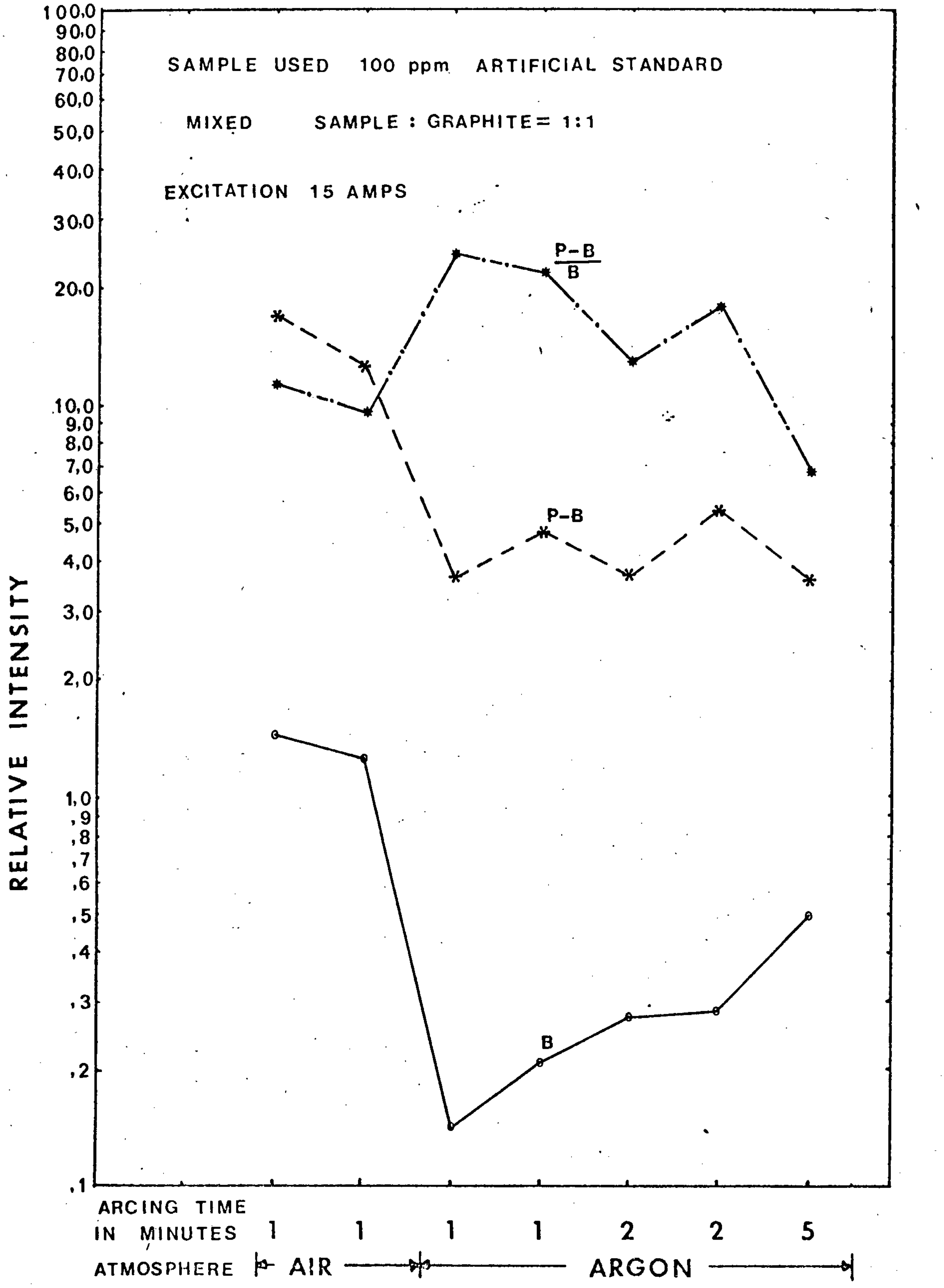
Pb 283,31 nm



COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ARCING TIMES IN ARGON

FIGURE 20

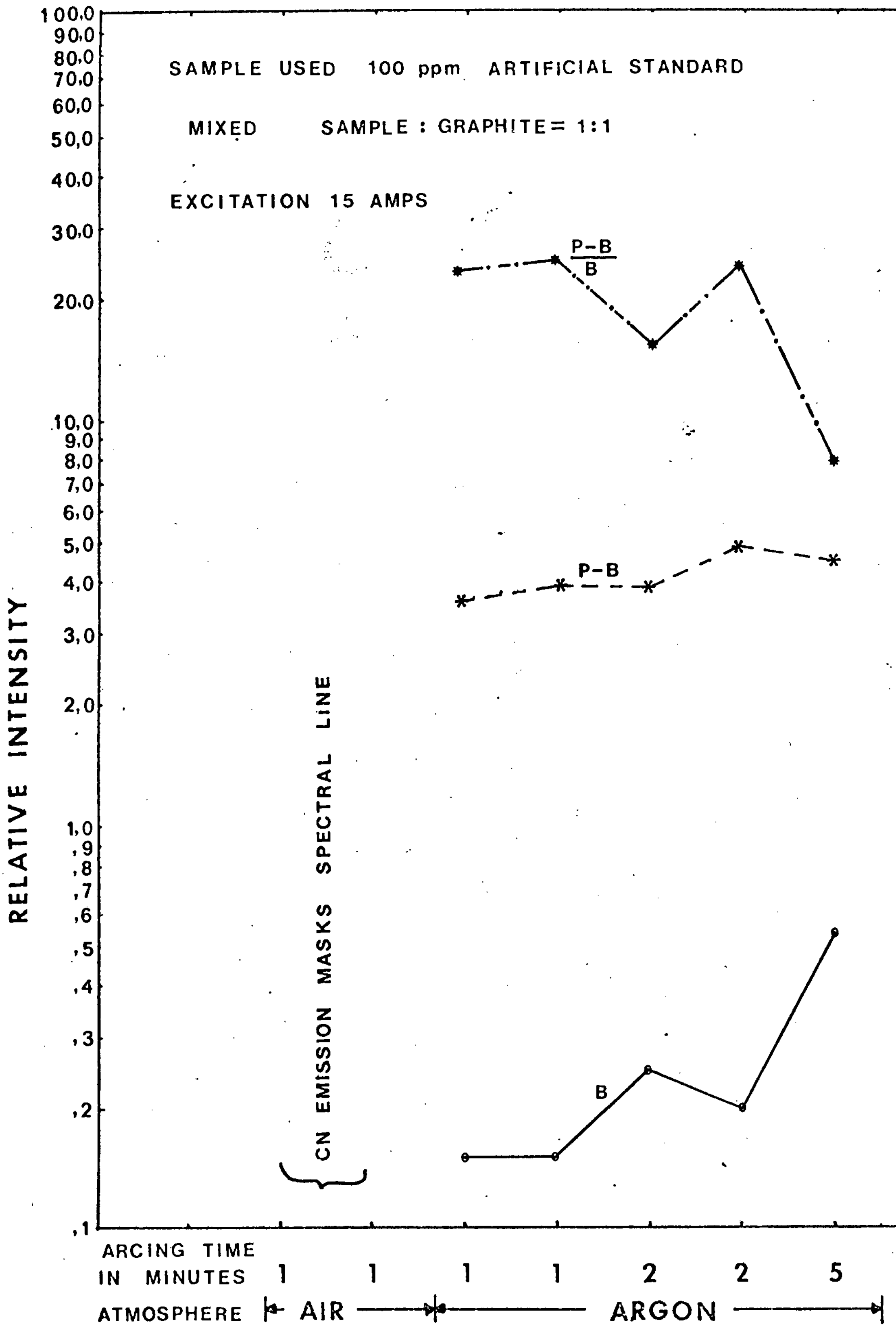
Sn 317,50 nm



COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ARCING TIMES IN ARGON

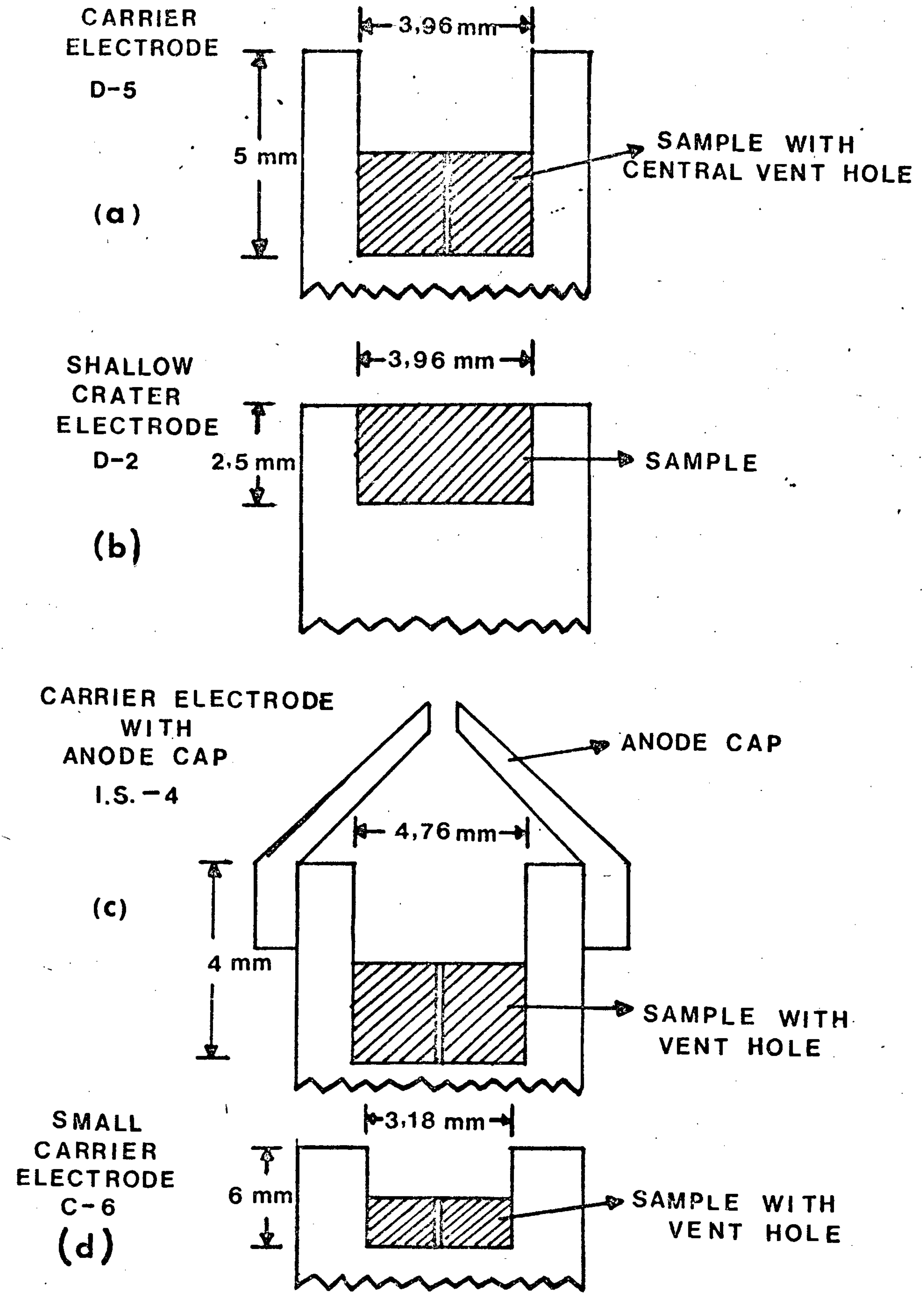
FIGURE 21

Zn 334,50 nm



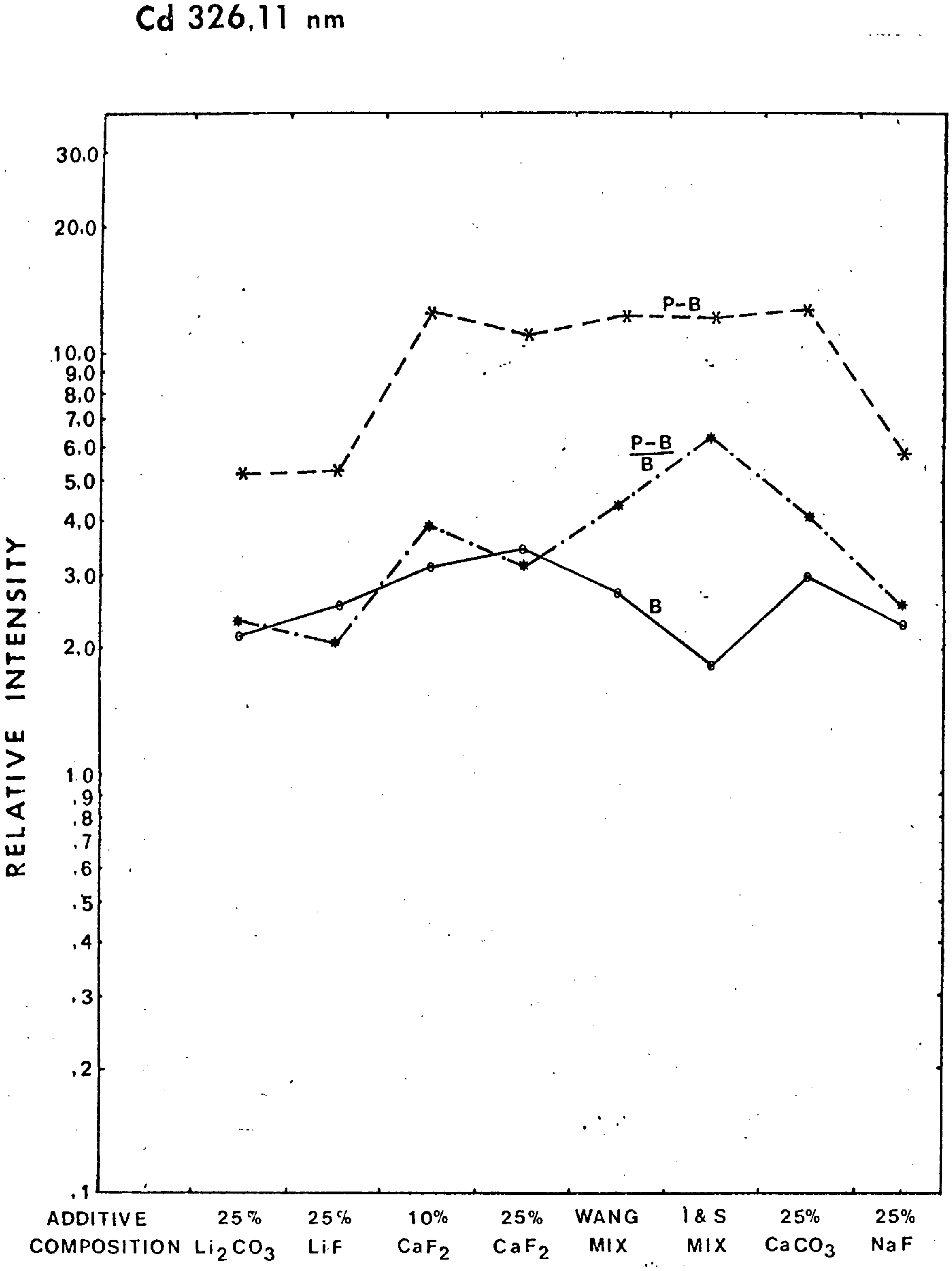
COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ARCING TIMES IN ARGON

FIGURE 22



ELECTRODE SHAPES & SIZES

FIGURE 23


Cd 326,11 nm

WANG MIX = 90% SAMPLE, 5% Li_2CO_3, 5% GRAPHITE

I & S MIX = 80% SAMPLE, 8% K_2SO_4, 12% GRAPHITE

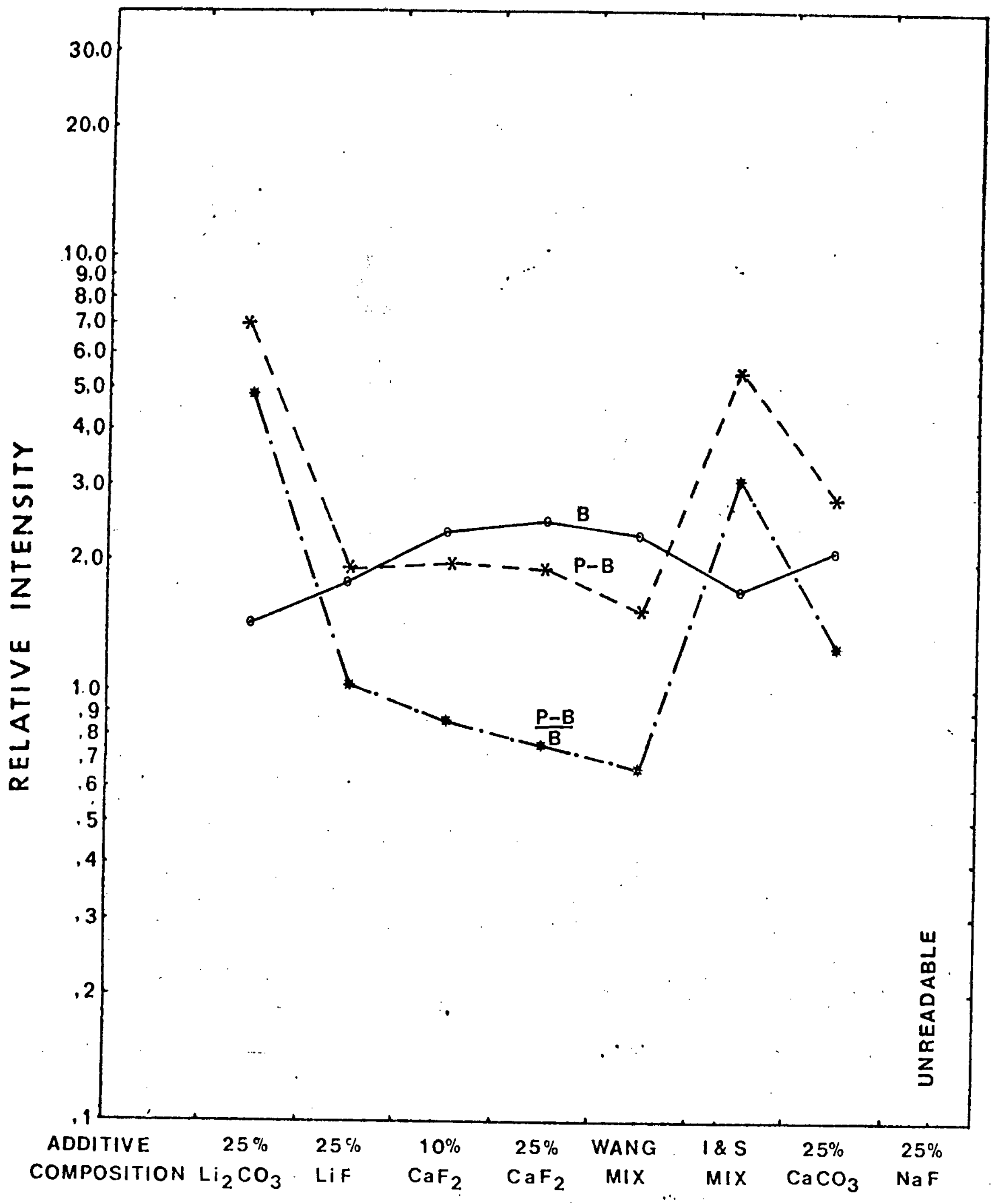
General Conditions

Sample	Bushveld Granite	Atmosphere	Argon
Electrode	Carrier 8mm deep	Excitation	15 amps

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ADDITIVE MIXTURES

FIGURE 24

Sn 317,50 nm



WANG MIX = 90% SAMPLE, 5% Li_2CO_3, 5% GRAPHITE

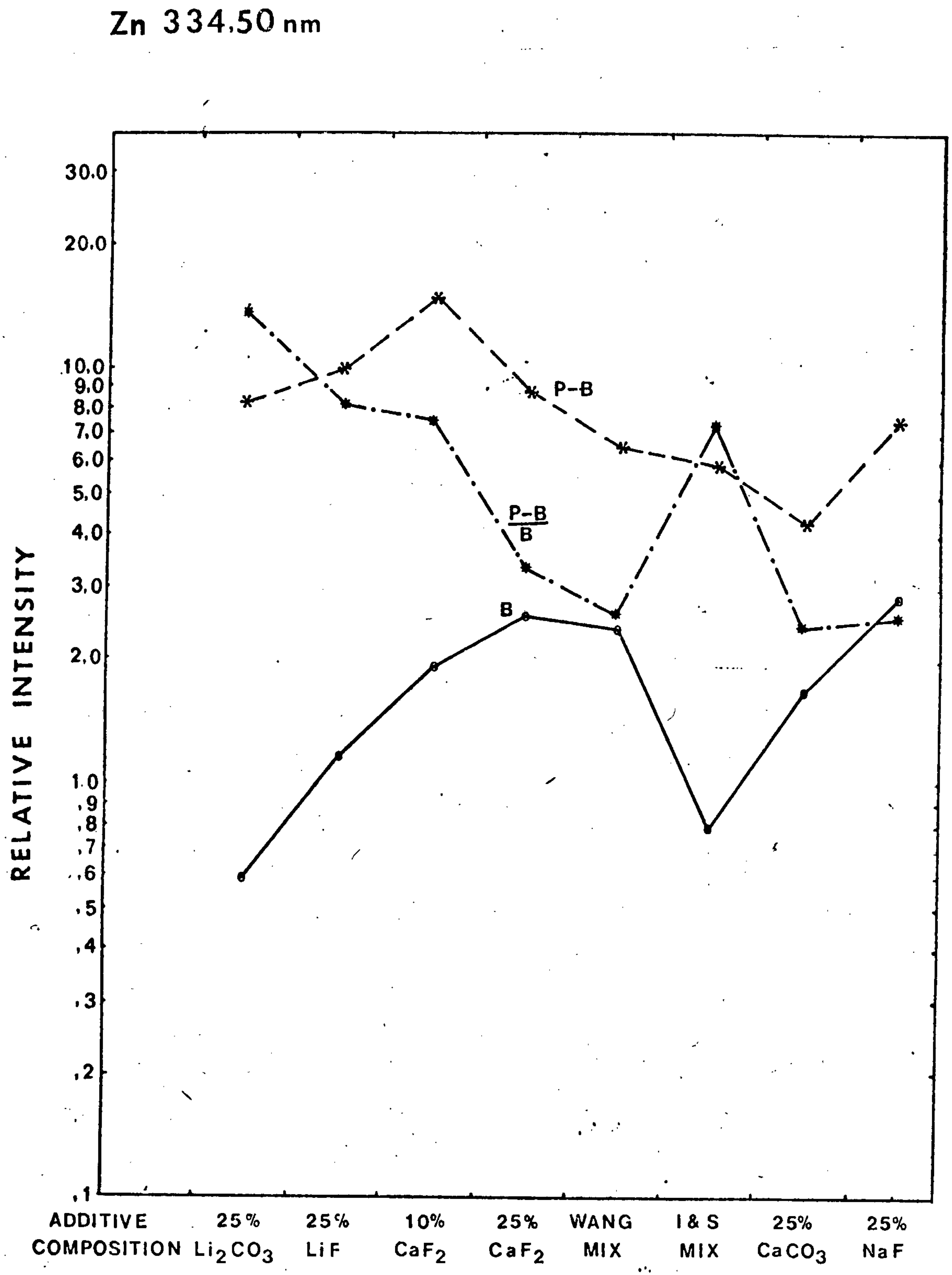
I & S MIX = 80% SAMPLE, 8% K_2SO_4, 12% GRAPHITE

General Conditions

Sample	Bushveld Granite	Atmosphere	Argon
Electrode	Carrier 8mm deep	Excitation	15 amps

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ADDITIVE MIXTURES

FIGURE 25


Zn 334.50 nm

WANG MIX = 90% SAMPLE, 5% Li_2CO_3, 5% GRAPHITE

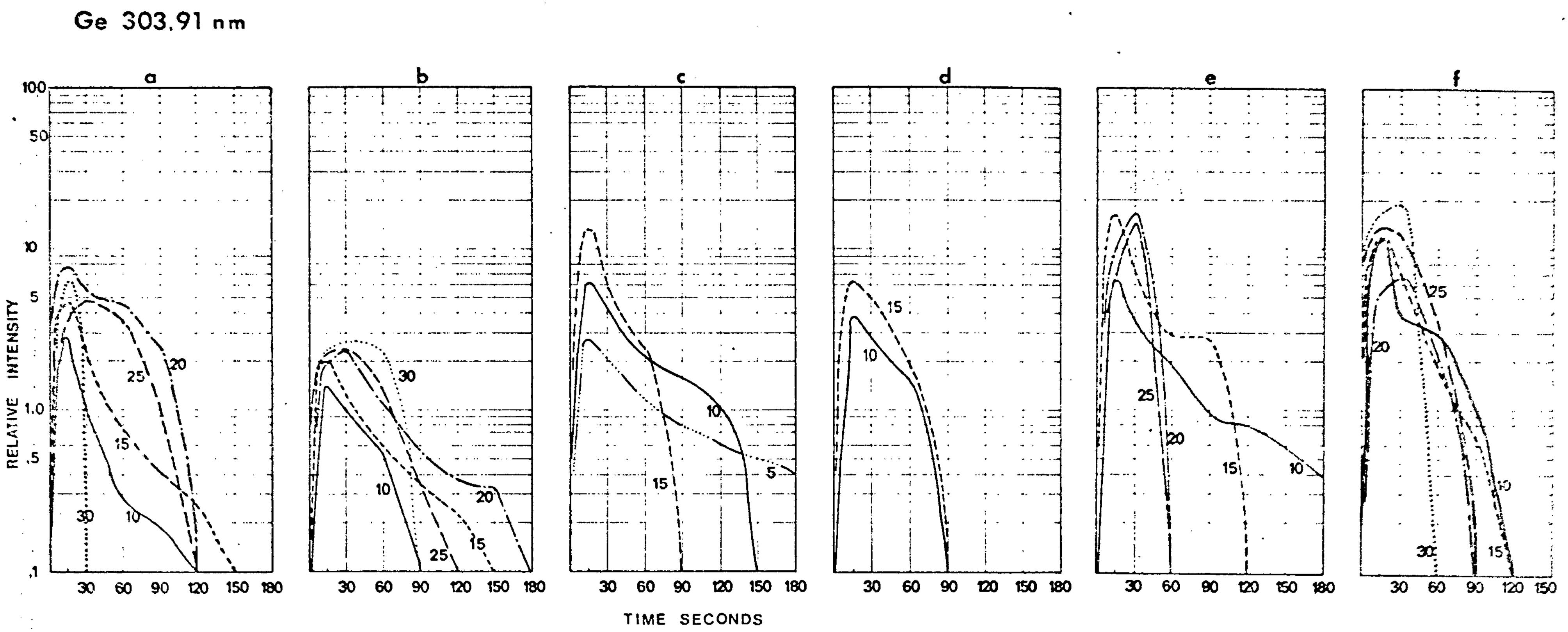
I & S MIX = 80% SAMPLE, 8% K_2SO_4, 12% GRAPHITE

General Conditions

Sample	Bushveld Granite	Atmosphere	Argon
Electrode	Carrier 8mm deep	Excitation	15 amps

COMPARISON OF NETT PEAK TO BACKGROUND RATIO $\left(\frac{P-B}{B}\right)$ NETT PEAK (P-B) & BACKGROUND (B) FOR VARIOUS ADDITIVE MIXTURES

FIGURE 26



MOVING PLATE STUDY AT VARIOUS AMPERAGES

AMPERAGE LEGEND	
5 AMPS	——·········——
10 AMPS	————————
15 AMPS	- - - - - - -
20 AMPS	—·—·—·—
25 AMPS	— — — —
30 AMPS	···········

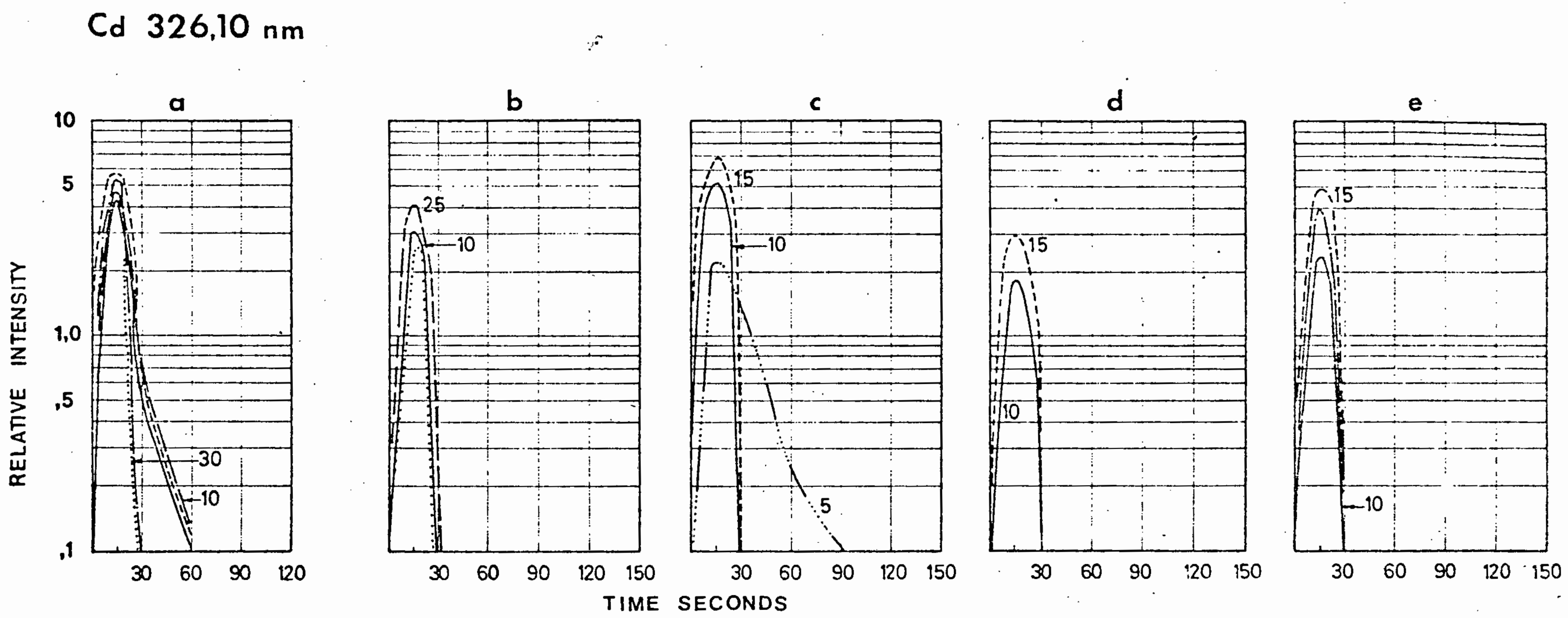
	ADDITIVE	ATMOSPHERE
a	20:2:3	ARGON
b	1:1	ARGON
c	20:2:3	ARGON-OXYGEN
d	1:1	ARGON-OXYGEN
e	20:2:3	NITROGEN
f	1:1	NITROGEN

ADDITIVE LEGEND

$20:2:3 =$ 80 % SAMPLE, 8 % K_2SO_4, 12 % GRAPHITE

$1:1 =$ 50 % SAMPLE, 50 % GRAPHITE

FIGURE 27



MOVING PLATE STUDY AT VARIOUS AMPERAGES

AMPERAGE LEGEND
5 AMPS ——⋯⋯——
10 AMPS ————
15 AMPS - - - - - - -
20 AMPS —·—·—·—
25 AMPS — — — —
30 AMPS ⋯⋯⋯⋯⋯

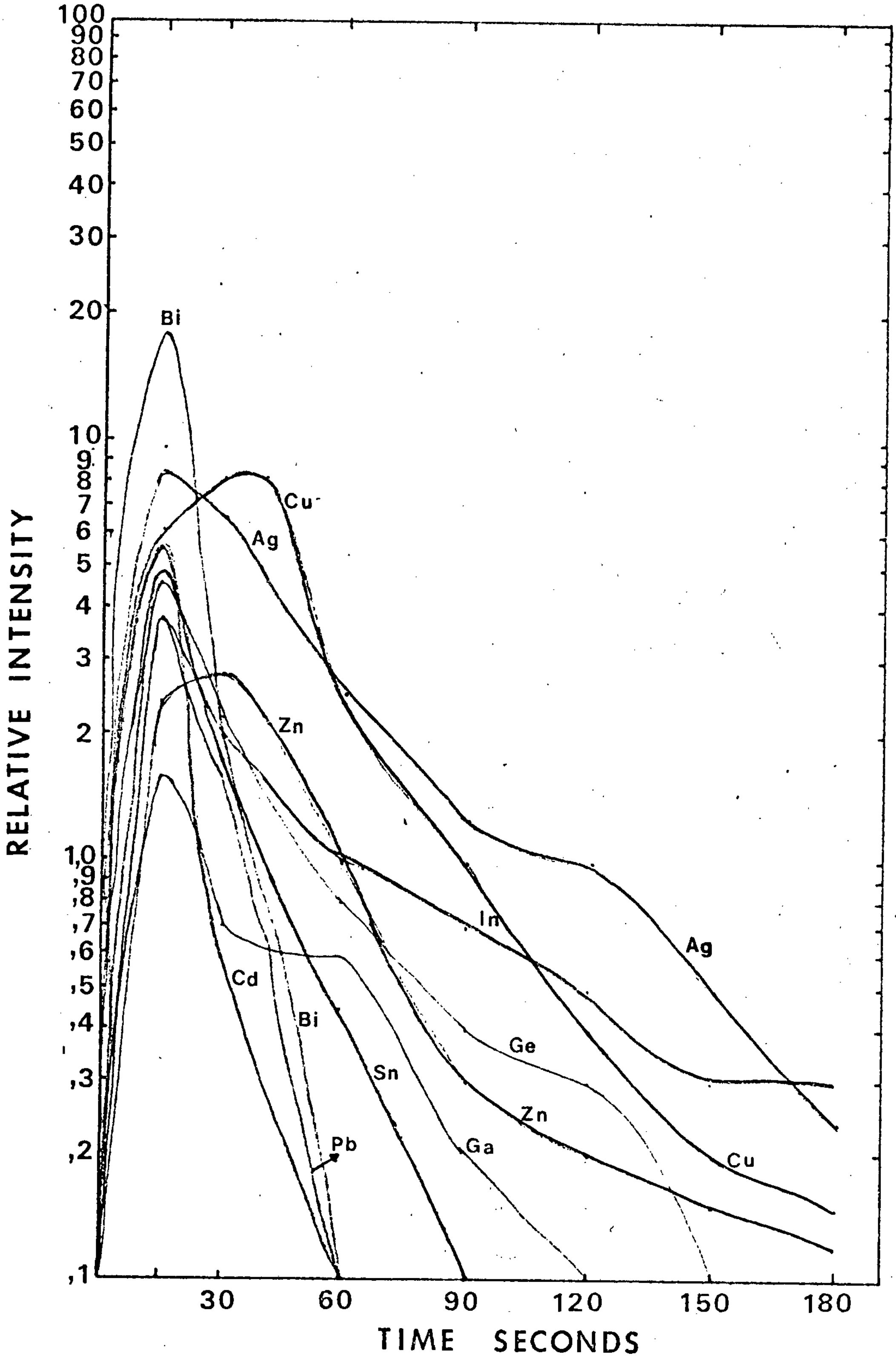
	ADDITIVE	ATMOSPHERE
a	20:2:3	ARGON
b	1:1	ARGON
c	20:2:3	ARGON - OXYGEN
d	1:1	ARGON - OXYGEN
e	20:2:3	NITROGEN
f	1:1	NITROGEN

ADDITIVE LEGEND

20 : 2 : 3 = 80 % SAMPLE, 8 % K_2SO_4, 12 % GRAPHITE

1 : 1 = 50 % SAMPLE, 50 % GRAPHITE

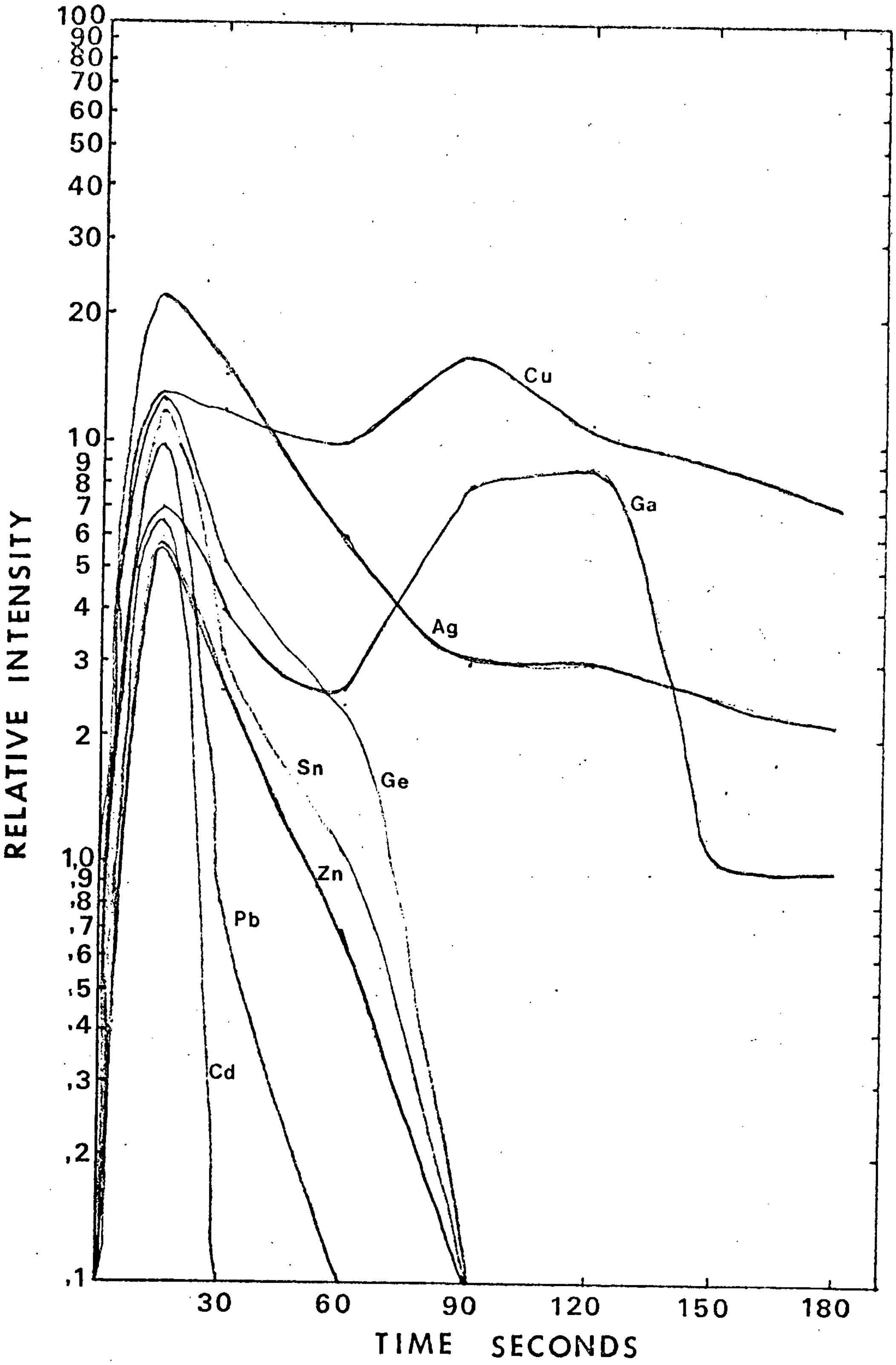
FIGURE 28



COMPOSITE MOVING PLATE STUDY

ARGON	ATMOSPHERE
EXCITATION	15 AMPS
ELECTRODE	D-5 CARRIER
ADDITIVE	8% K_2SO_4 12% GRAPHITE

FIGURE 29



COMPOSITE MOVING PLATE STUDY

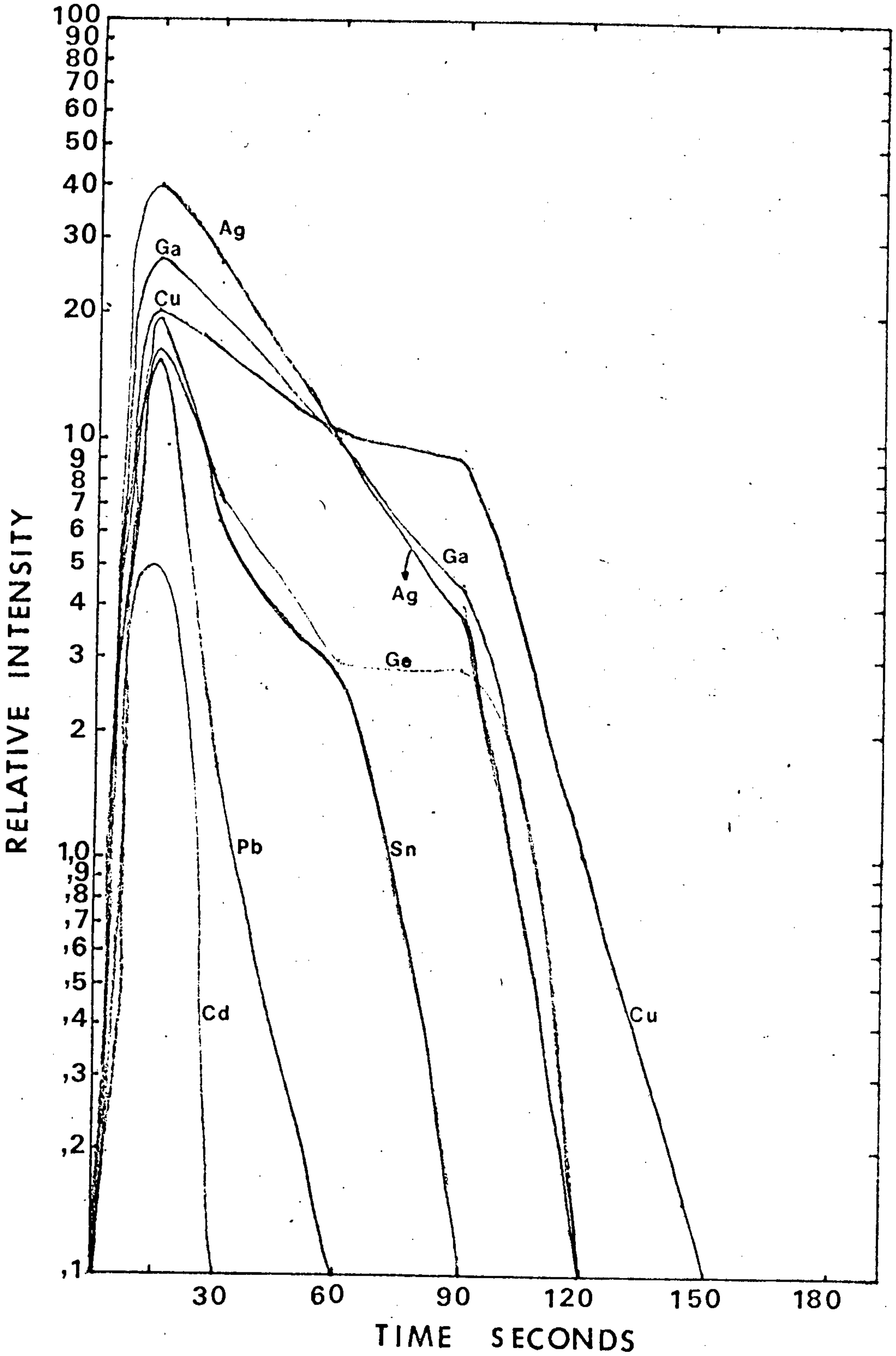
ARGON-OXYGEN ATMOSPHERE

EXCITATION 15 AMPS

ELECTRODE D-5 CARRIER

ADDITIVE 8% K_2SO_4 12% GRAPHITE

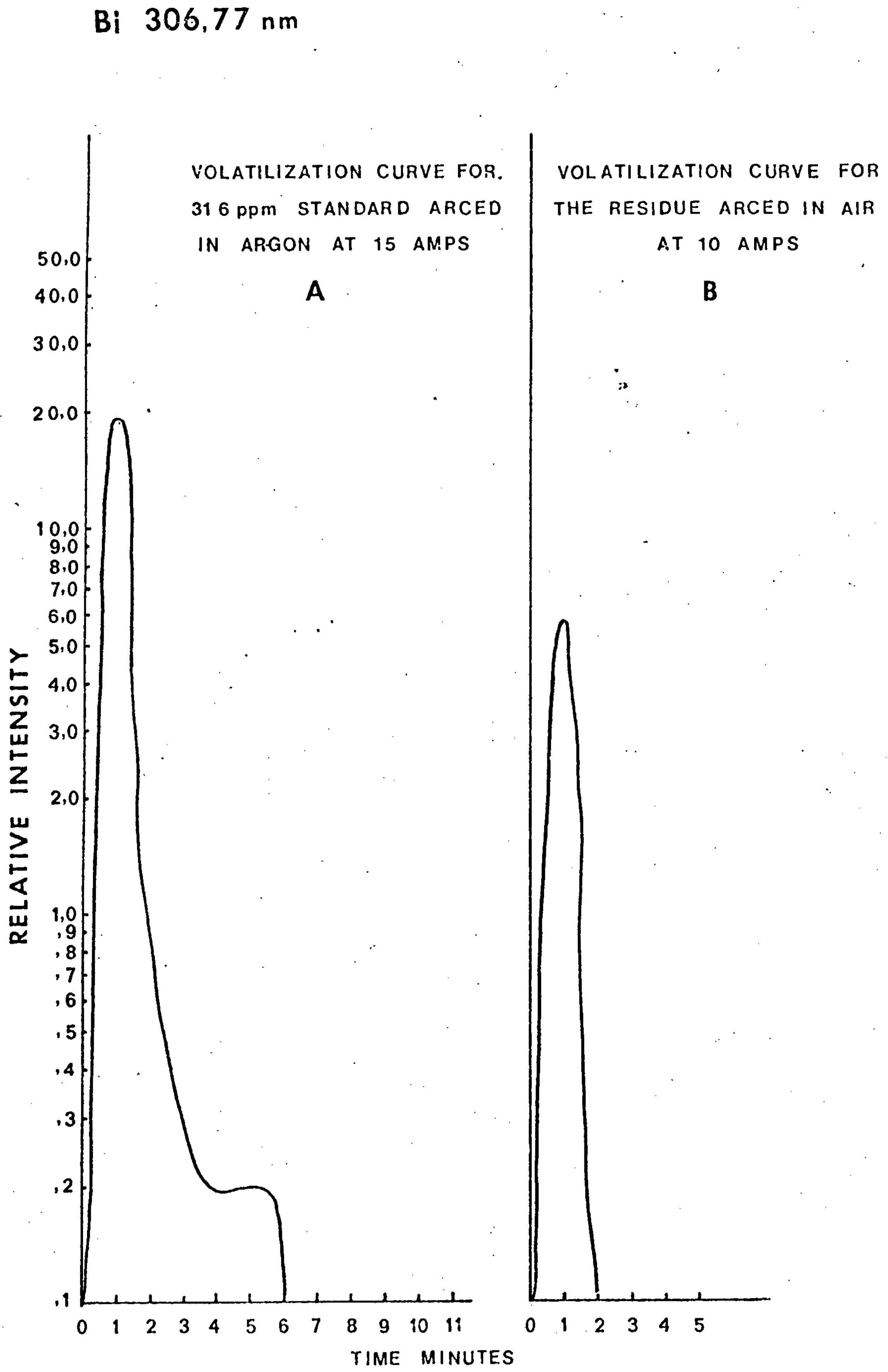
FIGURE 30



COMPOSITE MOVING PLATE STUDY

NITROGEN ATMOSPHERE
EXCITATION 15 AMPS
ELECTRODE D-5 CARRIER
ADDITIVE 8% K_2SO_4 12% GRAPHITE

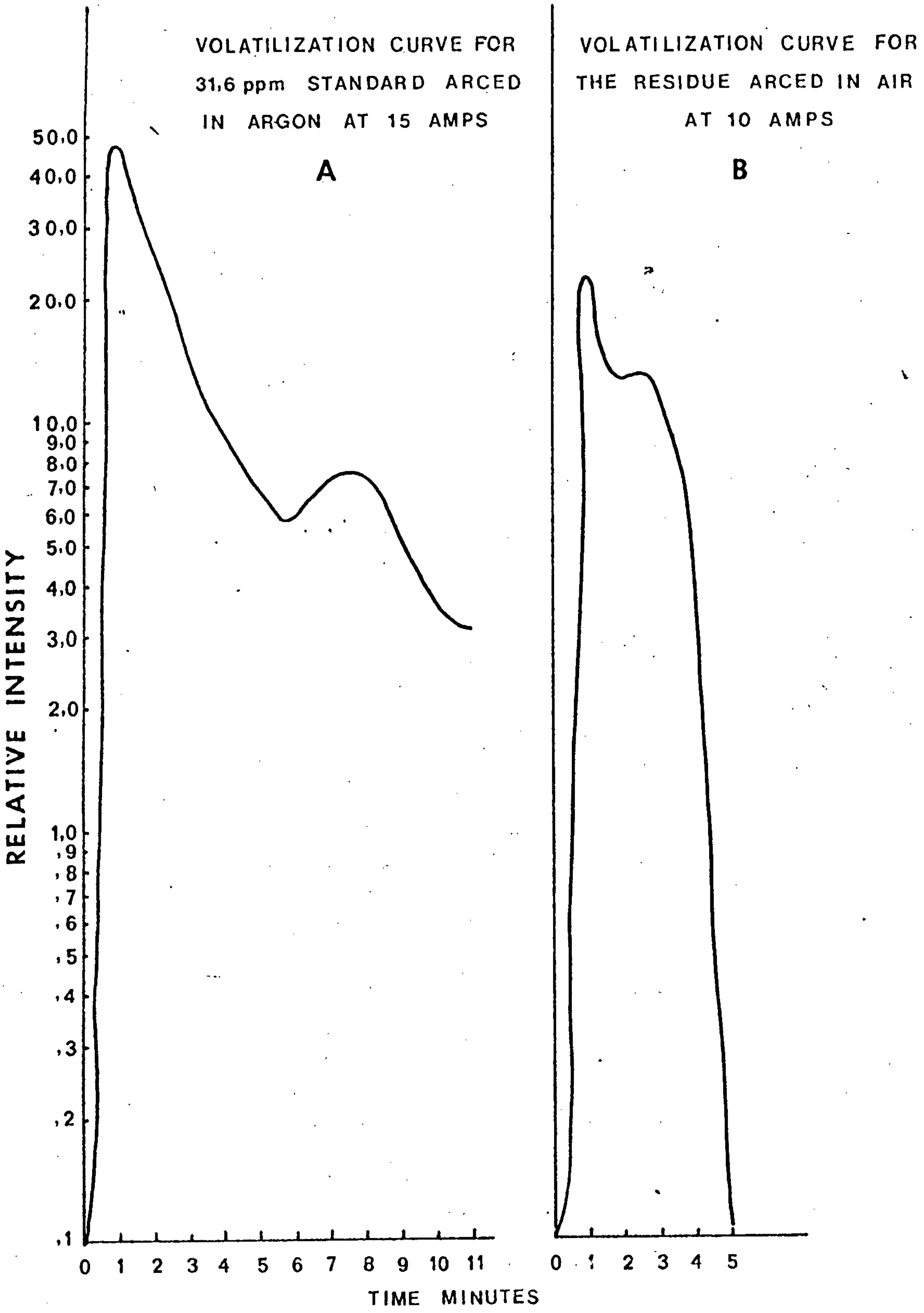
FIGURE 31



EVIDENCE OF ELEMENT RETENTION DUE TO CARBIDE FORMATION
CURVE 'A' ILLUSTRATES ELEMENT VOLATILIZATION FROM SAMPLE
CURVE 'B' ILLUSTRATES ELEMENT RECOMMENCING ITS
VOLATILIZATION FROM THE RESIDUE

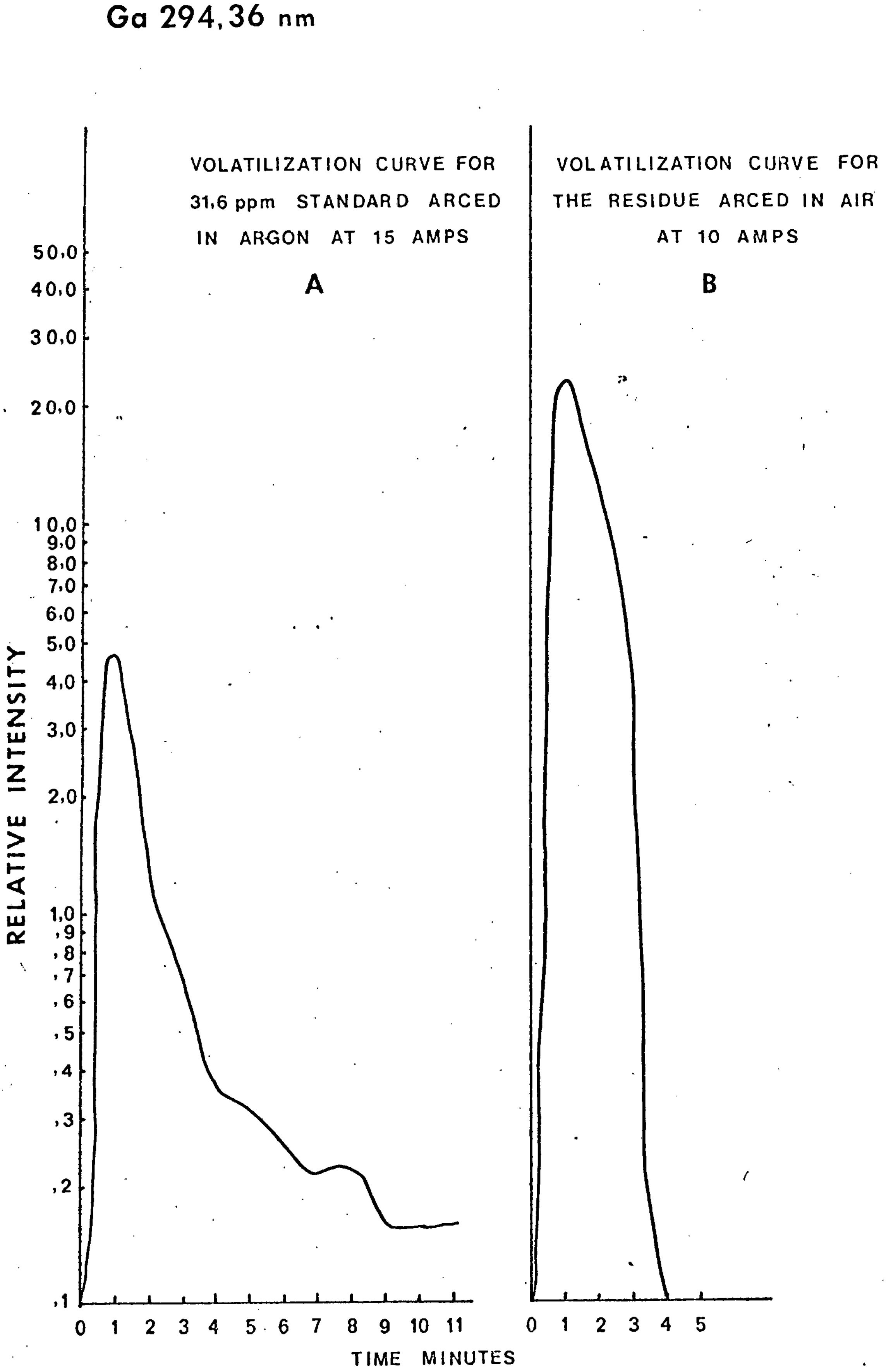
FIGURE 32

Cu 327,39 nm



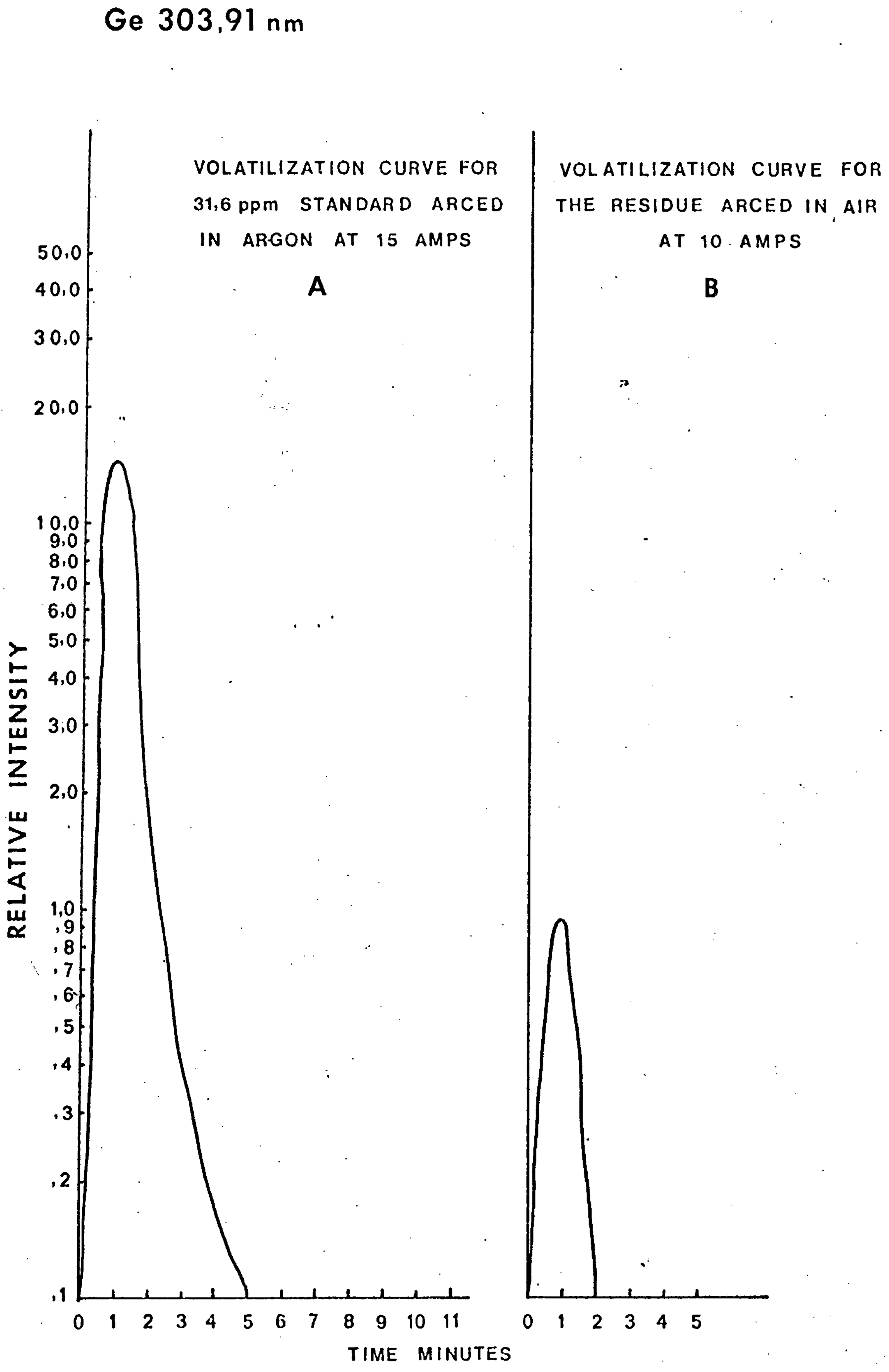
EVIDENCE OF ELEMENT RETENTION DUE TO CARBIDE FORMATION
CURVE 'A' ILLUSTRATES ELEMENT VOLATILIZATION FROM SAMPLE
CURVE 'B' ILLUSTRATES ELEMENT RECOMMENCING ITS
VOLATILIZATION FROM THE RESIDUE

FIGURE 33



EVIDENCE OF ELEMENT RETENTION DUE TO CARBIDE FORMATION CURVE 'A' ILLUSTRATES ELEMENT VOLATILIZATION FROM SAMPLE CURVE 'B' ILLUSTRATES ELEMENT RECOMMENCING ITS VOLATILIZATION FROM THE RESIDUE

FIGURE 34



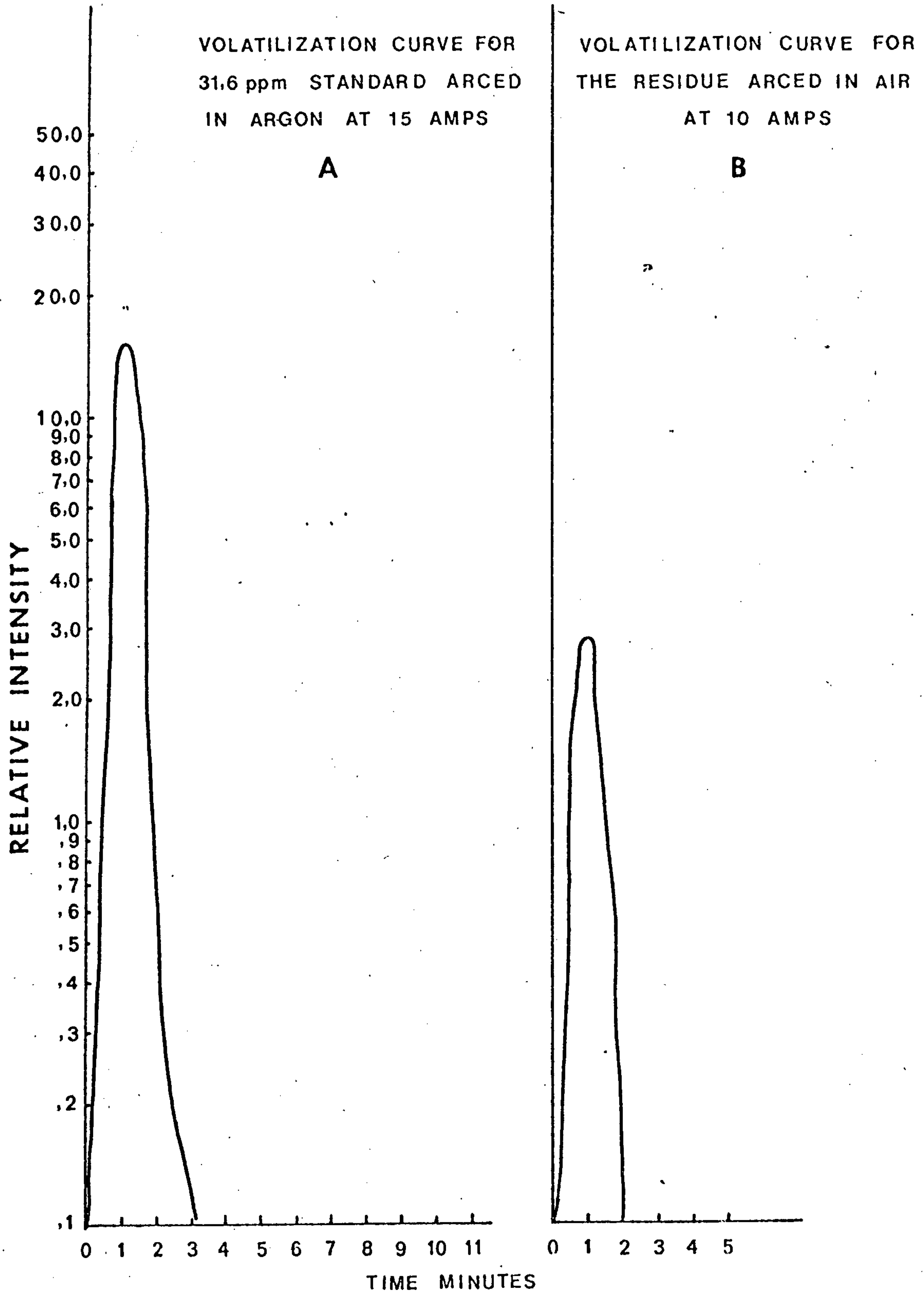
EVIDENCE OF ELEMENT RETENTION DUE TO CARBIDE FORMATION

CURVE 'A' ILLUSTRATES ELEMENT VOLATILIZATION FROM SAMPLE

CURVE 'B' ILLUSTRATES ELEMENT RECOMMENCING ITS VOLATILIZATION FROM THE RESIDUE

FIGURE 35

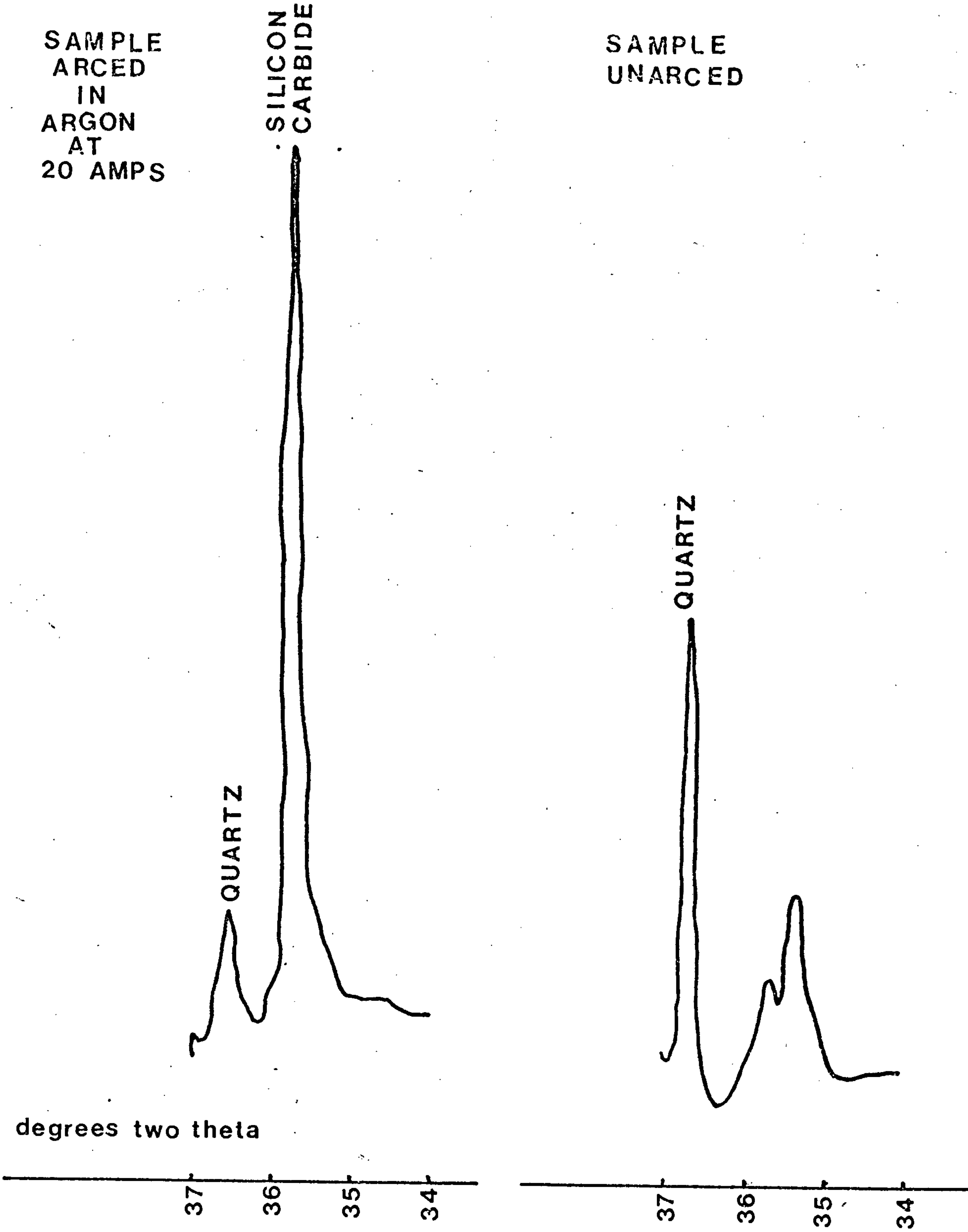
Sn 317,50 nm



EVIDENCE OF ELEMENT RETENTION DUE TO CARBIDE FORMATION
CURVE 'A' ILLUSTRATES ELEMENT VOLATILIZATION FROM SAMPLE
CURVE 'B' ILLUSTRATES ELEMENT RECOMMENCING ITS
VOLATILIZATION FROM THE RESIDUE

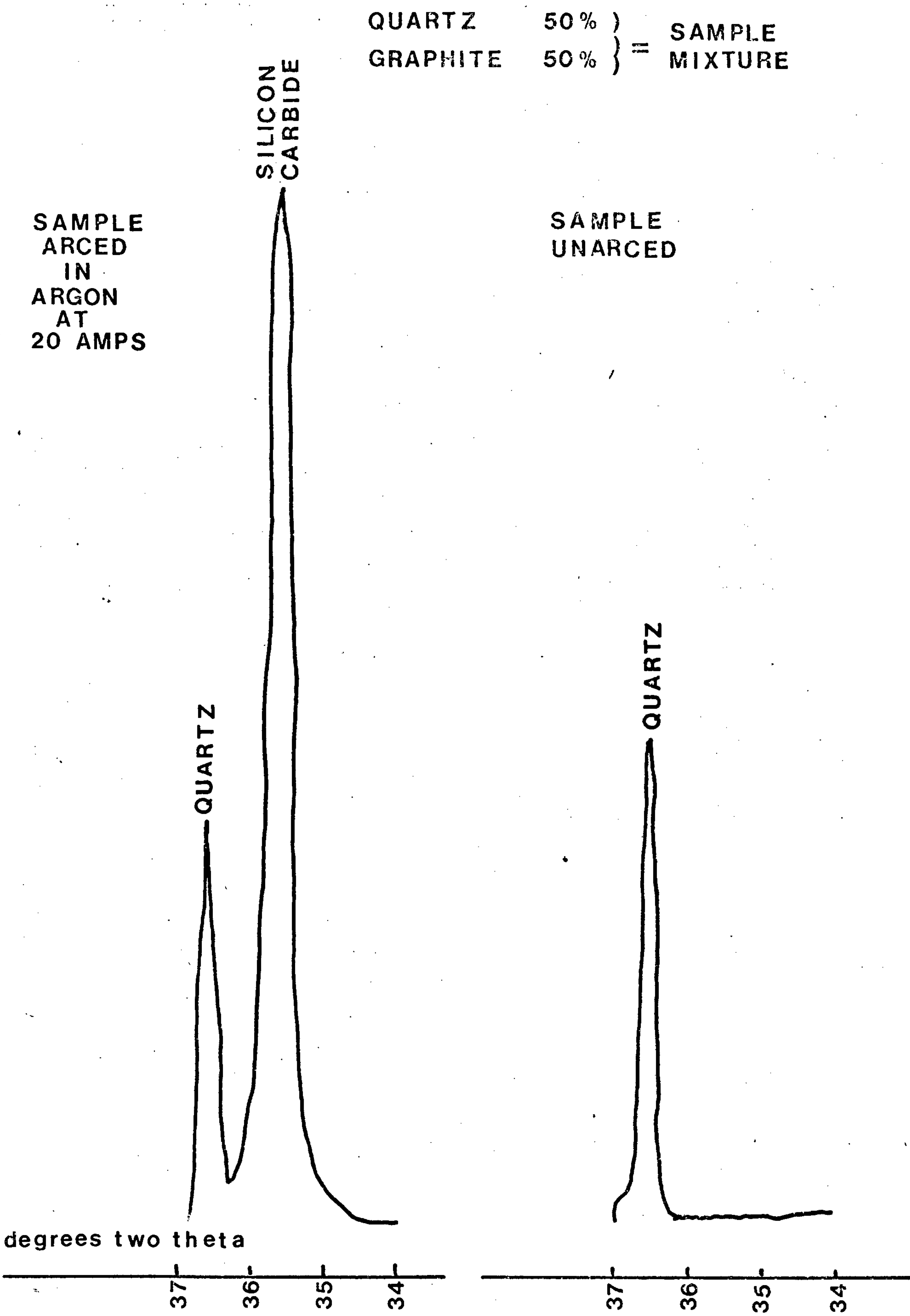
FIGURE 36

BUSHVELD GRANITE 46%)
GRAPHITE 46%) = SAMPLE MIXTURE
$BaSO_4$ 8%)



COMPARISON OF DIFFRACTOGRAMS DEMONSTRATING THE FORMATION OF SILICON CARBIDE DURING EXCITATION IN ARGON

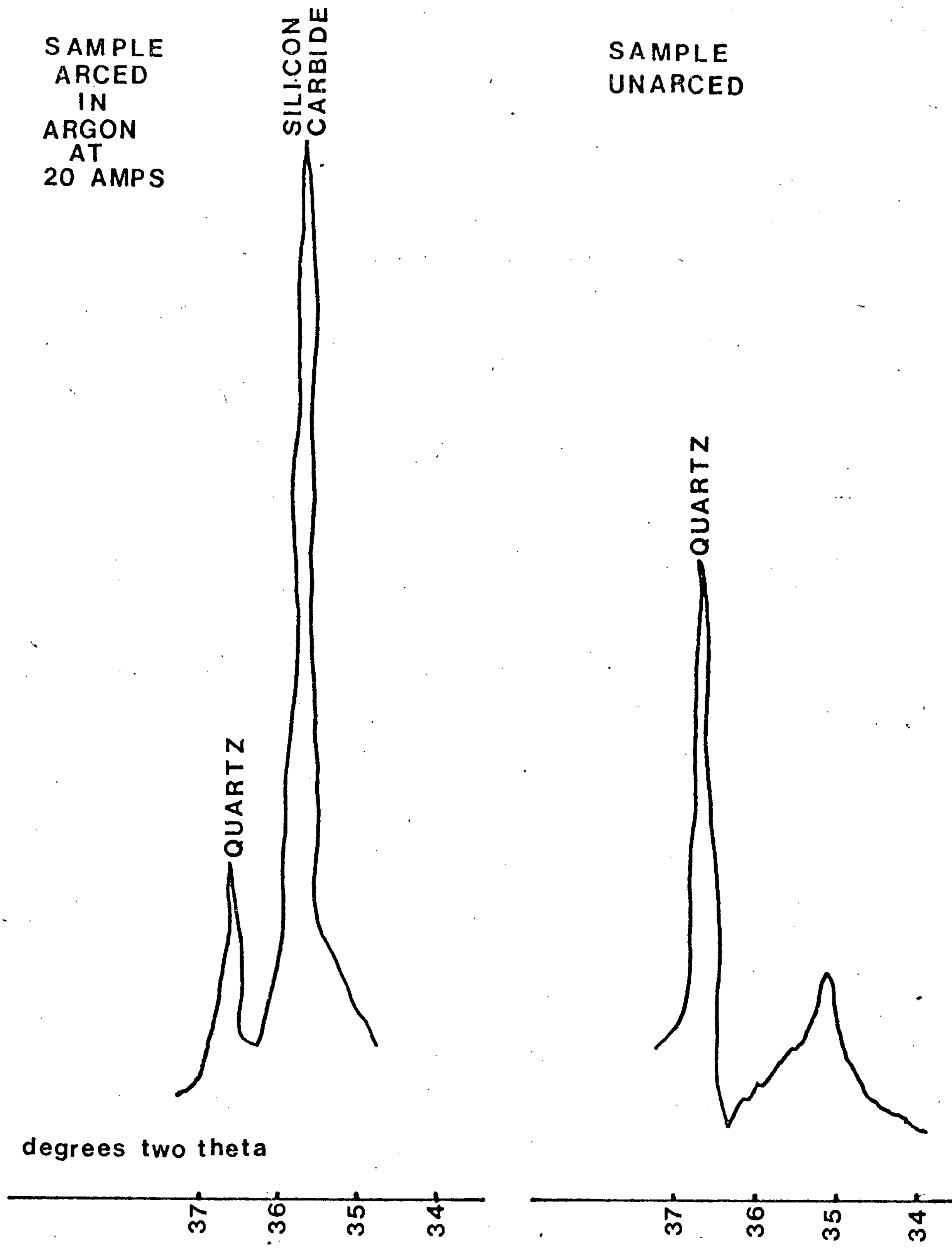
FIGURE 37



COMPARISON OF DIFFRACTOGRAMS DEMONSTRATING THE FORMATION OF SILICON CARBIDE DURING EXCITATION IN ARGON

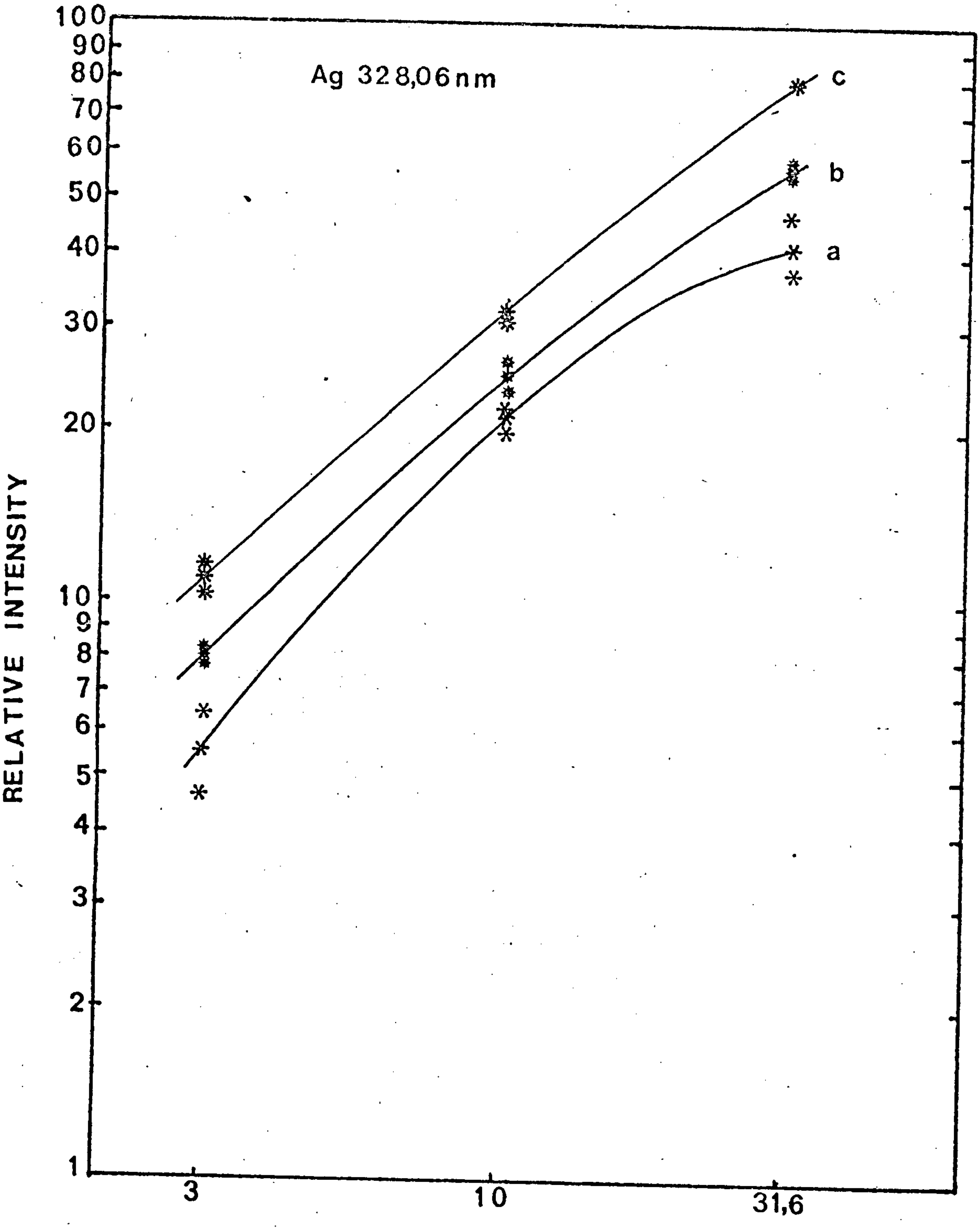
FIGURE 38

BUSHVELD GRANITE 50%) = SAMPLE
GRAPHITE 50%) MIXTURE



COMPARISON OF DIFFRACTOGRAMS DEMONSTRATING THE FORMATION OF SILICON CARBIDE DURING EXCITATION IN ARGON

FIGURE 39



CALIBRATION CURVES

ARGON ATMOSPHERE

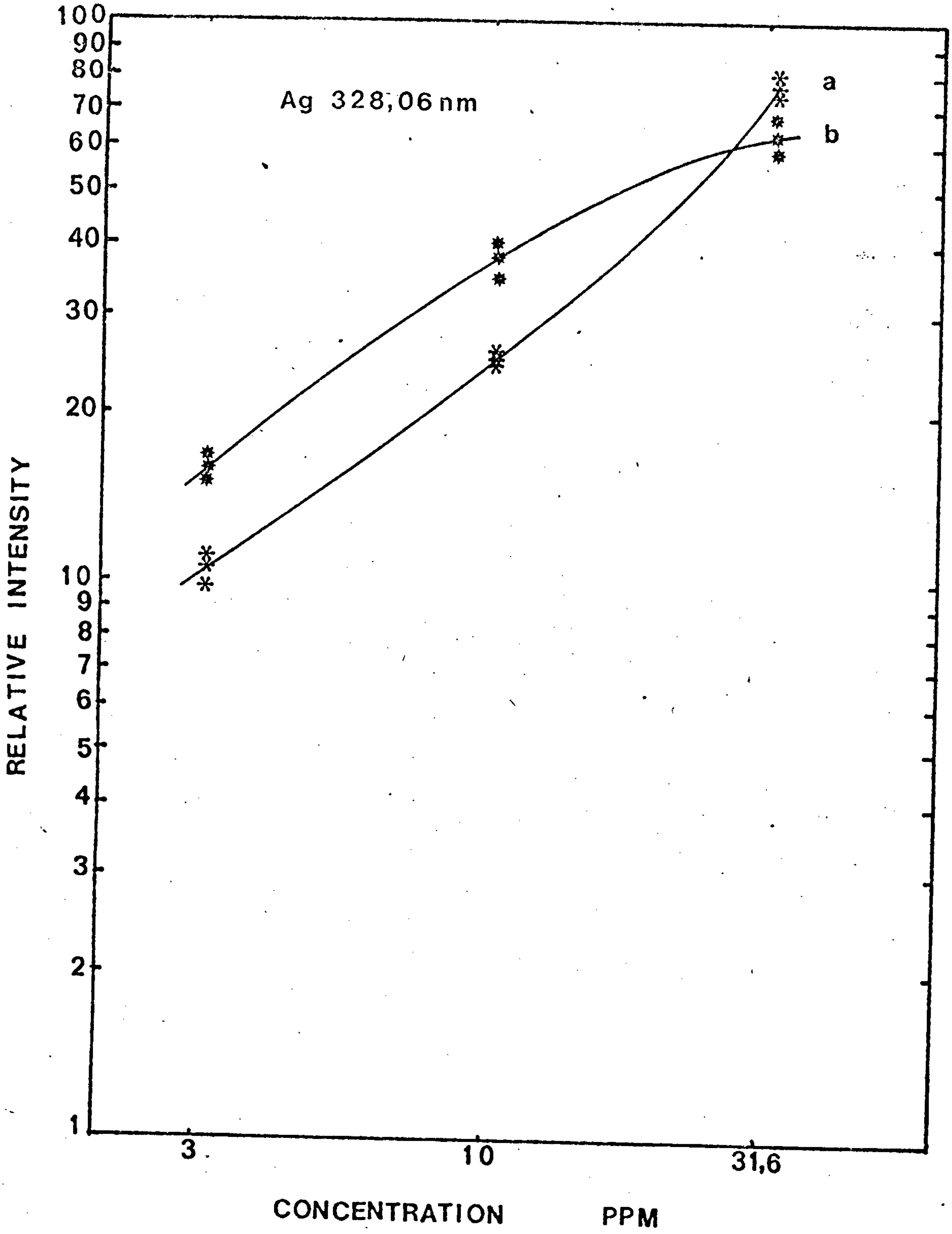
EXCITATION a 15 AMPS b 20 AMPS c 25 AMPS

EXPOSURE a 90 SECONDS b 60 SECONDS c 60 SECONDS

ELECTRODE D-5 CARRIER

ADDITIVE 8% K_2SO_4 12% GRAPHITE

FIGURE 40



CALIBRATION CURVES

ARGON – OXYGEN ATMOSPHERE

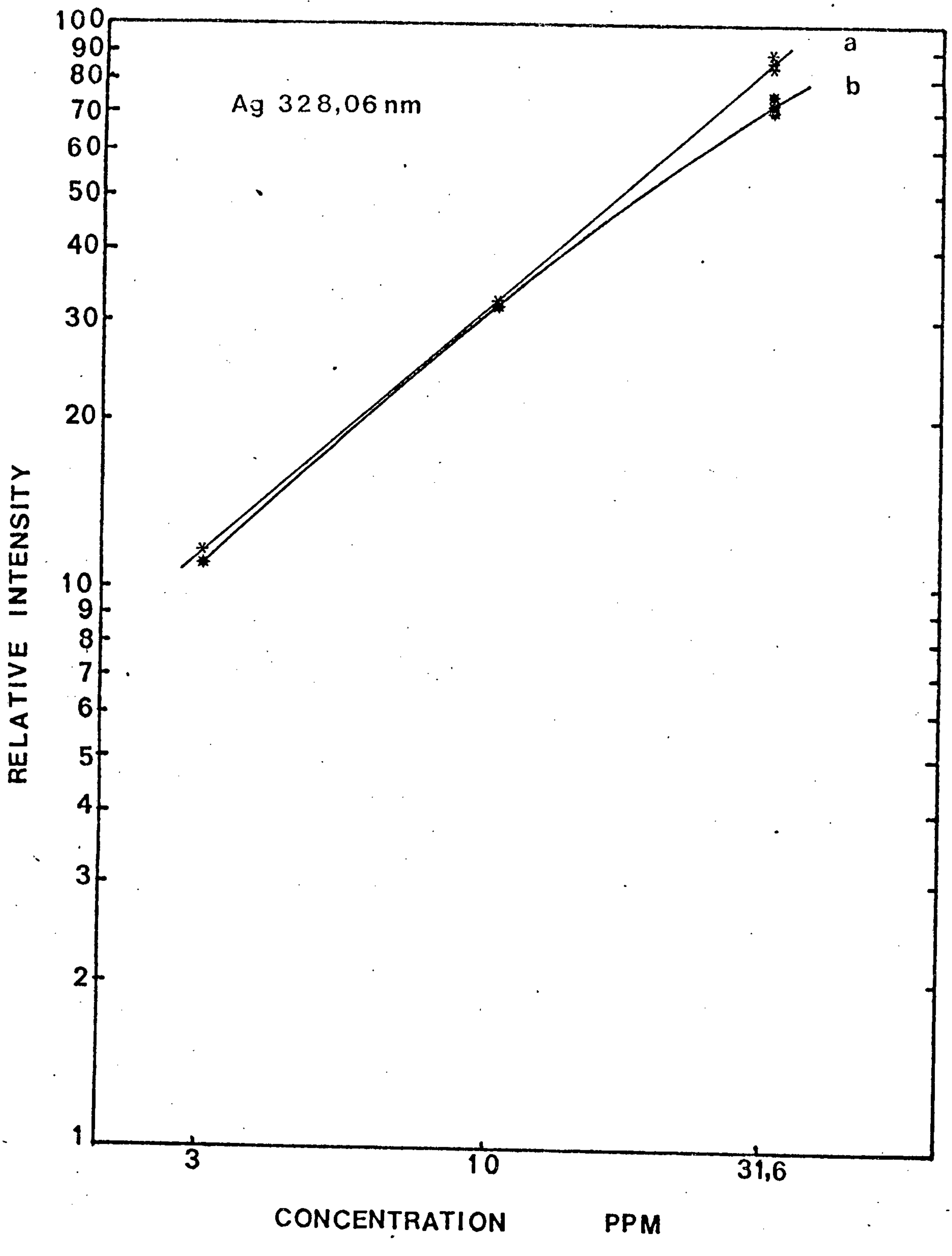
EXCITATION a 15 AMPS b 20 AMPS

EXPOSURE a 120 SECS b 90 SECS

ELECTRODE D-5 CARRIER

ADDITIVE AS PER FIGURE 40

FIGURE 41



CALIBRATION CURVES

NITROGEN ATMOSPHERE

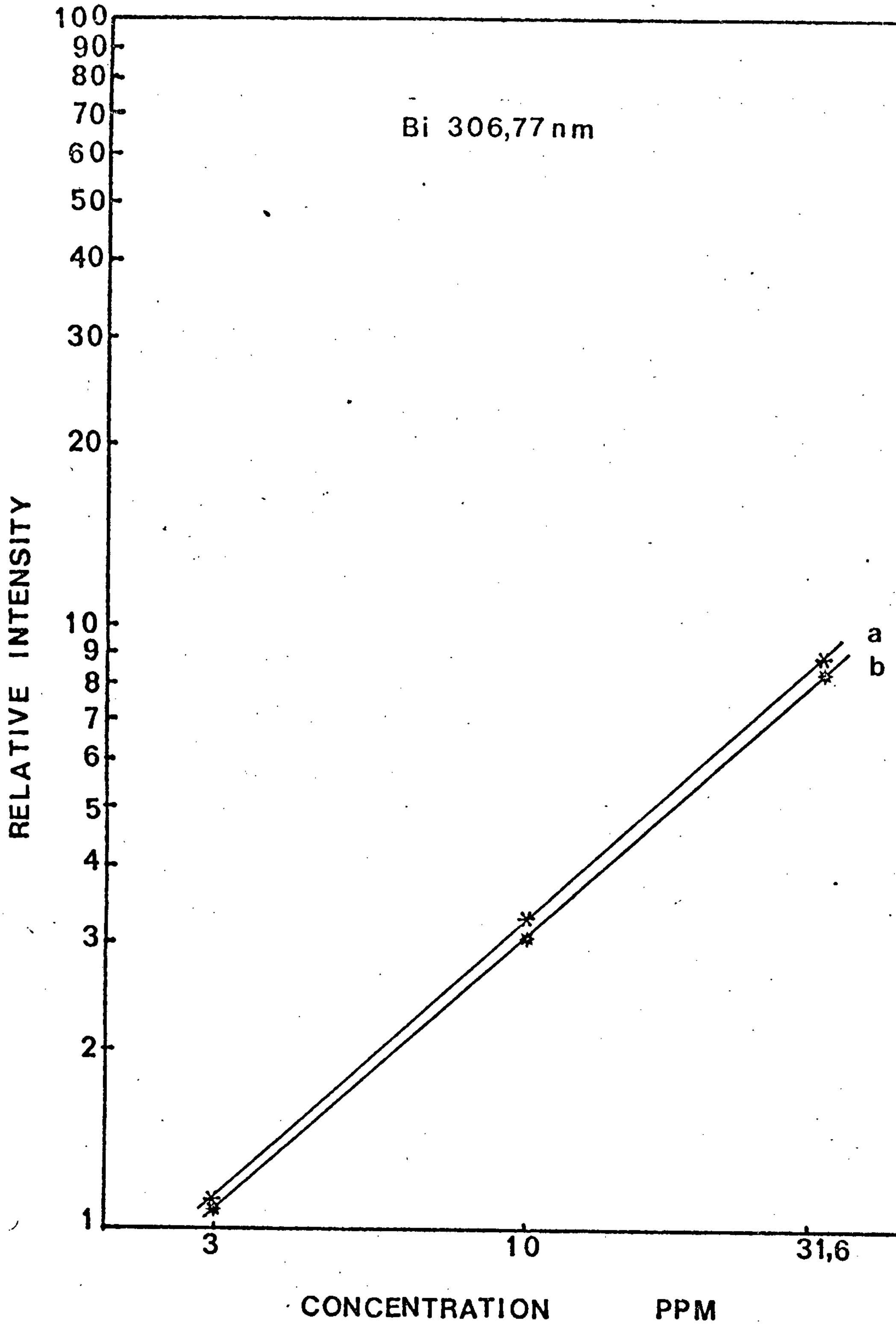
EXCITATION a 15 AMPS. b 20 AMPS.

EXPOSURE a 60 SECS. b 40 SECS.

ELECTRODE D-5 CARRIER

ADDITIVE AS PER FIGURE 40

FIGURE 42



CALIBRATION CURVES

ARGON ATMOSPHERE

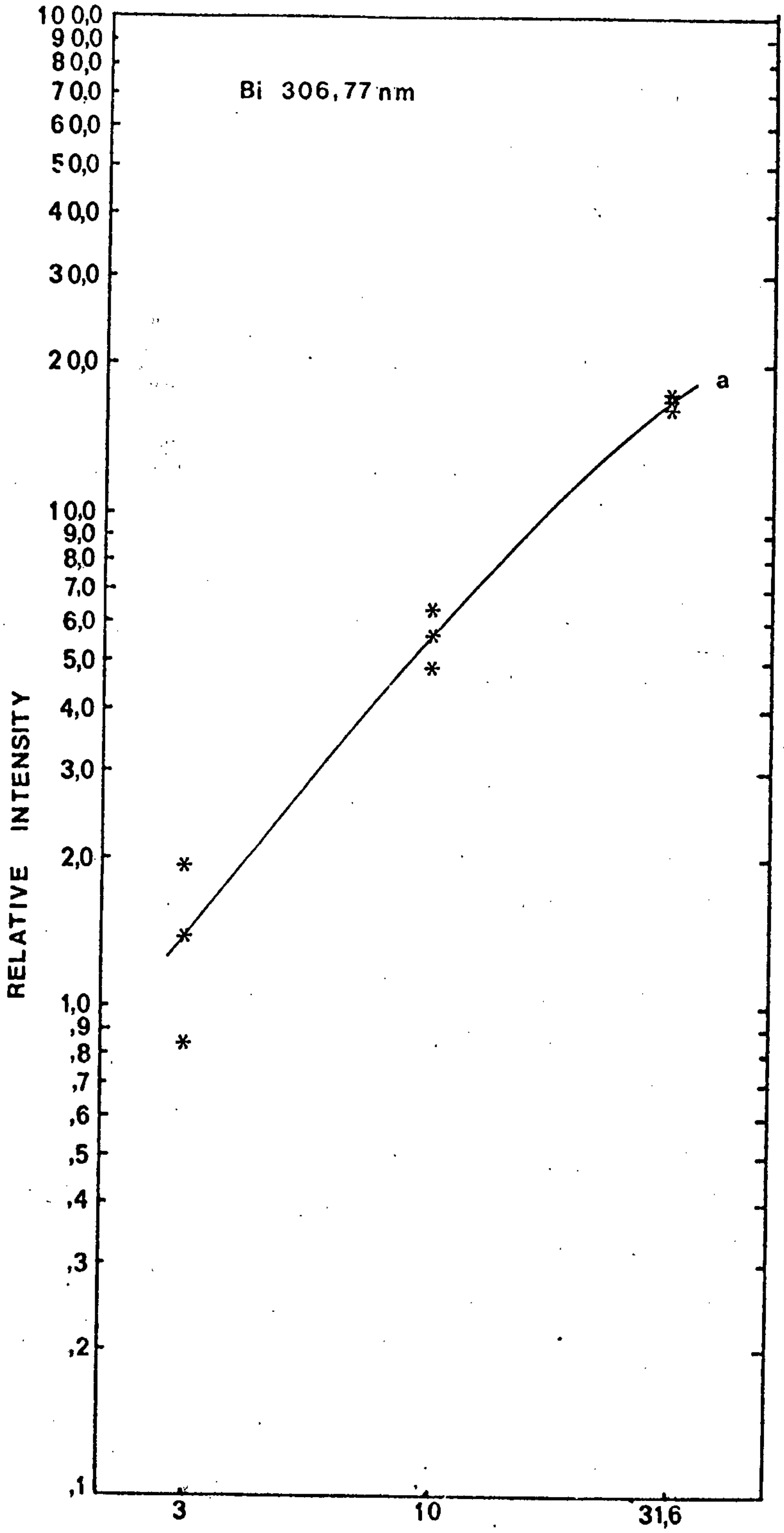
EXCITATION a 15 AMPS b 20 AMPS

EXPOSURE a 90 SECONDS b 60 SECONDS

ELECTRODE D-5 CARRIER

ADDITIVE AS PER FIGURE 40

FIGURE 43



CONCENTRATION PPM

CALIBRATION CURVES

ARGON-OXYGEN ATMOSPHERE

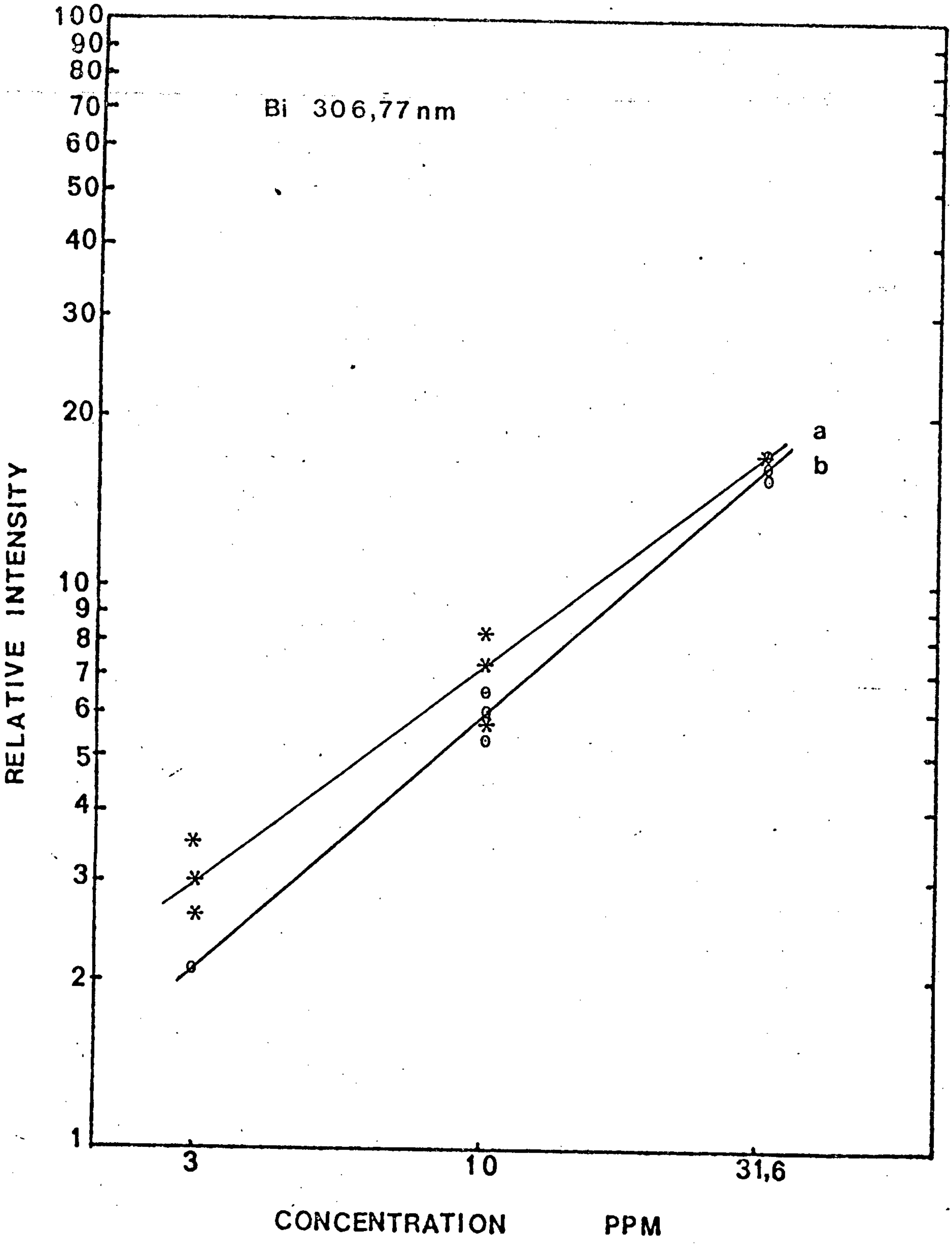
EXCITATION a 15 AMPS

EXPOSURE a 40 SECS

ELECTRODE D-5 CARRIER

ADDITIVE AS PER FIGURE 40

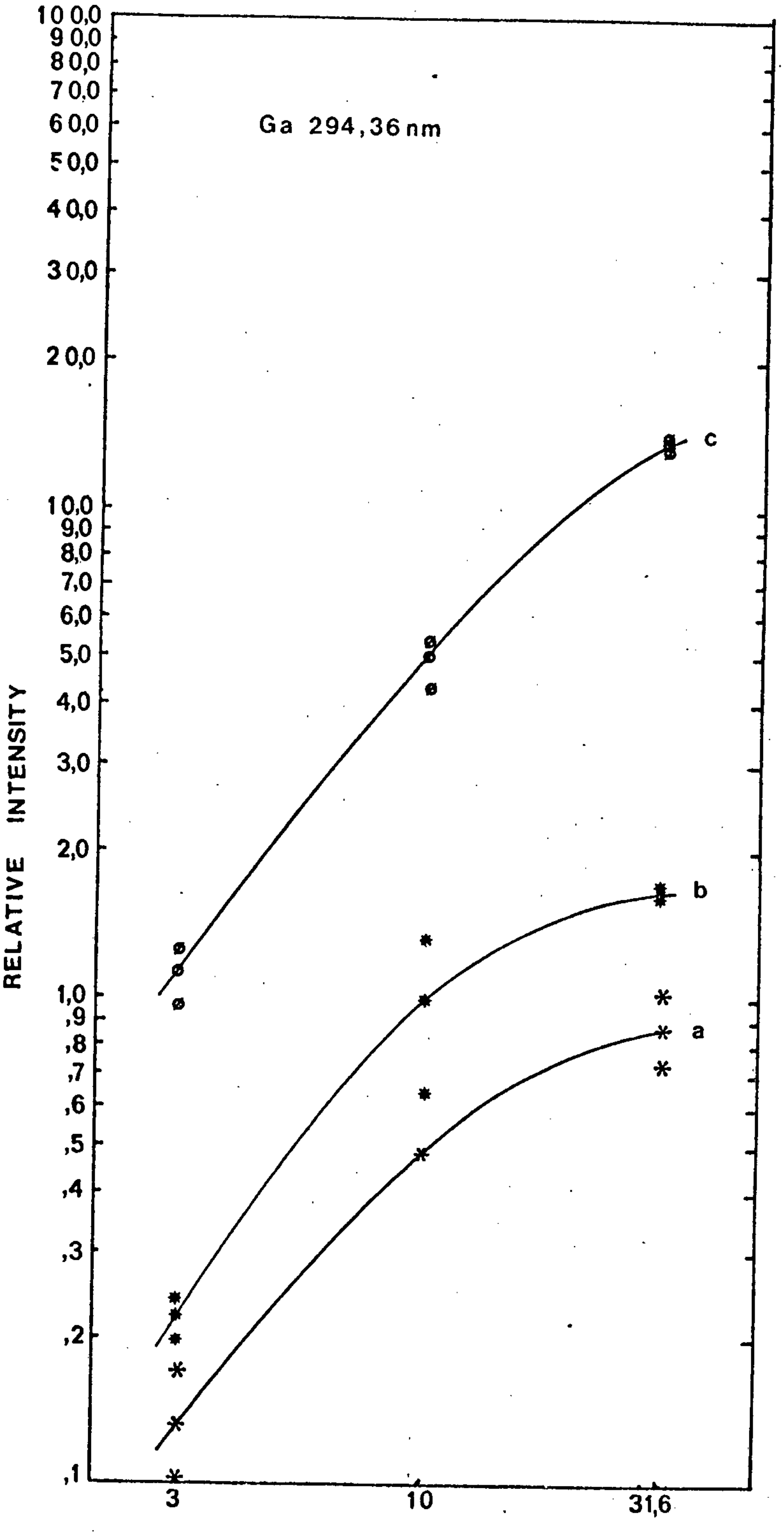
FIGURE 44



CALIBRATION CURVES

NITROGEN ATMOSPHERE
EXCITATION a 15 AMPS b 15 AMPS
EXPOSURE a 30 SECS b 60 SECS
ELECTRODE D-5 CARRIER
ADDITIVE AS PER FIGURE 40

FIGURE 45



CALIBRATION CURVES

ARGON ATMOSPHERE

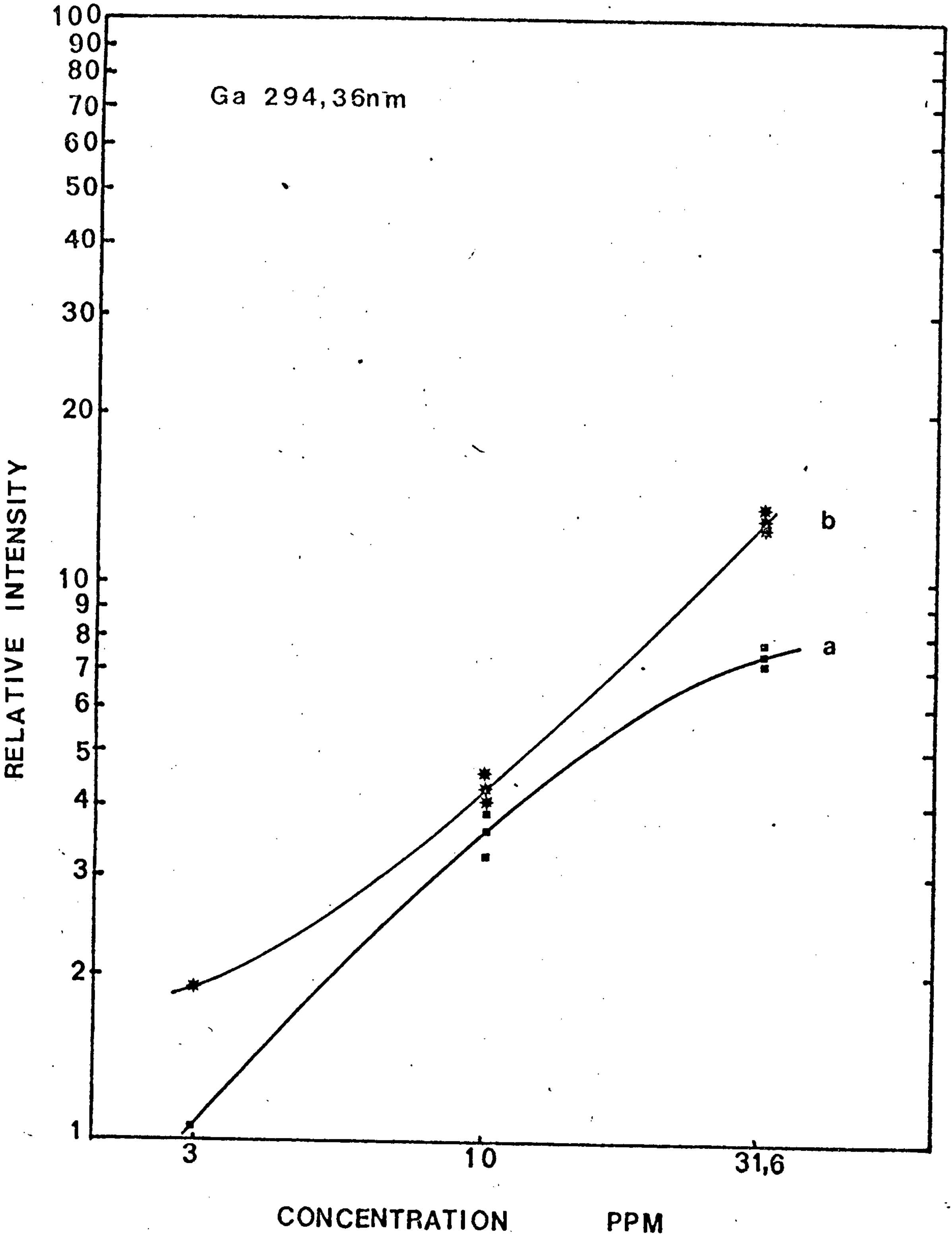
EXCITATION a 15 AMPS. b 20 AMPS. c 25 AMPS.

EXPOSURE a 90 SECS. b 60 SECS. c 60 SECS.

ELECTRODE D-5 CARRIER

ADDITIVE 8% K_2SO_4 12% GRAPHITE

FIGURE 46



CALIBRATION CURVES

ARGON – OXYGEN ATMOSPHERE

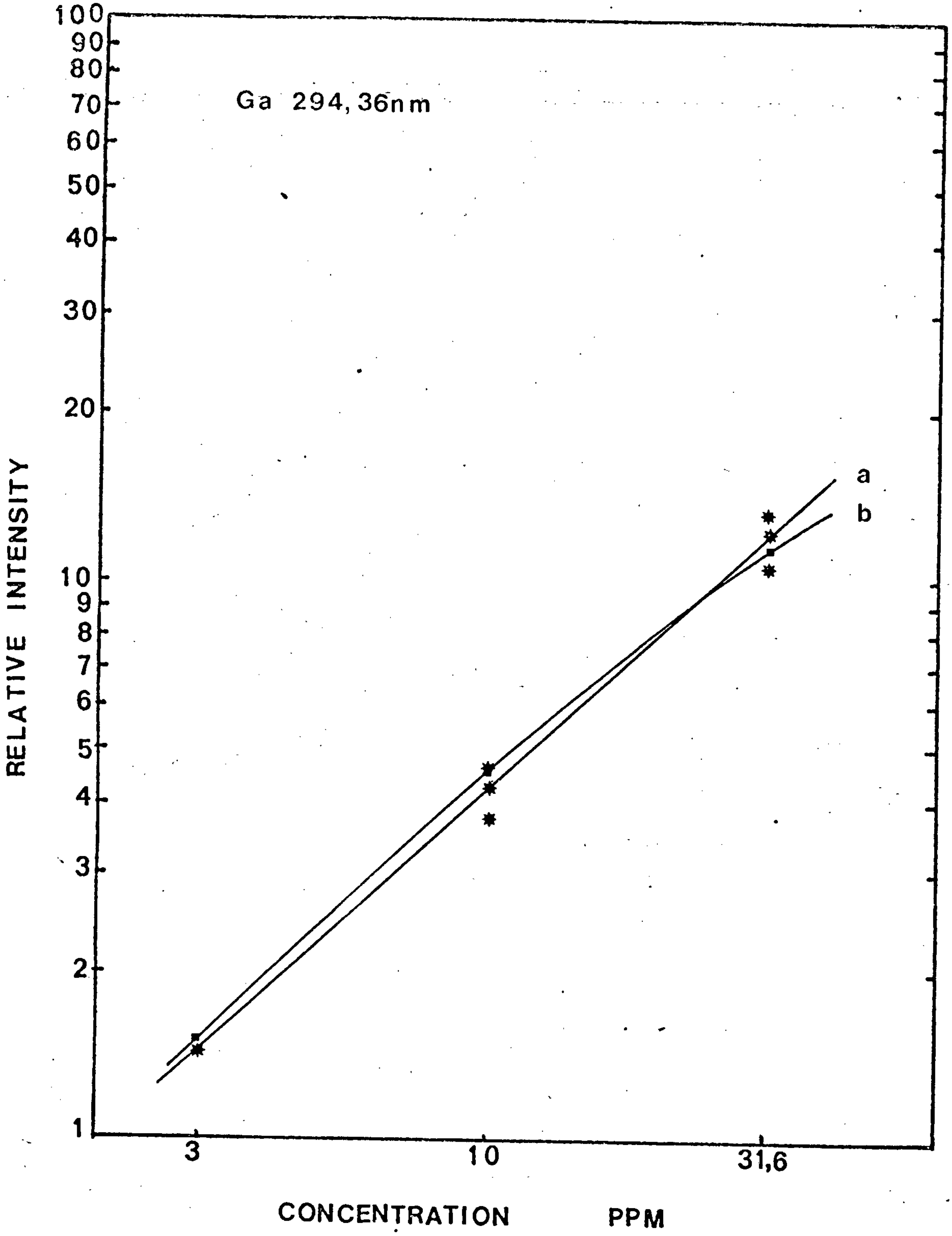
EXCITATION a 15 AMPS b 20 AMPS

EXPOSURE a 120 SECS b 90 SECS

ELECTRODE D-5 CARRIER

ADDITIVE AS PER FIGURE 40

FIGURE 47



CALIBRATION CURVES

NITROGEN ATMOSPHERE

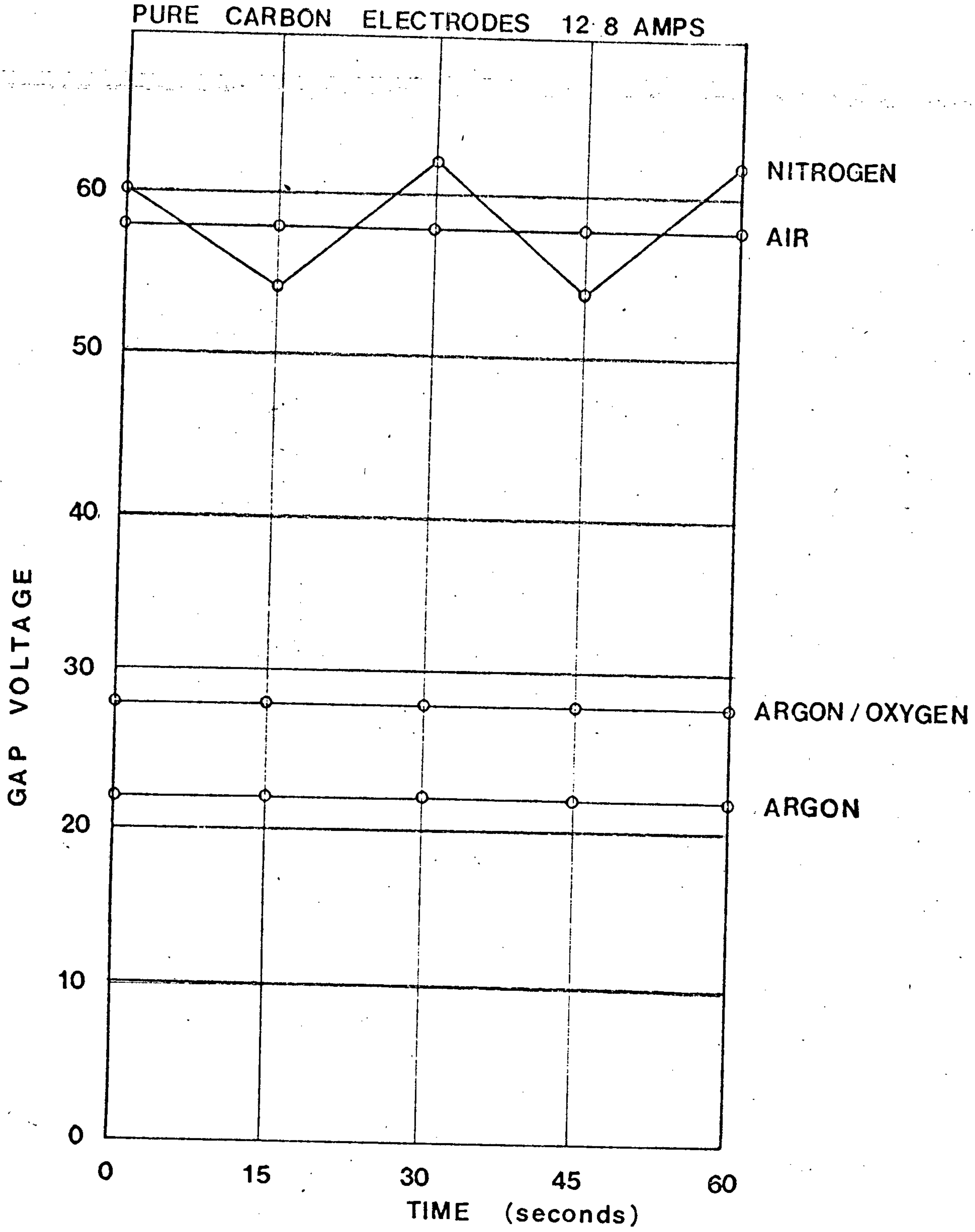
EXCITATION a 15 AMPS. b 20 AMPS.

EXPOSURE a 60 SECS. b 40 SECS.

ELECTRODE D-5 CARRIER

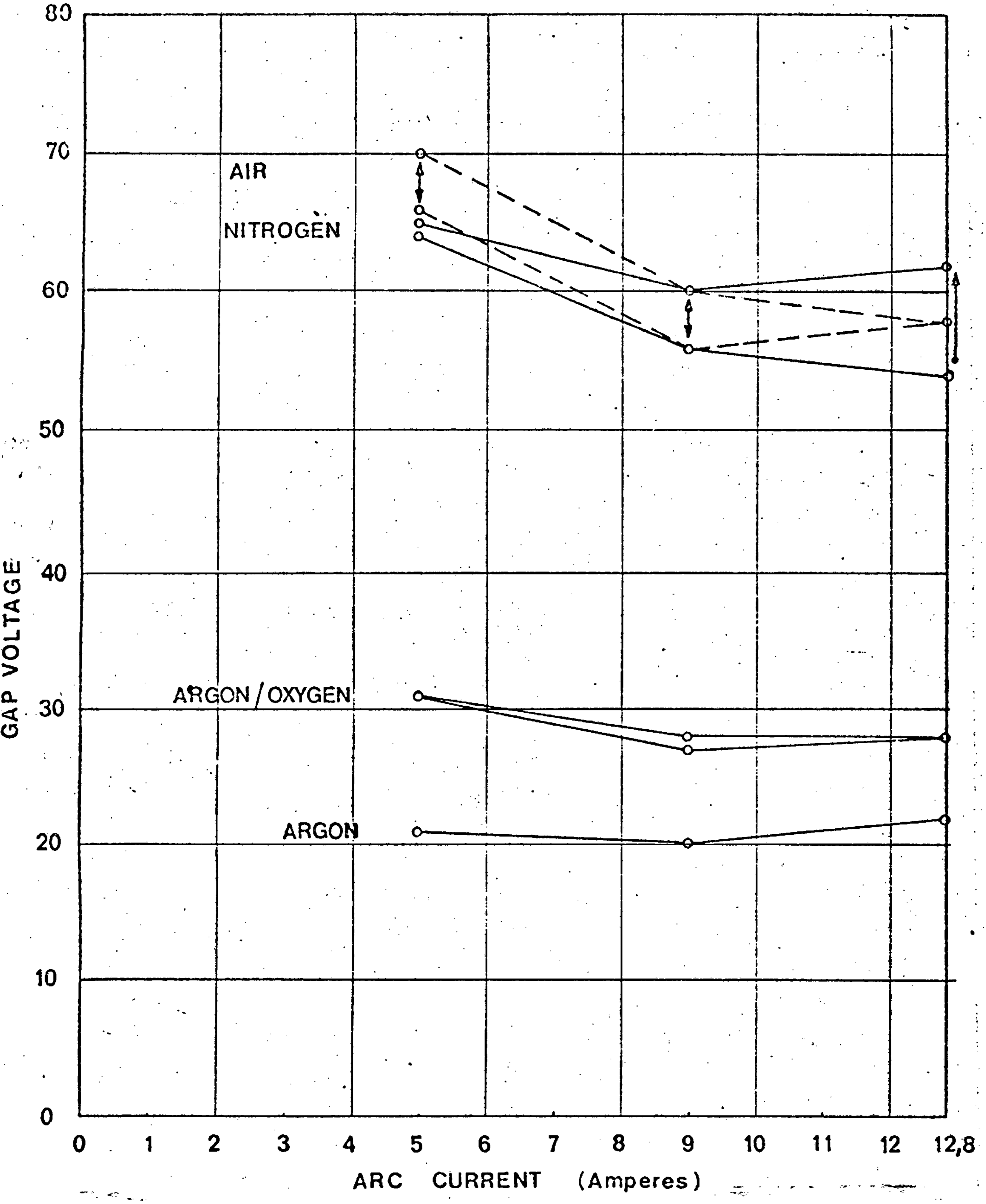
ADDITIVE AS PER FIGURE 40

FIGURE 48



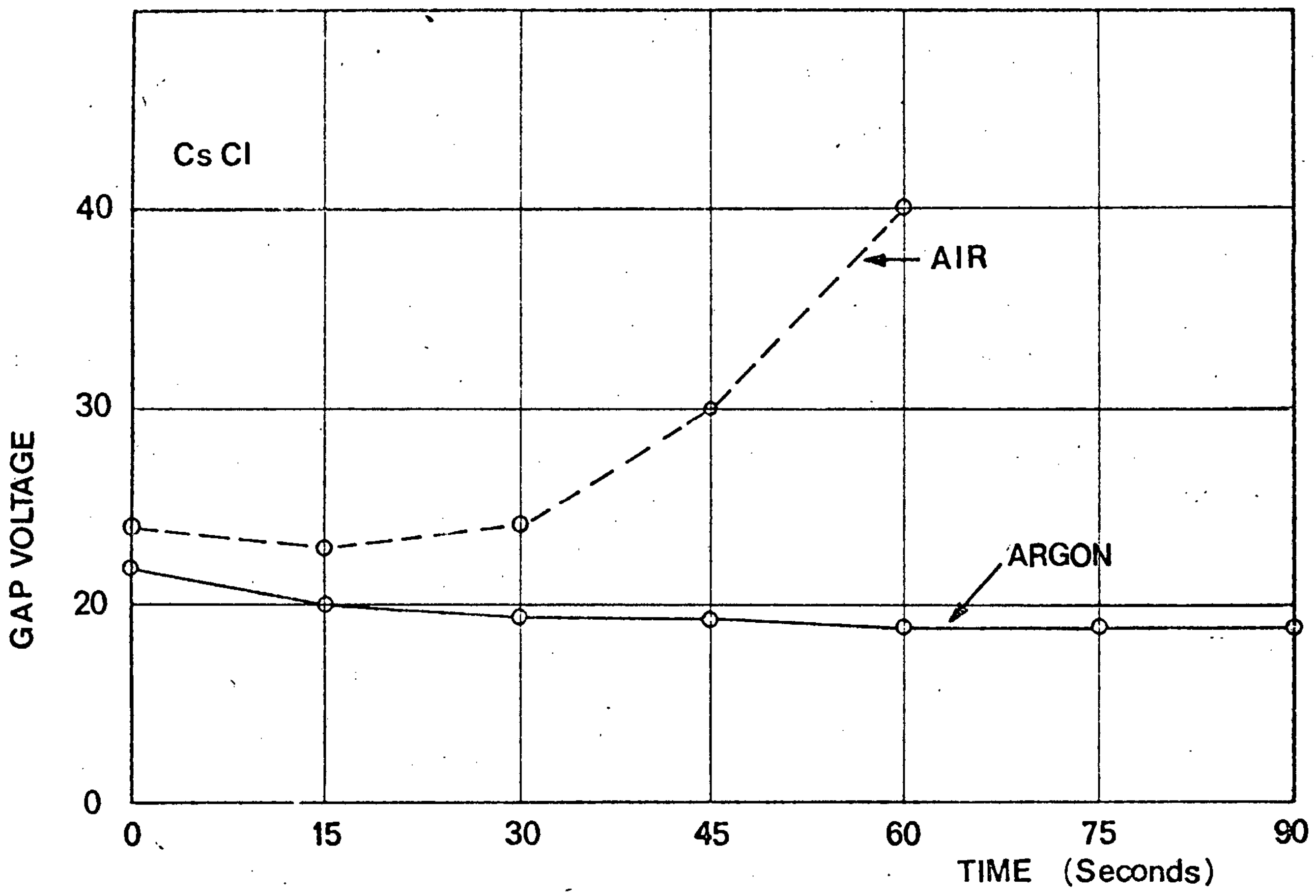
GAP VOLTAGE READINGS IN VARIOUS ATMOSPHERES (VOLTAGE USED AS AN INDICATION OF ELECTRODE TEMPERATURE)

FIGURE 49



VOLTAGE ACROSS ARC GAP VERSUS ARC CURRENT FOR AN ARC IN VARIOUS ATMOSPHERES

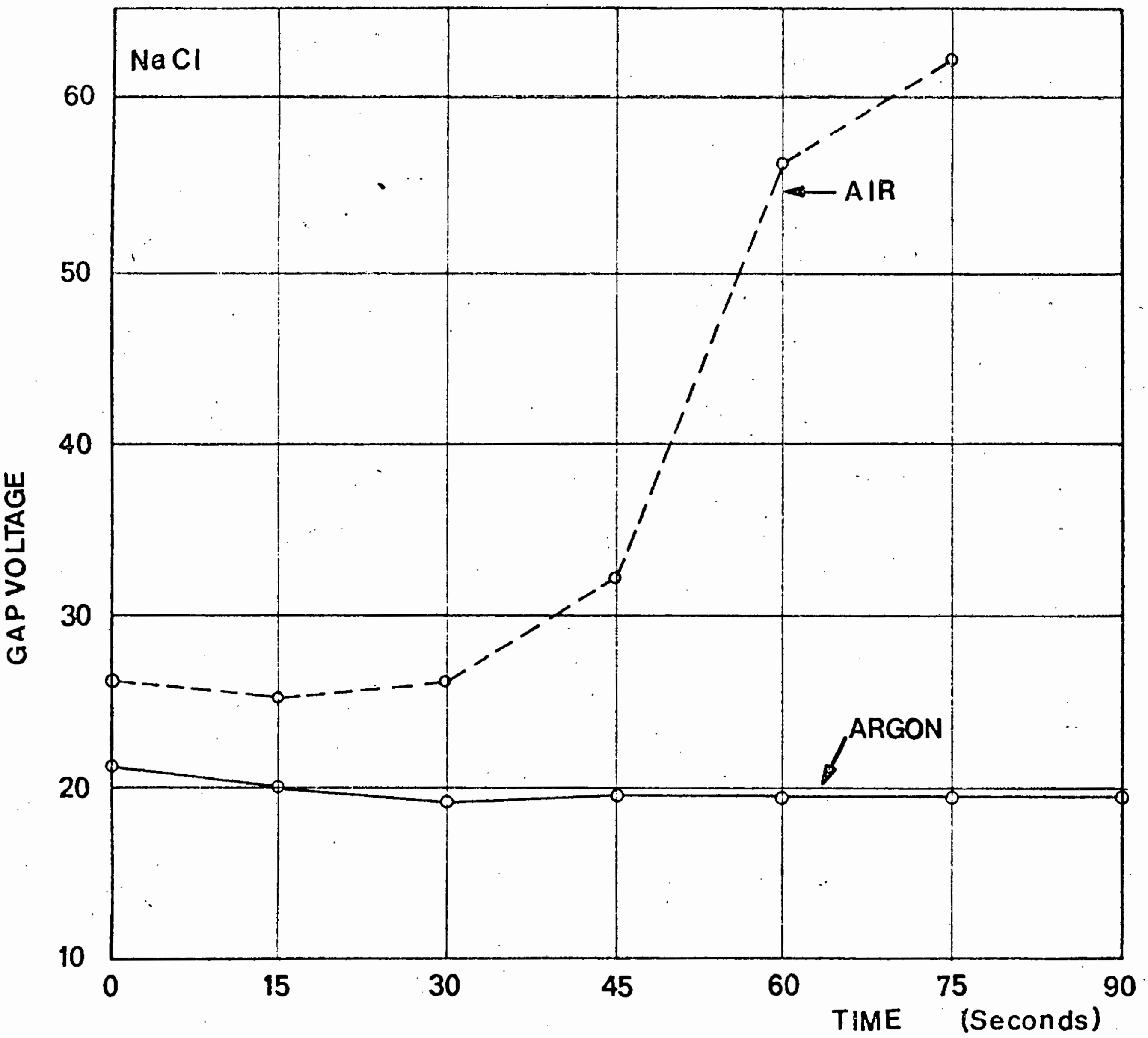
FIGURE 50



IONIZATION POTENTIAL OF Cs 3.89 volts

GAP VOLTAGE READINGS IN AIR & IN PURE ARGON FOR AN ELEMENT WITH LOW IONIZATION POTENTIAL

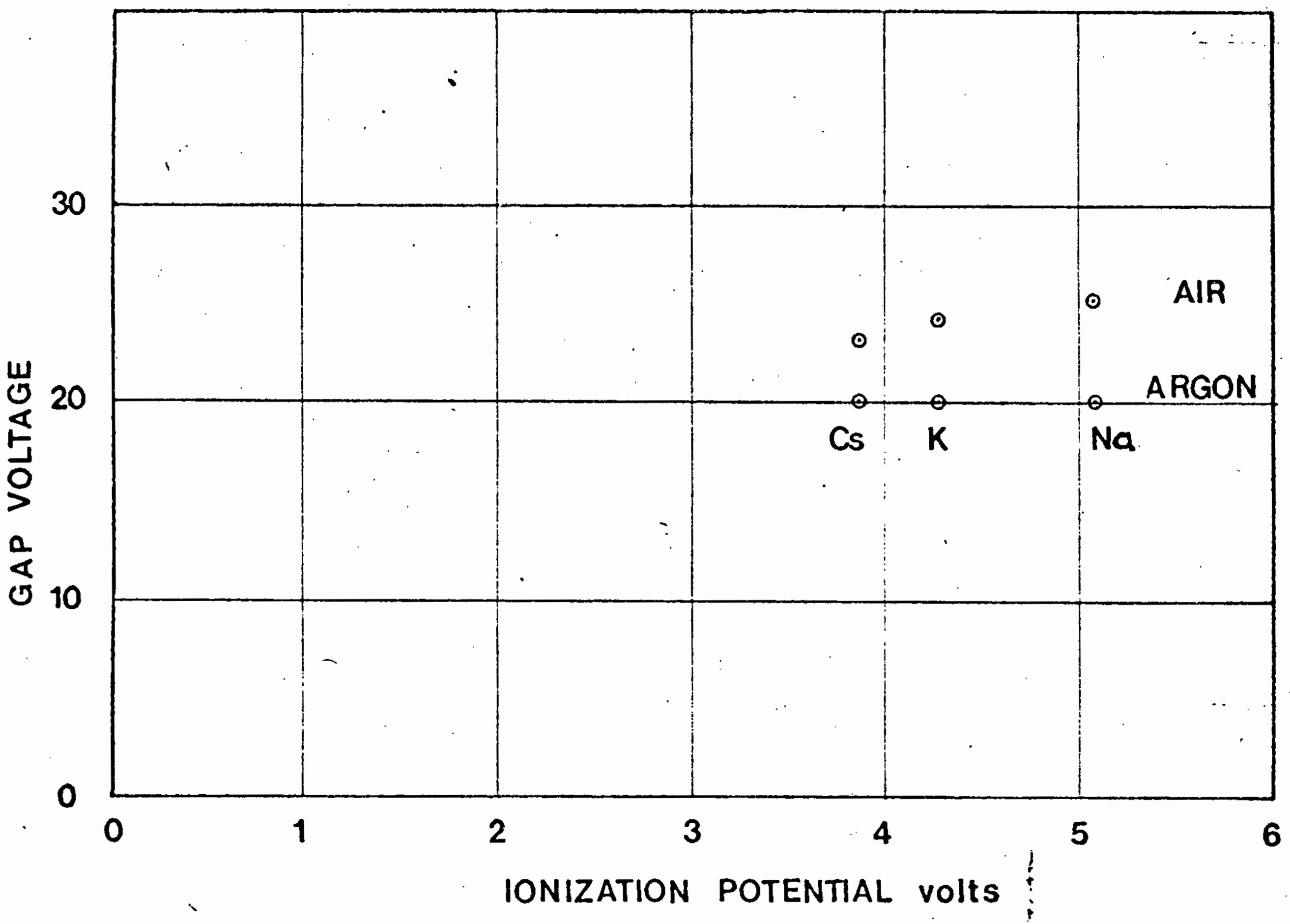
FIGURE 51



IONIZATION POTENTIAL OF Na 5,1 volts

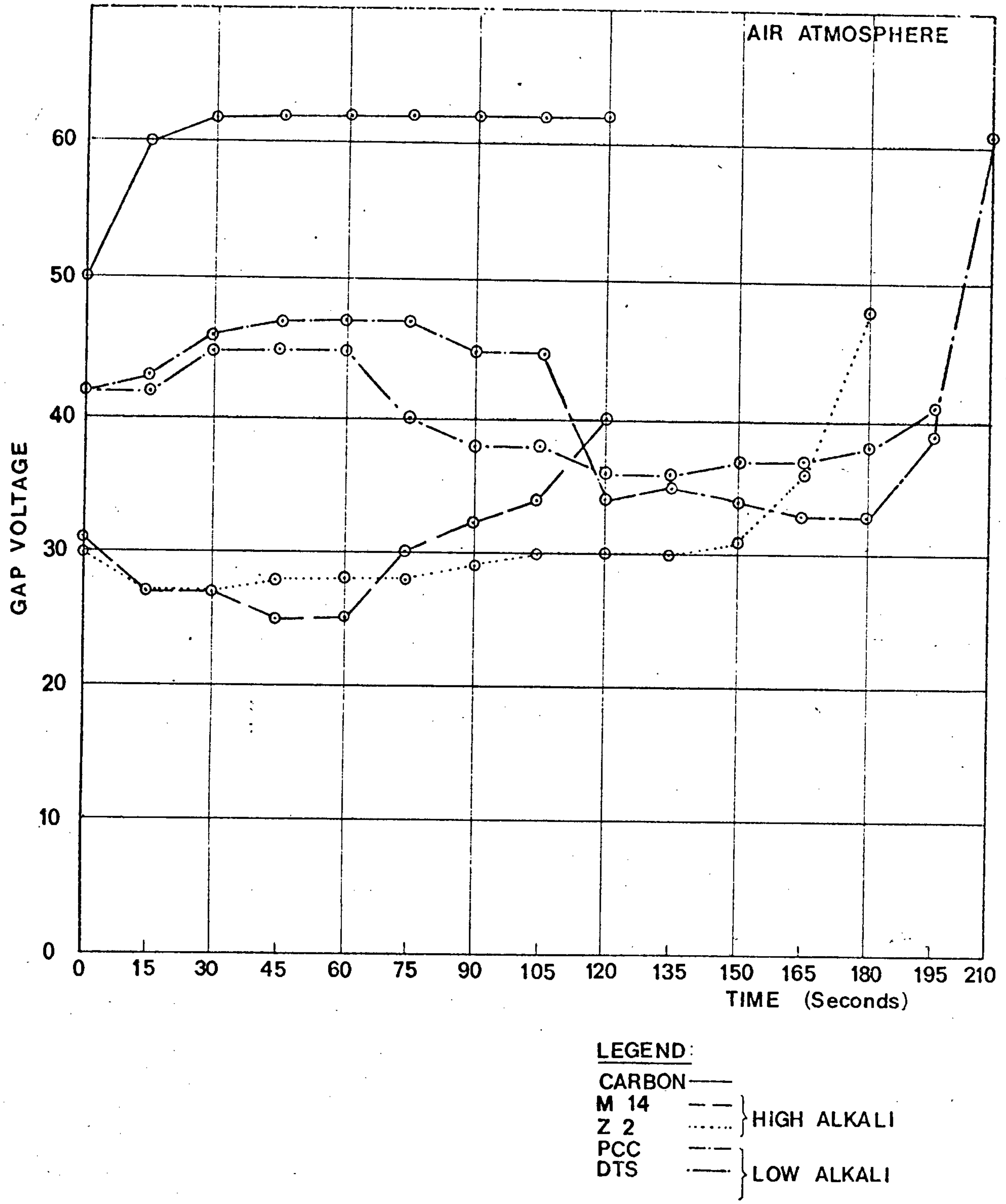
GAP VOLTAGE READINGS IN AIR & IN PURE ARGON FOR AN ELEMENT WITH HIGH IONIZATION POTENTIAL

FIGURE 52



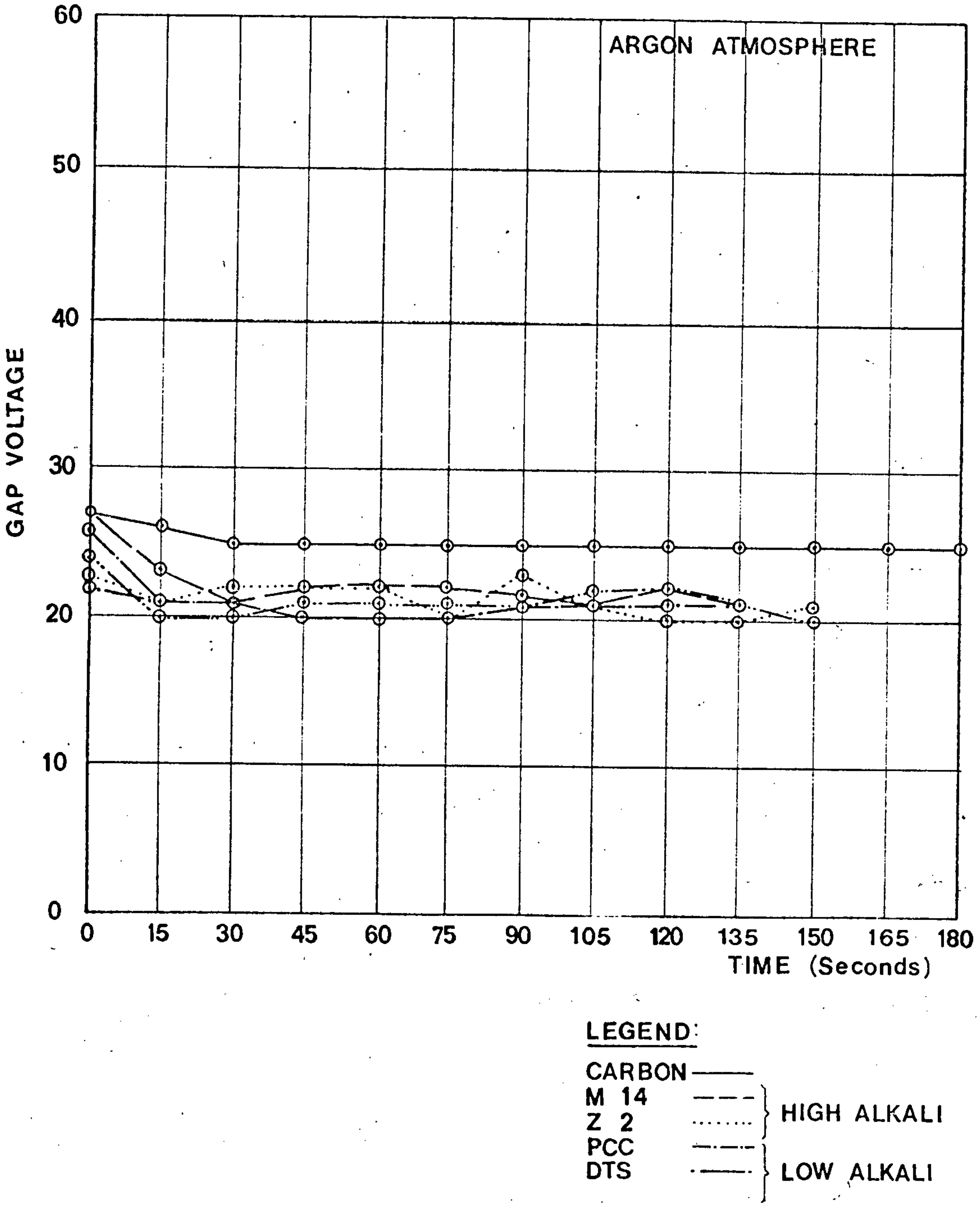
COMPARISON OF GAP VOLTAGE IN AIR & IN PURE ARGON FOR ALKALI ELEMENTS OF DIFFERING IONIZATION POTENTIAL

FIGURE 53



DEPENDENCE OF GAP VOLTAGE ON ALKALI METAL CONTENT OF SAMPLES ARCED IN AIR

FIGURE 54



INDEPENDENCE OF GAP VOLTAGE ON ALKALI METAL CONTENT OF SAMPLES ARCED IN ARGON

FIGURE 55

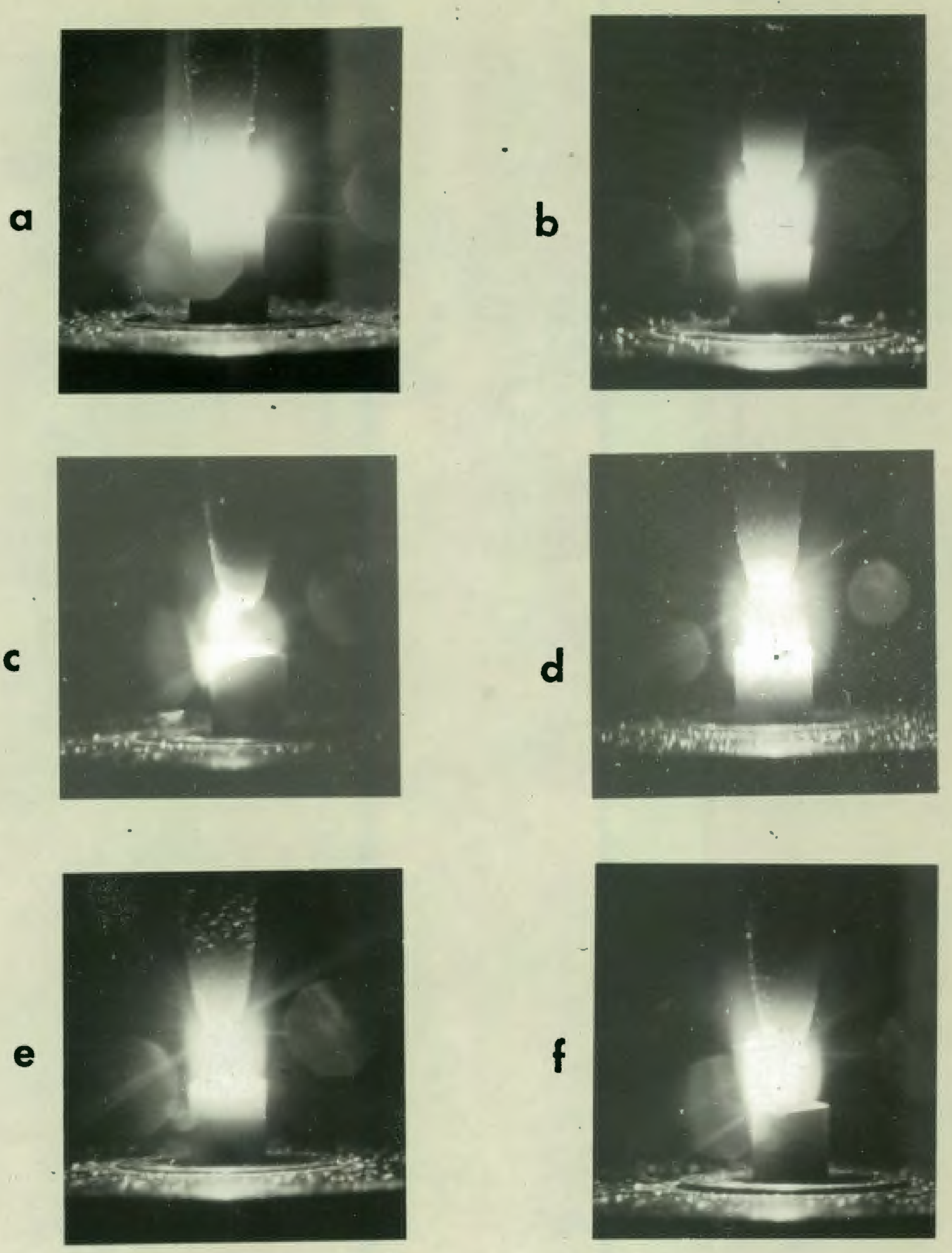


PLATE 1

a. 15 amp d.c. arc in air D-5 carrier electrode.
b. 15 amp d.c. arc in nitrogen D-5 carrier electrode.
c. 15 amp d.c. arc in argon D-5 carrier electrode.

d. 25 amp d.c. arc in argon D-5 carrier electrode.
e. 15 amp d.c. arc in argon-oxygen D-5 carrier electrode.
f. 15 amp d.c. arc in argon-oxygen D-5 carrier electrode filled.

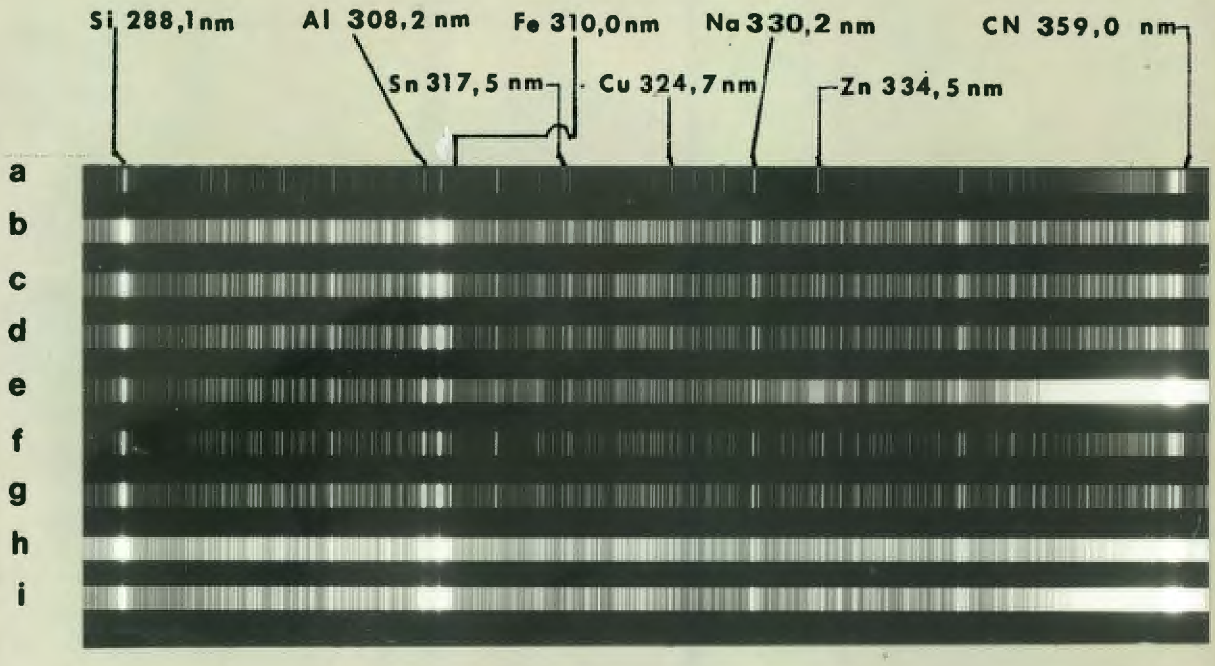


PLATE 2

15 amp d.c. arc using various atmospheres and electrodes and demonstrating the advantages obtained.

a. argon D-5 carrier electrode, Note selective distillation of Zn, Cu & Sn unaccompanied by matrix elements Na, Fe, Al & Si.

b. argon: oxygen = 80:20 D-2 electrode full.

c. argon: oxygen = 90:10 D-2 electrode full.

d. argon: oxygen = 95:5 D-2 electrode full.

Note superior CN 359.0 elimination using argon:oxygen mixtures.

e. nitrogen D-5 carrier electrode, superior Sn 317.5nm intensity

f. helium D-5 carrier electrode, low background

g. helium: oxygen = 80:20 D-2 electrode full. CN 359.0 elimination

h. carbon dioxide. D-2 electrode full.

i. air D-2 electrode full. High background. Zn 334.5nm swamped by CN emissio

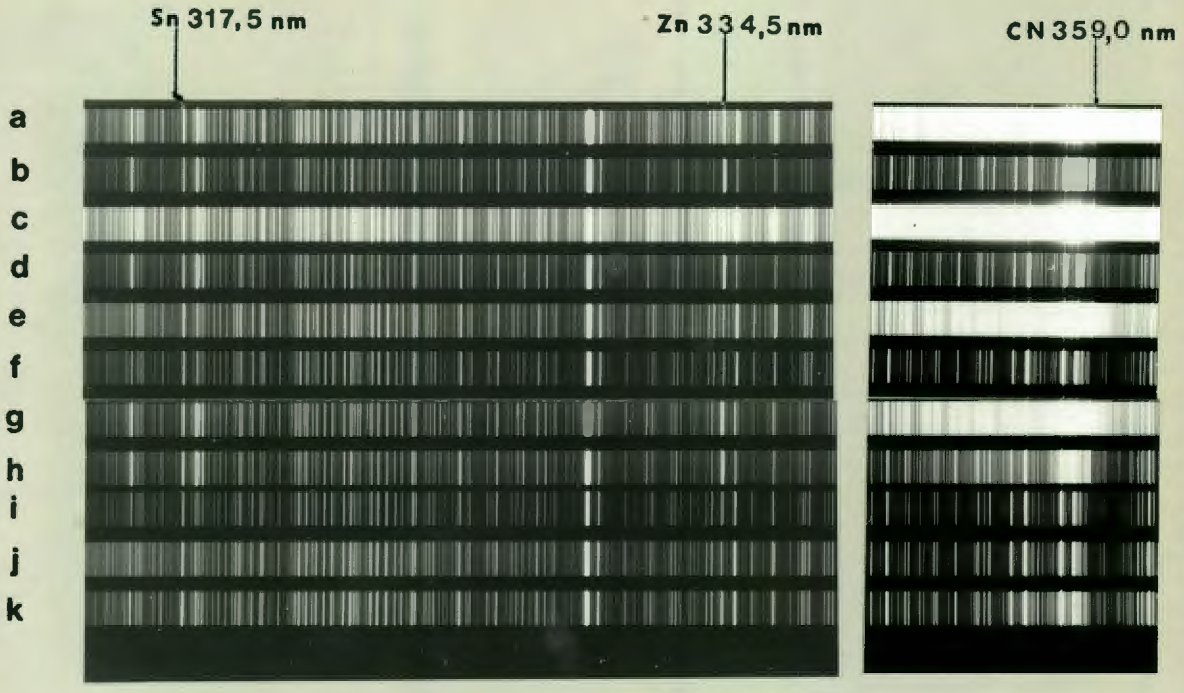


PLATE 3

a.	Stallwood jet	Argon 5L/min.	25 amps
b.	Stallwood jet plus canopy	Argon 5L/min.	25 amps
c.	Stallwood jet	Argon 9L/min.	25 amps
d.	Stallwood jet plus canopy	Argon 9L/min.	25 amps
e.	Stallwood jet	Argon+Oxygen = 9+1L/min.	10 amps
f.	Stallwood jet plus canopy	Argon+Oxygen = 9+1L/min	10 amps
g.	M & S gas jet	Argon 5L/min.	25 amps
h.	M & S gas jet	Argon 9L/min.	25 amps
i	M & S gas jet	Argon+Oxygen = 9+1L/min.	10 amps
j	M & S gas jet	Argon+Oxygen = 8+2L/min.	10 amps
k	M & S gas jet	Argon+Oxygen = 9+½L/min.	10 amps

Bushveld granite mixed with graphite 1:1 loaded into D-4 electrodes full.

APPENDIX - C

Preparation of artificial standards

APPENDIX C

A detailed description of the preparation of the artificial standards employed during the systematic study of the use of artificial atmospheres.

It was intended that the method of analysis developed should be applicable to a wide range of silicate matrices. For this reason the base mix composition selected was intermediate between the compositions of the United States Geological Survey (U.S.G.S.) standard silicate materials G-1 and W-1. This composition was: SiO_2 63.0%, Al_2O_3 15.0%, Fe_2O_3 6.5%, MgO 3.5%, CaO 6.0%, Na_2O 3.0% and K_2O 3.0%.

As the lower level of concentration of the artificial standards was 0.032ppm it was essential that stringent precautions against contamination be taken. The individual matrix constituents were examined using optical spectrography to determine the presence of the volatile elements. (Details of method to follow). Johnson Matthey specpure chemicals were used in all cases, except for SiO_2, which was carefully prepared from natural quartz chips.

After crushing and grinding the quartz chips, the quartz powder was repeatedly washed with 6N HCL (to removed Fe contamination), until the supernatant liquid became colourless. The washed quartz powder plus the individual base mix oxides, carbonates (Na_2CO_3, $CaCO_3$) and sulphate (K_2SO_4) were dried at 110°C in a drying oven overnight.

After weighing, the base mix components were placed in a specially cleaned glass jar and mixed in a mechanical shaker. Further homogenization was effected by grinding in a mechanical agate mortar.

This base mix was then sintered in a silica basin in a muffle furnace at 1000°C to drive off the carbon dioxide and sulphur dioxide. The sintered material was reground in the mechanical agate mortar.

The volatile element oxides to be added to the base mix were individually examined by optical spectrography for the presence of other members of the volatile group. Cu was found to be present in the CdO, Ga_2O_3 and In_2O_3. It was also present in the Li_2CO_3, LiF and K_2SO_4 which were used as additives during the investigation.

A standard containing 1% of all the volatile element oxides was prepared and successive dilutions made using the method described by Ahrens and Taylor (1961). A mechanical agate mortar was used in the dilution procedure. The series of standards contained 0.032, 0.10, 0.32, 1.00, 3.16, 10.0, 316, 1000ppm of each of the volatile elements.

Details of the optical spectrographic method used to determine the presence of contaminant volatile elements in the base mix components and the volatile element oxides is as follows:

a. The samples were mixed with graphite powder in the ratio 1 part sample to 1 part graphite.

b. The samples were loaded into C-2 electrodes.

c. Excitation at 20 amps in an argon atmosphere was employed.

d. Kodak 103-0 photographic plates were used to record the spectra obtained from a 10 sec. and a 30 sec. exposure.

e. The spectra were visually examined for the presence of contaminant volatile elements.

APPENDIX - D

Diagram and description of M & S gas jet

APPENDIX - D

DETAILED DESCRIPTION OF NEW MARGOSHES AND SCRIBNER GAS JET CONSTRUCTED FOR THIS INVESTIGATION

Refer to figure next page for detailed drawing of M & S gas jet.

A:- Stainless steel top section machined to allow complete circulation of water necessary for cooling when high amperage excitation is used with pure argon flowing through the device.

B:- Aluminium section inserted between water cooled top and perspex body. Necessary as water leaks developed when perspex body was in direct contact with stainless steel top.

C:- Perspex body of gas jet.

D:- Electrode holder machined from stainless steel. Water cooled. Different diameter electrodes can be accommodated by changing the collet (G).

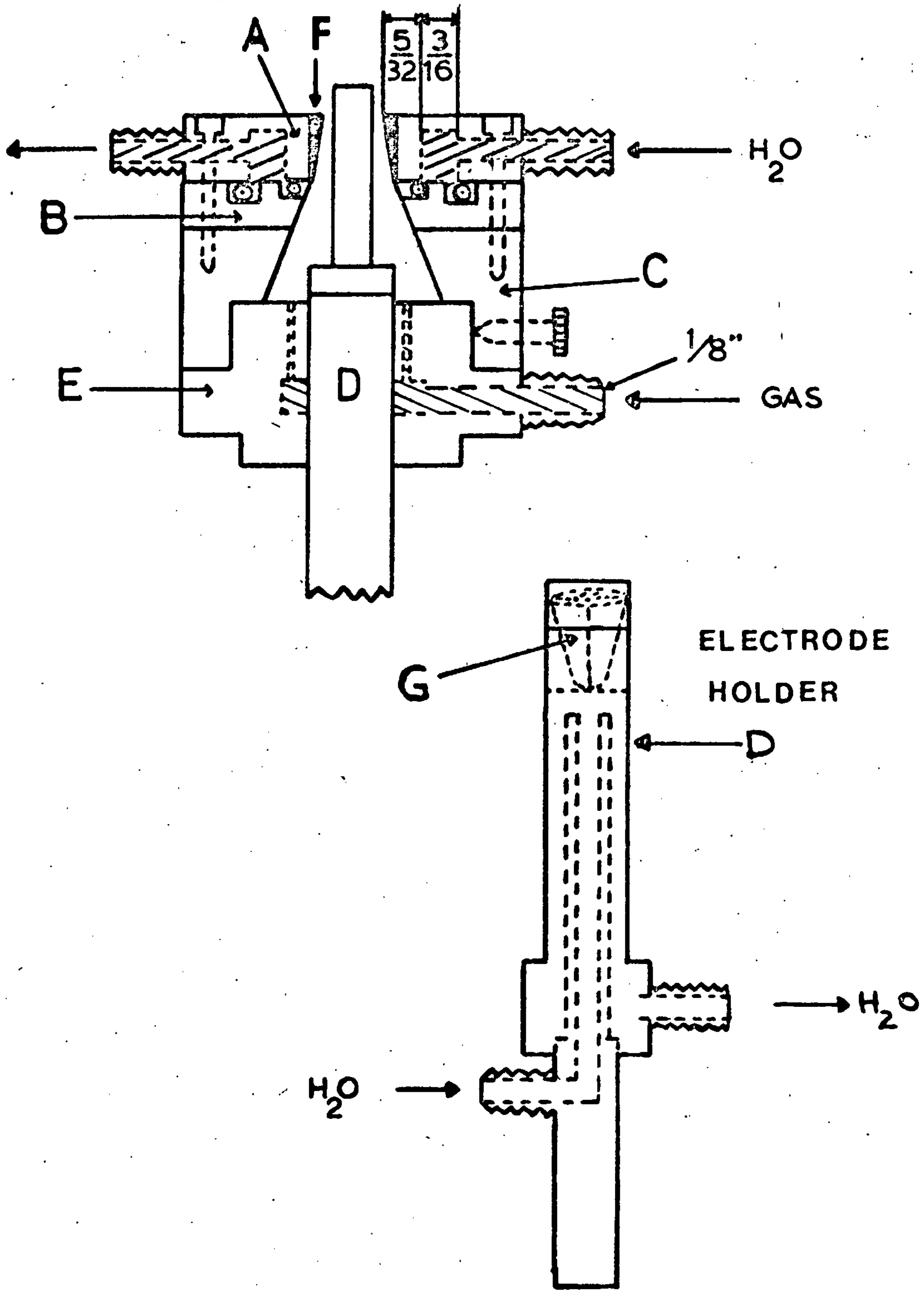
Electrode holder is clamped in lower electrode jaws of arc stand. Gas device is mounted to side walls of arc stand and thus the lower electrode holder can be adjusted independently. It is possible to maintain a constant arc gap during excitation.

E:- The base plate machined from aluminium rod and designed to ensure laminar flow of gas up past the lower electrode.

F:- Variable size ring insert which ensures that gas flow past electrodes of different diameter is similar.

There are two neoprene O rings between the stainless steel top (A) and aluminium section (B). These O rings form the watertight seal between section (A) and (B).

APPENDIX - D



M&S GAS JET