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CENTRO DE ENGENHARIA QUÍMICA
CEQ APE 009

INSTITUTO DE ENERGIA ATÔMICA
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ABSTRACT

A method has been developed for the determination of trace elements in horse hair The hair is cleaned with acetone and EDTA and dried The clean hair is ashed inside a muffle furnace The ash is dissolved in pure nitric acid and the solution is dried on graphite powder Standards are prepared on graphite powder synthetically, Standards and samples are loaded in an under cut shallow cup electrode of Scribner Mullins type A DC arc excitation is used and the spectra are recorded on a Jarrel Ash grating spectrograph Elements found in the hair are Ag Al B Ca Cu Fe Mg Mn Na P Pb Si Ti V and Zn The precision of the determinations has been calculated

1 – INTRODUCTION

The analysis of human hair has been reported in literature extensively On the other hand there is a lack of knowledge about the trace elements in the hair of farm animals like horse In veterinary science the knowledge of trace elements in biological materials of farm animals is important from the point of view of their production feeding and health requirements The trace element analysis of hair has a further possibility of helping forensic sciences as hair seem to be capable of storing the quantities of elements in excess concentration

1 1 – Scope

The method is intended for the quantitative detection and subsequent quantitative determination of trace elements in horse hair By adjusting the amount of hair being ashed the determination range can be varied If proper ashing methods are used the method will be useful for the analysis of all biological materials like human hair tissues urine blood etc

1.2 – Previous Instrumental Methods

Many instrumental methods have been used for the analysis of human hair and other biological samples The methods include among others the atomic absorption spectrophotometry (AAS), optical emission spectroscopy (OES), mass spectrometry (MS) neutron activation analysis (NAA) and X-ray fluorescence (XRF) spectrometry Of these, the AAS and NAA have been more frequently used

Table I give the elements determined by various workers using AAS The number of elements determined by AAS depends on the availability of hollow cathode lamps (HCL) It is necessary to change the HCL every time a new element is to be determined and thus the AAS has a limited scope for multielemental analysis

Table II lists the elements determined by NAA method For NAA analysis the samples have to be irradiated in a reactor, at times for as long as 2 to 3 days Though sensitivities obtained in NAA

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Table I

Elements Determined in Biological Materials by Atomic Absorption Spectrofotometry (AAS)

Nº	Author/s	Reference	Elements Determined
1	ALDER, J F	1	Ag Al, Co, Cr, Cu, Fe, Mn Ni and Si
2	ALDER, J F et alii	2	Al Co Cr, Fe, Mn, Ni, Pb and Si
3	ANDERSON, D H et alii	3	Hg
4	BACKER E T	4	Zn
5	CLARK A N and WILSON, D J	8	Pb
6.	GIOVANOLI, T J et alii	12	Hg
7	GRAEF V	13	Pb
8	HARRISON, W W et alii	17	Ca, Cu, Fe, Mg and Zn
9	HARRISON, W W et alii	18	Cu, Fe, Mg and Zn
10	HELSBY C.A.	20	Hg
11	HENDZEL, M R	21	Hg
12.	HILDEBRAND, D.J and WHITE, D H	23	Ca, Cu, Mg and Zn
13.	HOELLERER, G	24	Hg.
14	LAN, H K Y and ASHMEAD, H	28	Ca, Cd, Co, Cr, Cu, Fe, K, Li Mg Mn, Na, Pb and Zn
15	SORENSON, J R.J	41	Cu, Cd, Pb and Zn.
16	ULLICI, P A and HWANG, J Y	43	Cd

Tabela II

Elements Determined in Biological Materials by Neutron Activation Analysis (NAA)

Nº	Author/s	Reference	Elements Determined
1	BADER H and HEDRICH E	6	Hg
2	BETTERIDGE D	8	Se
3.	BYRNE A R	7	Sn
4	COLEMAN R F et alii	9	Ag Au Be, Br, Ca, Cl, Cr, Cu Hg I, Mn Na Sb, Sc and Zn
5	HEALY W B and BATE L C	19	Mo
6	HUANG C W et alii	25	Ag As, Au, Cd Co Cu Fe Ga Hg In La Mn Ni, Sb Se Sr and Zn
7	JERVIS R E et alii	26	Cd
8	MAGNO P J and KNOWLES F E	30	Sr
9	MINAGAWA Y and KAMEGAYA K.	32	As.
10	NAUMANN M and ZIMMERSCHIED K	33	Pb
11	QUITTNER P et alii	36	Al Cl Mg Mn and Na
12.	RUF, H and ROHDE H	37	Hg
13	SAVEL P	39	As.
14	SMITH H	40	Sr
15	SIVERSEN, T M and SYVERSEN, G B	42	Cd
16.	WYTTENBACH A. et alii	46	As.
17	YEH S J et alii	47	Hg

analysis are very low the associated problems of activity and chemical separation necessitate the determination of only one or two elements at a time

Table III gives the elements determined in biological sample using XRF MS spectrophotometry combustion and other methods

Table III

Elements Determined in Biological Samples Using X-Ray Fluorescence (XRF), Mass Spectrometry (MS) And Other Methods

Nº	Author/s	Reference	Method Used	Element Determined
1	CORTIVO, L.A D et alii	10	Spectrofotometry	As
2	FUJITA M et alii	11	Combustion	Hg
3	GRIFFON, H	14		As
4	HARRISON W W and CLEMENA G G	16	MS	Cu Fe, Mg and Zn
5	HEN KENS C H and MEBIUS L J	22		Mn
6.	KAMEL S H	27	Colorimetry	Ca and P
7	MENKE, H et alii	31	XRF &NAA	Comparison
8.	NISHI S et alii	34	Combustion	Hg
9	VOLKOVIC, V et alii	44	XRF	Trace along hair
10	WALTER, R L. et alii	46	XRF	Co, Cu, Pb, Mn and Zn
11	YURACHEK, J P et alii	48	MS	20 elementes.
12	ZEITZ, L. et alii	49	XRF	Ca, S and Zn

Using OES only four methods are reported for human hair analysis There is no method reporting the analysis of horse hair

SAKAMOTO[38] has determined As, Cd Cu, Pb and Zn in human hair by evaporating them on a filament exciting the sample vapour in an electrodeless discharge tube (after mixing it with argon) by microwave source and subsequent OES analysis

LICHTE[29] has determined only As in water, blood, hair and leaves by converting it to AsH_3 passing it through a microwave plasma in a silica tube and measurement at 2350 Å

PRAKASH and HARRISON[35] have determined Pb in hair and liver tissues employing a demountable hollow cathode tube for the excitation of the residues of these samples and further OES analysis

HAMBIDGE[15] has used an AC arc between graphite electrodes for the OES determination of Cr in serum red cells hair and urine

2 – EXPERIMENTAL

2 1 – Outline of the Method

The hair is cleaned with acetone and EDTA (Ethylene diaminetetracetic Acid) and dried The clean hair is ashed in a muffle furnace and the ash is dissolved in nitric acid Pure graphite powder is added to the acid solution and dried on a hot plate The graphite which now contains the trace elements from hair is loaded in an under cut shallow cup electrode The sample is excited in a DC arc and the light from it is dispersed by a 15 000 lines/inch grating and subsequently recorded on photographic plates The intensities of trace elements are compared with those of standards prepared synthetically Palladium is used as an internal standard The working curves are prepared by plotting the element concentration against the intensity ratio of the element to that of internal standard

Intensities of the element line and the internal standard line are calculated

2 2 – Cleaning of the Sample

As there was no literature on the cleaning of horse hair to remove its grease and superficial contaminants contaminants a survey was done to find out the methods used for cleaning the human hair for analytical purposes Table IV shows the reagents used for cleaning human hair by previous workers

Table IV

Method Used for Cleaning the Human Hair

Nº	Author/s	Reference	Reagent/s Used
1	BETTERIDG, D	6	Acetone and Water
2	CLARK, A N and WILSON, D J	8	Hot ethyl ether or detergent or EDTA
3	COLEMAN, R F et alii	9	Ethyl ether
4	GIOVANOLI, T J et alii	12	Detergent and water
5	HARRISON, W W et alii	18	Detergent and water
6.	HILDEBRAND, D D and WHITE, D H	23	Normal treatment.
7	KAMEL, S H	27	Water and light petroleum
8.	SORENSON, J R.J et alii	41	Water, acetone and ethyl ether
9	YEH, S.J et alii	47	Acetone and metanol mixture.

We preferred to use acetone to remove any grease from hair and then wash it with EDTA to remove the superficial contaminants EDTA was earlier used by CLARK and WILSON[8] for the determination of Pb in human hair and they found it to be better than ethyl ether and detergent in removing the surface contamination

The method of washing used in the present study is that hair is put in a pyrex beaker and immersed in acetone for one hour During this period the hair is agitated by a spatula intermittently The acetone is then thrown out and the hair is immersed in EDTA solution for another hour being agitated intermittently The EDTA solution is drained the hair is taken out put on a filter paper and allowed to dry

2 3 – Preconcentration of the Sample

Five hundred milligrams of washed sample is weighed and placed in a platinum crucible The crucible containing the sample is put inside a muffle furnace (Thermolyne type 2000) This furnace has a Dubuque II temperature controller and can operate up to a maximum temperature of 1200°C The temperature of the furnace is first adjusted to 300°C and the hair is allowed to burn at this temperature for 30 minutes The temperature of the furnace is then raised to 450°C and the sample is allowed to stay at this temperature for 4 hours The sample is taken out of furnace and dissolved in pure nitric acid (minimum amount) One hundred milligrams of pure graphite powder is added to the acid solution and a minimum amount of distilled water is added enough to wet the sample The sample is then put for drying on a hot plate The graphite is taken out of the crucible and it now contains trace elements from hair concentrated five times

2 4 – Preparation of the Standards

As the number of elements present in horse hair was not known it was decided to use Spex Mix powder to prepare standards so that there is wide scope for detection and determination of many elements The Spex Mix contains 49 common elements listed in Table V

Table V

Elements Present in Spex Mix Powder

Ag, Al, As, B, Ba, Be, Bi Br, Ca, Cd, Ce, Cl Co, Cr, Cs, Cu, F, Fe, Ga, Ge Hg, I, In Li, Mg, Mn, Mo, Na, Nb Ni, P, Pb, Rb, Sb, Se, Si, Sn Sr Ta Te Tl Th Ti U, V, W Zn and Zr

In this powder the compounds of elements are mixed so that each element is present at the concentration of 1 28% in the mixture When 100 parts of Spex Mix powder are added to 1180 parts of graphite powder, this results in a standard which contains 0 1% (1000 ppm) of each element Further standards containing 500 200 100 50, 20 10, 5, 2 and 1 ppm for each element are prepared by dilution of higher standards with graphite

2 5 – Choice of Internal Standard

As the standards contained most of the common elements and the matrix element graphite could not provide a suitable line wich could be used as an internal standard the choice was left to rare earth elements or the noble metal elements Of these, a noble metal element palladium was preferred from other elements as it gives only 6 lines in the region 2400 to 3300 Å when present at the concentration of 0 001% Therefore, an internal standard mixture containing 0 002% of Pd, added as ammonium chloropalladite ($(NH_4)_2PdCl_4$), on graphite was prepared This mixture is added to sample and standards in the ratio 1 1 to provide 0 001% Pd as internal standard

2 6 — Choice of the Electrode and Volatilisation Studies

As the trace elements expected in horse hair were of both volatile and refractory nature it was necessary to use the complete burn method of spectrographic analysis in order not to lose any element Electrodes of Scribner Mullins type like L 4030 of Union Carbide Corporation New York are suitable for this purpose A volatilisation study using racking plate method with this electrode showed that the refractory elements continue to volatilise from the graphite matrix even up to 75 seconds An exposure of 75 seconds was considered high because it produces excessive background for the spectrum This electrode was therefore modified by under cutting it This modification resulted in quicker volatilisation and most of the intesity even for the refractory elements was obtained in 30 seconds Table VI shows the comparative volatilisation behaviour of these electrodes viz a deep cavity electrode a shallow cup electrode and an under cut shallow cup electrode The deep cup electrode used in these volatilisation studies was specially prepared in the laboratory and has a crater wall depth of 4 mm as against 0 8 mm for commercially available L 4030 electrode Based on this study L 4030 electrodes were used for the analysis after under cutting them

2 7 — Experimental Conditions and Equipment

Spectrograph	Jarrell Ash Company 3 4 m grating spectrograph with an Ebert mount
Grating	15 000 lines/inch having a reciprocal linear dispersion of 5 Å/mm in the first order and 2 5 Å/mm in the second order
Grating angle	10 00
Wavelength region	2300 — 3500 Å in the Second order
Slit Width	10 μ
Pre exposure	Nil
Exposure time	30 seconds
Electrodes	Anode, AGKSP L 4030 of Union Carbide Corporation (UCC) under cut at 4 mm from the top of the cup Pedestal, AGKSP 9068 UCC Cathode AGKSP L 4038 UCC
Excitation Source	DC arc from Standard Varisource of Jarrel Ash Co
Current	10 amperes
Charge	10 mg
Analytical gap width	4 mm
Photographic plates	Kodak SA 1 two plates
Photographic processing	Plates are developed for 3 minutes at 18°C using Kodak D 19 developer fixed in Kodak F-5 fixer, washed and dried
Densitometer	Comparator microphotometer of Jarrel Ash Co, non-recording type having both transmission and density scales

Table VI

Percent Volatilisation of Impurities from Graphite for Diferent ARC Periods Using Scribner Mullins Electrodes of Different Cup Depths and Shapes

Element	Arc period, Seconds	Percent Volatilisation		
		Deep Cup	Shallow Cup L 4030	L 4030 Under Cut
Fe	0 – 15	38 8	65	92 2
	15 – 30	13 2	18 3	7 8
	30 – 45	13 6	7 8	0
	45 – 60	15 4	4 9	0
	60 – 75	19 1	3 8	0
Mg	0 – 15	48 3	85 8	92
	15 – 30	23 2	7 8	8
	30 – 45	16 1	3 8	0
	45 – 60	8 4	3.1	0
	60 – 75	3 9	0	0
Mn	0 – 15	52 4	92 7	93 3
	15 – 30	25 5	4 1	5 1
	30 – 45	11 4	1 3	1 8
	45 – 60	6 3	1 0	0
	60 – 75	4 1	0 9	0
Si	0 – 15	42	66	81
	15 – 30	17 3	11	11
	30 – 45	15.7	8 3	8
	45 – 60	13 3	7 5	0
	60 – 75	11 6	7 1	0

Calibration of plates — Emulsion is calibrated by an iron spectrum photographed through a seven step rotating sector with a step ratio of 2 1

2 8 – ANALYTICAL LINES

The analytical lines and the estimation range in which these lines are useful are given in Table VII Two internal standard lines one for each plate were used and the same are also listed in this table

Table VII

Analytical Lines and Estimation Range

nº	Element	Analytical Line Å	Estimation Range ppm	Remarks
1	Aluminium	2567 99	100–1000	–
2	Antimony	2598 06	20–1000	SQ
3.	Arsenic	2780 20	50–1000	SQ
4	Beryllium	3131 07	1– 50	SQ
5	Bismuth	3067 72	5– 500	SQ
6.	Boron	2497 73	4– 100	–
7	Cadmium	3261 06	50–1000	SQ
8	Calcium	3158 87	20–1000	–
9	Chromium	2835 63	5–1000	SQ
10	Cobalt	2424 93	10–1000	SQ
11	Copper	3273 96	1– 50	–
12	Gallium	2943 64	5– 500	SQ
13	Iron	2599 57	10– 500	–
14	Lead	2833 07	50– 500	–
15	Magnesium	2779 83	25– 520	20 ppm R
16	Manganese	2605 69	1– 100	–
17	Molybdenum	3132 59	10–1000	SQ
18.	Nickel	3050 82	10–1000	SQ
19	Phosphorus	2534 01	200–1000	–
20	Silicon	2435 16	60–1050	50 ppm R
21	Silver	3280 68	1– 20	–
22	Sodium	3302 99	100–1000	–
23.	Tin	2839 99	5–1000	SQ
24	Titanium	3199 91	10– 200	–
25	Vanadium	3183.41	35– 225	25 ppm R
26.	Zinc	3282 33	100–1000	–
27	Palladium	2476.42	Int. Std.	Low λ plate
28	Palladium	3242 70	Int. Std	High λ plate

SQ = Semi quantitative — R = Residual

All the 26 elements listed in Table VII were looked for and out of these 15 were found in horse hair

2 9 – Working Curves

The working curves for 15 elements found in horse hair were drawn and are shown in Figures 1 – 8 The working for Al and Ca were drawn but, as the amount of these elements in the sample was more than the highest standard only a semiquantitative estimate on extrapolated curve was done The working curves for other elements listed in Table VII can be drawn but were not drawn because these elements were not present in the horse hair

3 – RESULTS AND DISCUSSION

3 1 – Precision

The precision of the determinations was calculated in terms of relative standard deviation from 11 values of intensity ratios The relative standard deviation values for different elements are listed in Table VIII

3 2 – Analysis of Horse Hair

The analysis of horse hair in ppm and percent is given in Table IX

3 3 – Discussion

It is seen that the capability of OES method to do a simultaneous multielemental trace analysis was not utilised till now for the analysis of hair (human or animal) This capability of OES method has been utilised in this work In the present work 13 elements were determined quantitatively 2 elements semiquantitatively and 11 other elements were quantitatively looked for and found to be below our detection limits This 26 elements were looked for and 15 of these were found to be present and estimated in the horse hair

4 – CONCLUSIONS

Spectrographic trace element analysis is being reported for the horse hair for this first time A very simple method has been developed for the purpose This method can first qualitatively look for the elements present and then estimate them quantitatively This method will be suitable for all types of biological sample like liver, tissues, urine etc after these are ashed properly

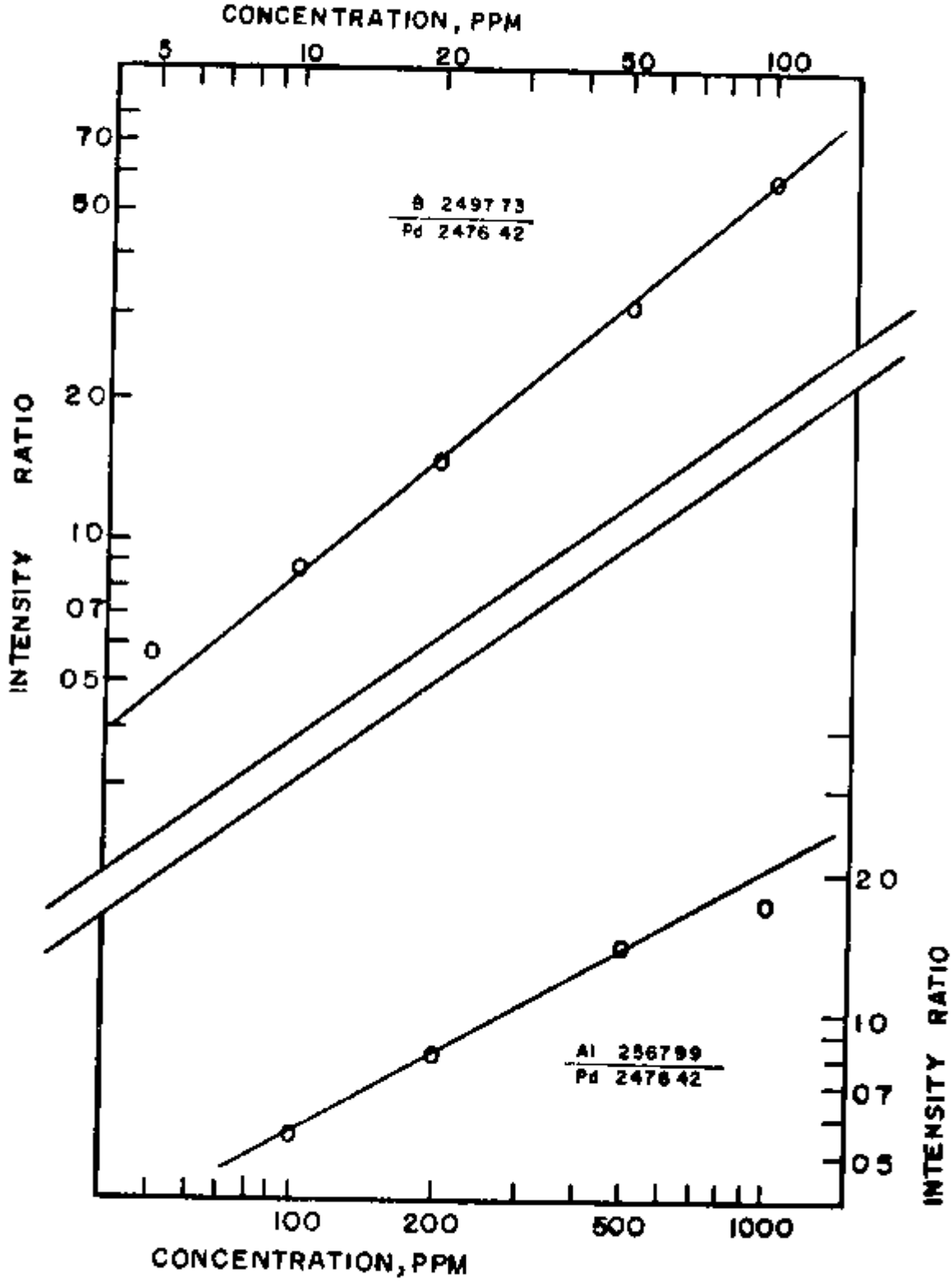

Figure 1 — Working Curves for Al and B

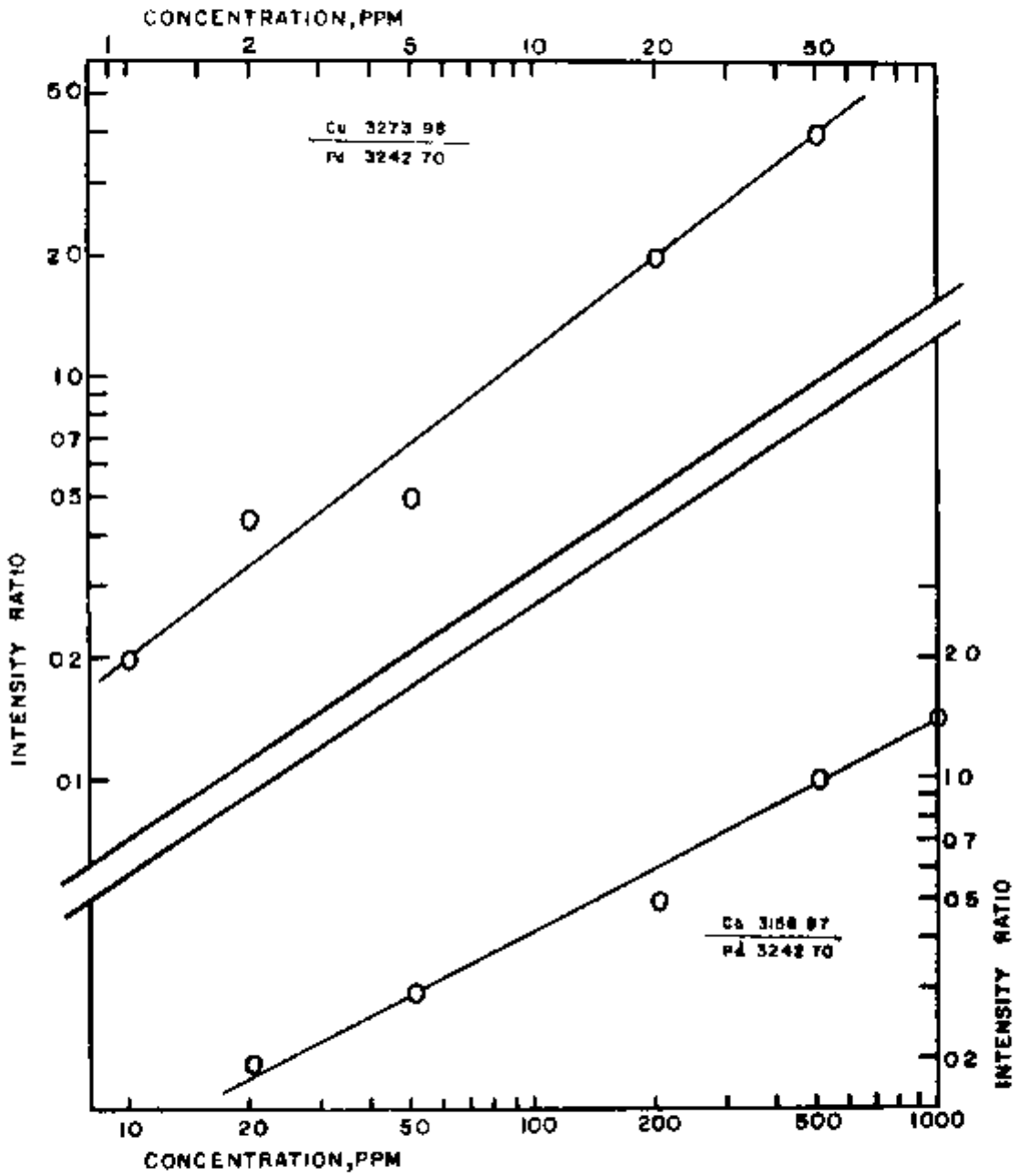

Figure 2 — Working Curves for Ca and Cu

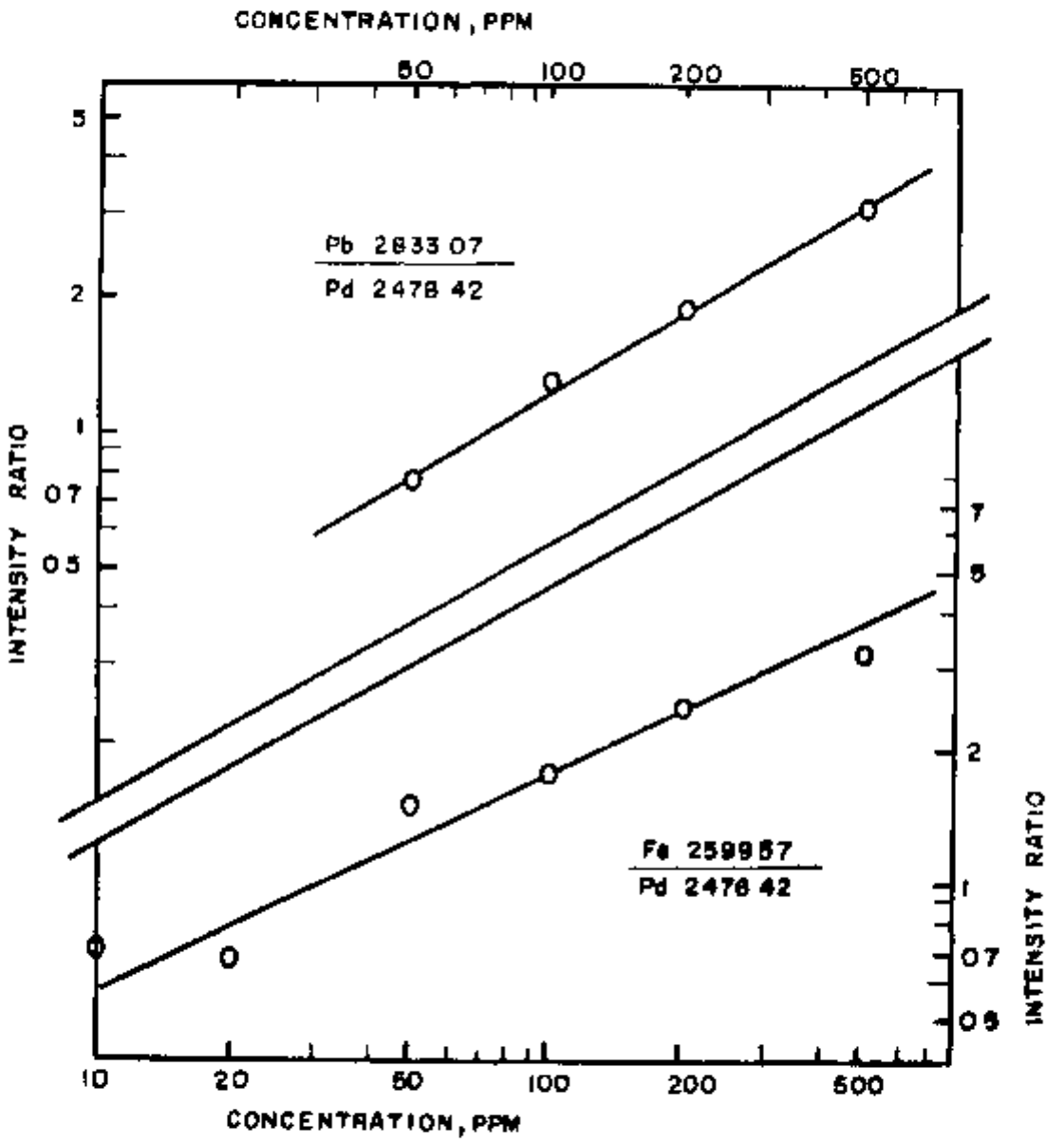

Figure 3 — Working Curves for Fe and Pb

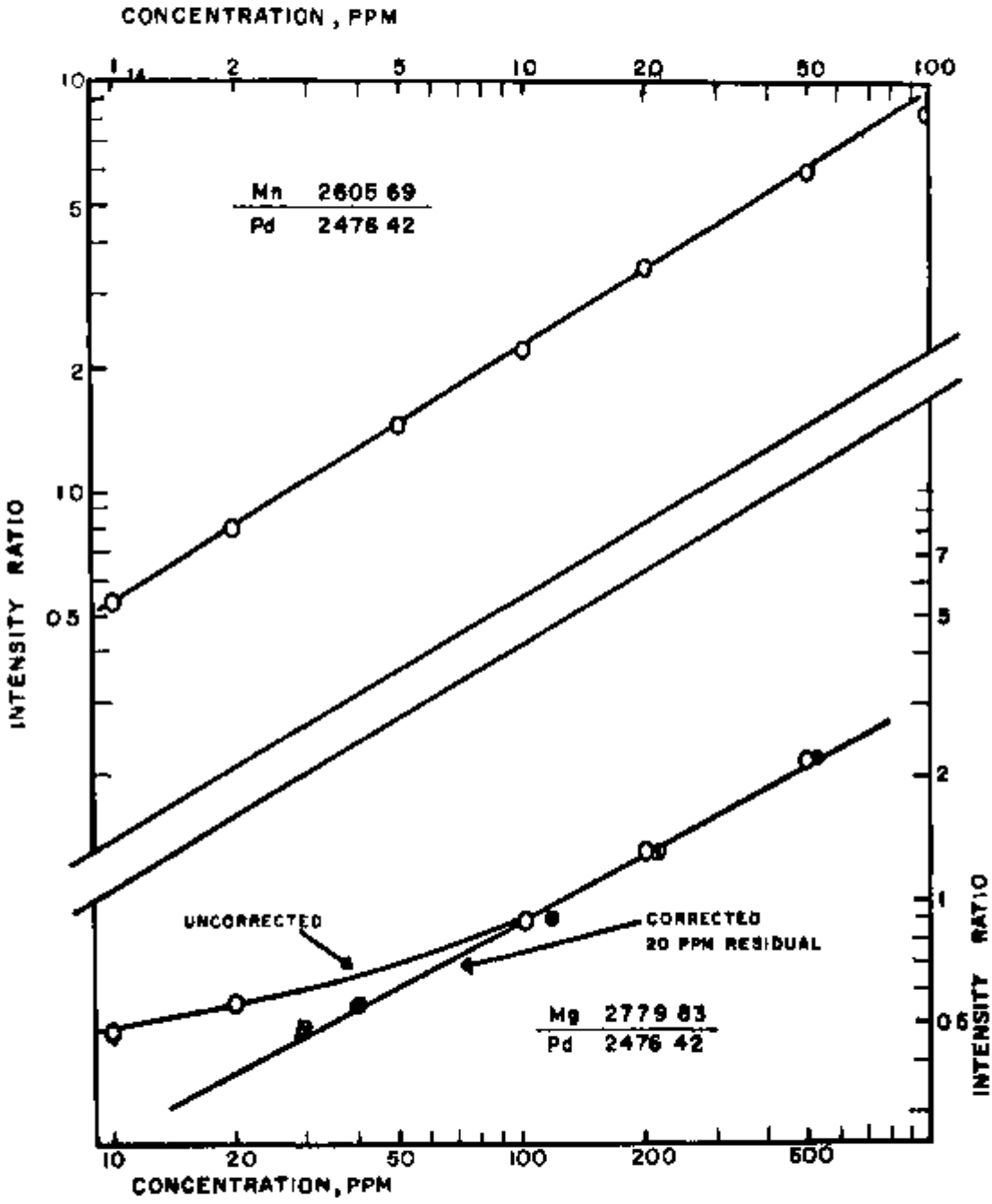

Figure 4 — Working Curves for Mg and Mn

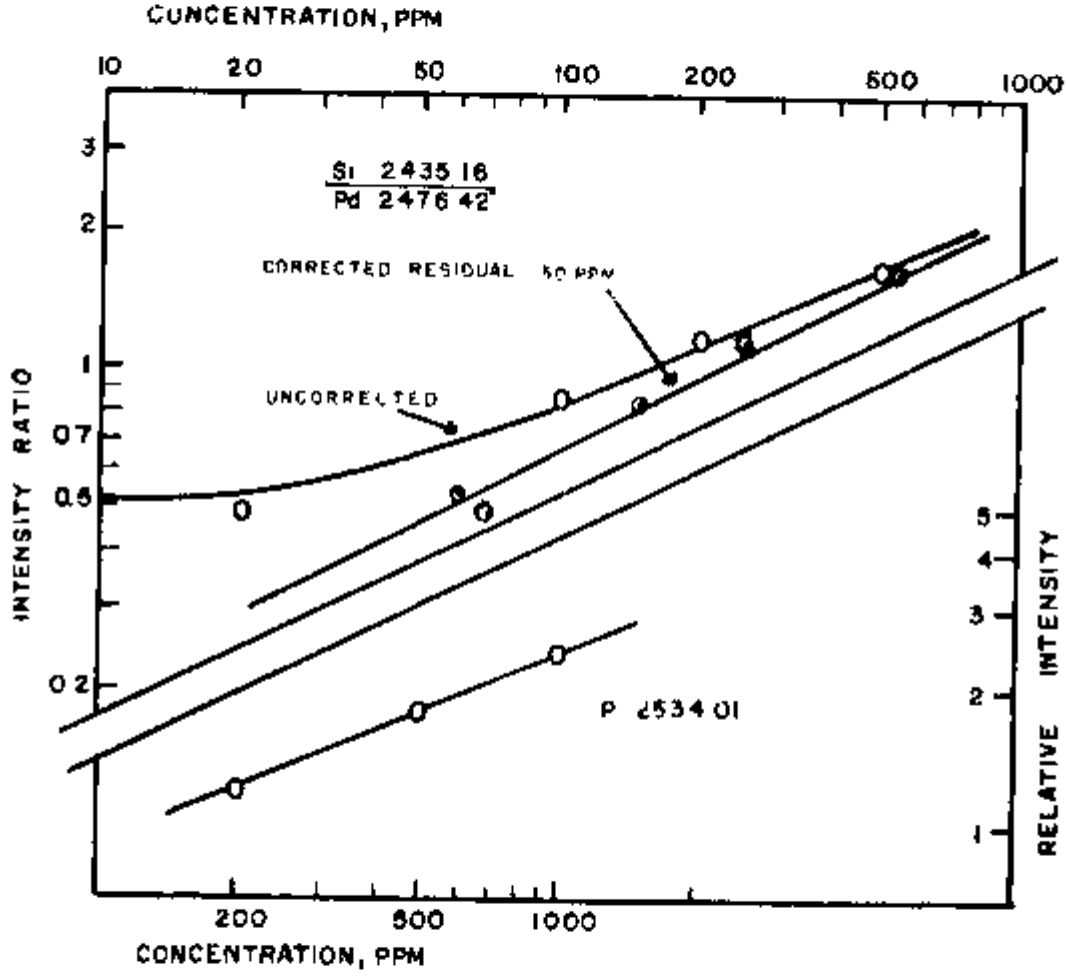

Figure 5 — Working Curves for P and Si

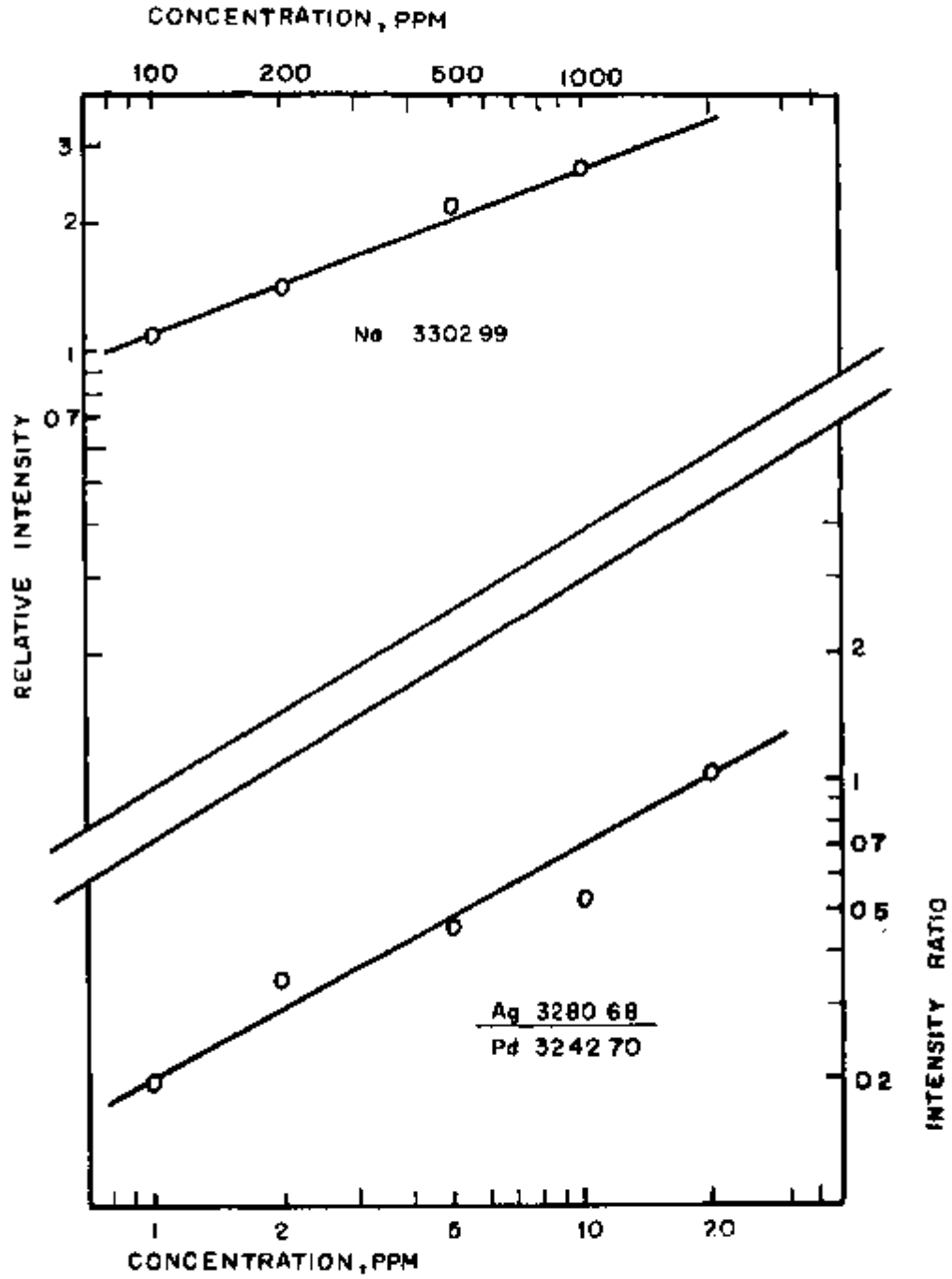

Figure 6 — Working Curves for Ag and Na

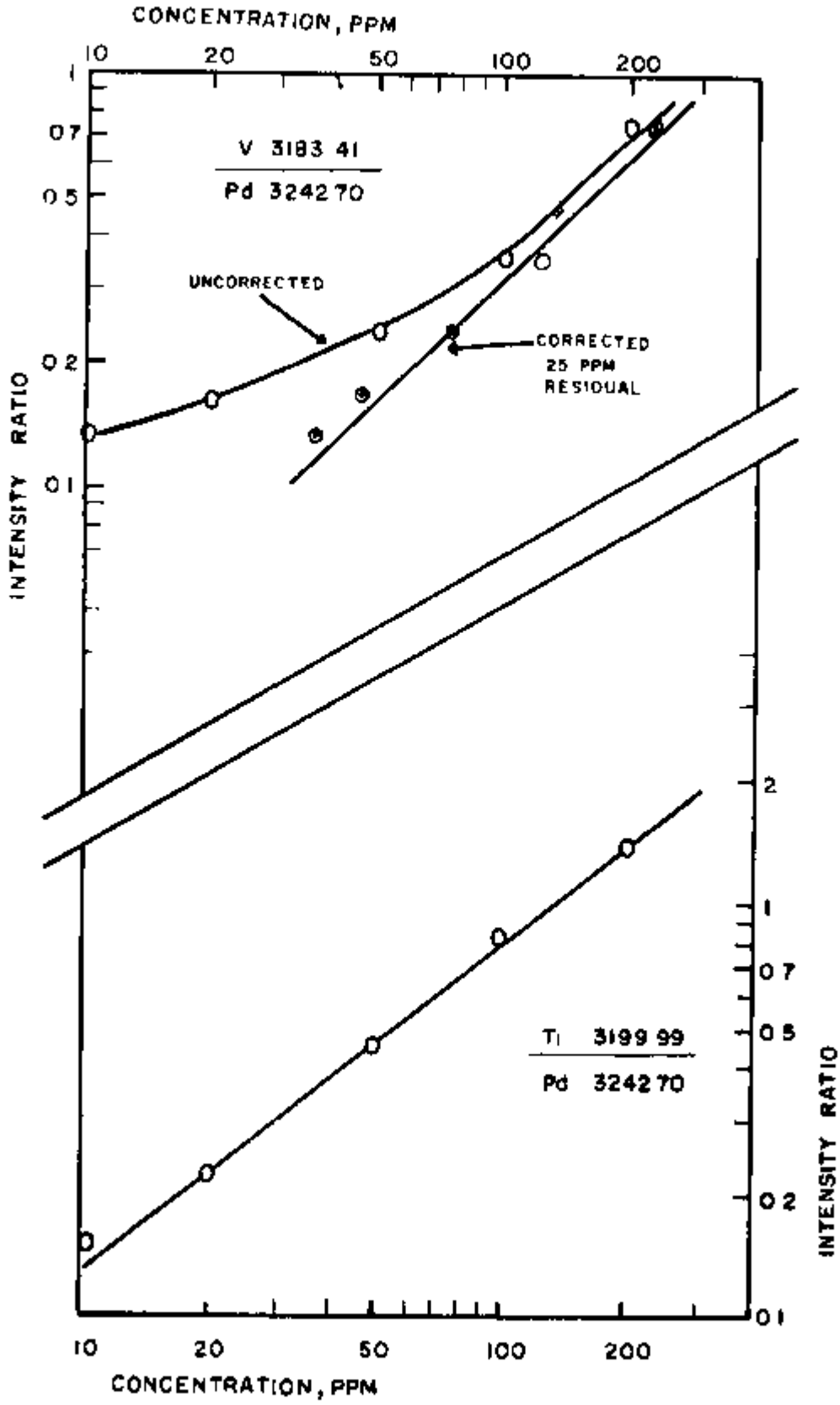

Figure 7 – Working Curves for Ti and V

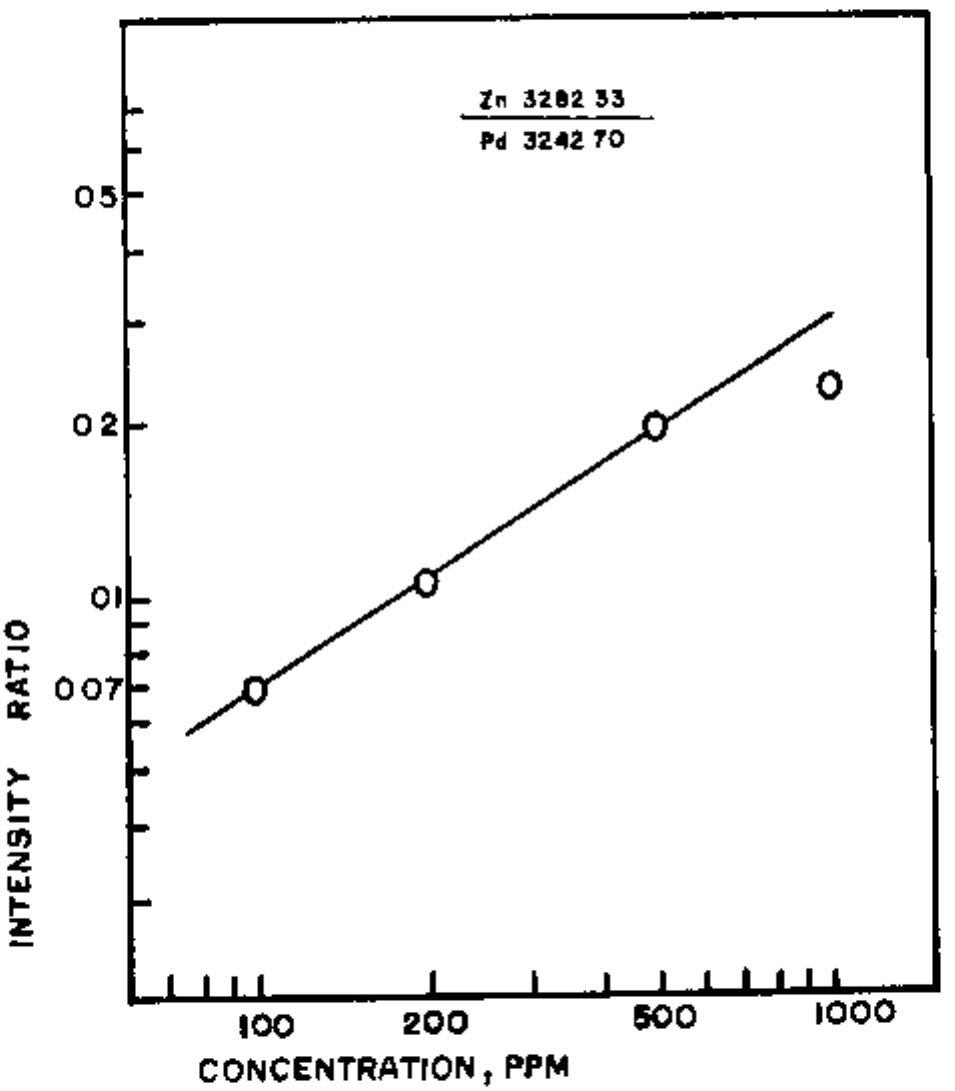

Figure 8 -- Working Curve for Zn

Table VIII

Precision

nº	Element	Standard Deviation %
1	Aluminium	15
2	Boron	14
3.	Calcium	24
4	Iron	16
5	Lead	10
6	Magnesium	10
7	Silicon	10
8.	Titanium	10
9	Vanadium	11

Table IX

Analysis of the Horse Hair

Nº	Element	Value on graphite	Value on hair	
			ppm	%
1	Aluminium*	4500	900	0 09
2	Boron	15	3	0 0003
3.	Calcium*	2000	400	0 04
4	Copper	50	10	0 001
5	Iron	350	70	0 007
6	Lead	300	60	0 006
7	Magnesium	1000	200	0 02
8.	Manganese	25	5	0 0005
9	Phosphorus	750	150	0 015
10	Silicon	1000	200	0 02
11	Silver	50	10	0 001
12.	Sodium	1000	200	0 02
13.	Titanium	25	5	0 0005
14	Vanadium	100	20	0 002
15	Zinc	1750	350	0 035

* only a semiquantitative analysis on extrapolated working curve was done.

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RESUMO

Apresenta-se um método para determinação espectográfica de elementos traços em pelo de cavalo Lava-se o pelo com acetona e EDTA seca se e calcina-se em uma mufla Dissolve-se a cinza em ácido nítrico e em seguida, seca-se a solução resultante em uma matriz de grafita em pó Os padrões são preparados sinteticamente com grafita em pó Utilizam se eletrodos do tipo Scribner Mullin de cratera pouco profunda com corte sob a base Emprega se um espectrógrafo de retículo plano da Jarrel Ash e a excitação se faz por meio de um arco de corrente contínua Detectaram se os seguintes elementos em uma amostra analisada Ag Al B Ca Cu Fe Mg Mn Na P Pb Si Ti V e Zn Apresentam se os resultados de precisão para vários elementos em termos do coeficiente de variação

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INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11049 – Pinheiros
CEP 05508
01000 – São Paulo – SP

Telefone 211-6011
Endereço Telegráfico – IEATOMICA
Telex – 011 23592 IENA BR