An analytical survey of raw bullion from South African gold mines by mass spectrography

A. STRASHEIM D.Sc. (Stellenbosch)* (Visitor),   P. F. S. JACKSON B.Sc. (Manchester)† (Visitor)

SYNOPSIS

In the survey "Analysis of South African raw bullion" the distribution of trace elements within the bullion have been shown to be distinctively dependent on the extraction process.
In general the amalgamation process produces the more impure bullion with respect to trace elements. Some chemical and physical explanations are given for the differences that have been observed in the raw bullion as received at the Rand Refinery.
The value of the spark source mass spectrographic technique in the study of the elemental impurities in bullion is demonstrated.

SINOPSIS

Die opname „Analise van Suid-Afrikaanse onbewerkte staafgoud" het aan die lig gebring dat die verspreiding van spoor elemente in staafgoud beslis afhanklik is van die herwinnings proses.
Staafgoud geproduseer deur die amalgamasie proses, is in die algemeen meer onsuiwer wat spoor elemente betref. Sekere chemiese en fisiese verklarings word dus aangewend vir die verskille wat opgemerk is by die onbewerkte staafgoud wat deur die Randse Raffinadery ontvang word.
Die waarde van die vonk bron massa spektrografiese tegniek by die studie van die elementêre onsuiwerhede in staafgoud word ook gedemonstreer.

INTRODUCTION

Gold is extracted from the parent rock at the mine by two processes, the amalgamation process and the cynide process. The raw bullion is then despatched to the Rand Refinery where it is further purified. Raw bullion thus received by the Rand Refinery is known to contain associated silver, copper, lead and other elements ranging in concentration from a few parts per thousand million to a few per cent.

With the advent of the electrolytic process of gold refining by which gold of ultra-pure (99.999+) quality can be produced, coupled with the increasing demand for such high purity from specialized industries, it was considered highly advisable that the trace elemental characterisation of South African gold be established. Such a project would enable the selection of the optimum starting material to be made not only in terms of initial purity of the raw bullion but also in terms of a prior knowledge of the refining time equilibrium of each element.

The work divides naturally into two parts:
1. The trace characterisation of South African bullion.
2. Refining time studies of selected elements.

In the first category the work further sub-divides into a study of the application of spark source mass spectrography to the analysis, a study of the ultimate precision

which may be attained and finally a commentary on the initial results. The advantages of the application of such a technique are obvious. No other technique displays simultaneously most of the naturally occurring elements to such a limit of detection (ca. 0,001 ppm). The elements all display approximately the same sensitivity and hence semi-quantitive analyses can be obtained rapidly with no corrections for blank values, etc., which are corollaries to most other analytical methods which achieve this detection limit. The technique produces a permanent record which can be consulted at a later date without re-analysis. It has only one disadvantage in that the cost of a suitable mass spectrograph is high, viz., approximately R100 000. Thus it can be seen that for such a project, where the concentrations of the elements cover such a wide working range, and the elements themselves range from the everyday elements to those normally considered as rare, the mass spectrographic technique is ideal for this particular application.

DESCRIPTION OF TECHNIQUE

The mass spectrographic technique relies upon the physical separation of charged particles (ions) by their successive interaction with an electric and magnetic field. The ions are produced in vacuum by initiating a low voltage discharge between electrodes of the sample material. The ions created by the discharge are accelerated and removed from the spark region by creating a positive electric field between the source and the earth

*Director — National Physics Research Laboratory, CSIR.
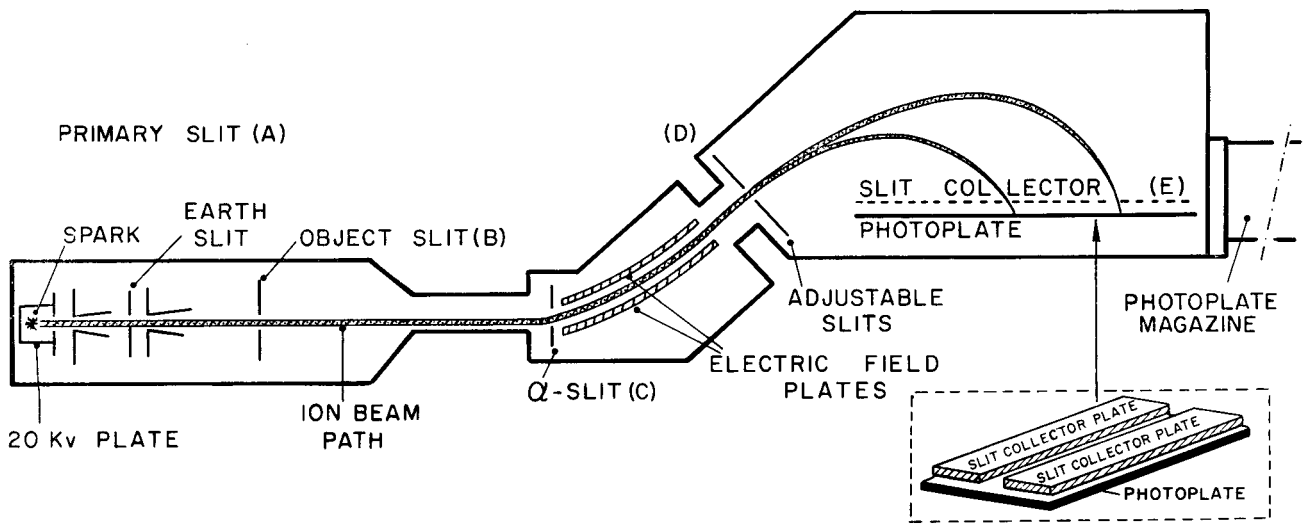†Research Officer, NPRL, CSIR.

PRIMARY SLIT (A)   (D)

SPARK   EARTH SLIT   OBJECT SLIT(B)   SLIT COLLECTOR   (E)
                                                       PHOTOPLATE

                                                       ADJUSTABLE SLITS   PHOTOPLATE MAGAZINE

                                              ELECTRIC FIELD PLATES
                                    α-SLIT (C)

20 Kv PLATE   ION BEAM PATH   PHOTOPLATE

Fig 1

slit. (See Fig. 1). This field drives the positive ions through the primary slit (A) and in doing so accelerates the ions towards the analysing region. The ions then pass through the object slit, (B), the image of which is to be focussed on the detector, a photoplate. These ions, which possess an energy distribution according to Druyvenstein,[1] enter the radial electric field at the α slit (C) of the electric field which causes them to travel along radial paths, the radii of which are reflections of their energy. At the exit of this field a slit (D) selects a small portion of this energy spectrum permitting it to pass undisturbed whilst all other energies are lost. The ion beam may now be considered parallel, and of low energy band width.

In order to bring these slightly differing energies to point focus, a magnetic field is used to curve the ions in the opposite direction. The penetration into this field is a function of the energy of the ion. The radius of curvature of the ions is proportional to the square root of the ion-mass and, hence, as the ions are almost mono-energetic, their relative positions in the direction of the ion path on the detector defines the ion-mass. Two

rectangular collector plates (E), between which is a small gap (1,5 mm), are placed parallel to each other just above and parallel to the emulsion surface. An imaginary cross-section through any one of the incoming ion-beams taken normal to the resultant direction of motion would indicate a rectangular profile. The ions contained within the upper and lower ends of this rectangle, whose length, dependent on mass, is approximately 3 mm and whose width, again dependent on mass, approximately 0,05-0,1 mm, are thus seen to impinge on the collector plates, thereby imparting their charge to them. This charge is dissipated to earth through a high resistance and the instantaneous current flowing at any time is taken as a relative beam intensity indication. This current, electrically integrated with respect to time, becomes the relative exposure at that position on the photoplate. A series of exposures is made, such that a very small exposure is followed by increasing exposure length, until all the available thirty vertical positions of the photoplate have been exposed. Thus the mass spectrum appears as a two dimensional representation of concentration and mass (Fig. 2).
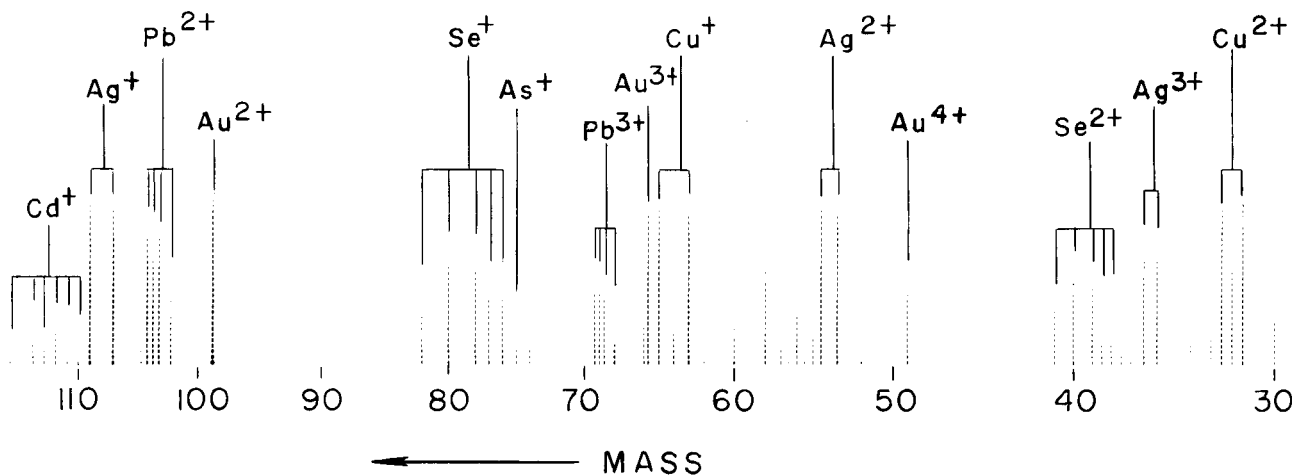

MASS

Fig 2

INSTRUMENT CONDITIONS

The instrument is fitted with two object slit positions. These enable a slit width of either 10 microns or 300 microns to be selected externally. In the case of the 10 micron slit, resolutions of greater than 25 000 can be recorded. However, under these conditions the spectral line width is reduced to two or three grain widths of the emulsion, and hence any value obtained for the transmission of such a line will be subject to large error. The total ion-current is reduced together with the slit width, and to obtain a detection level of 0,1 ppm, exposure times of several hours would have become necessary.

In the case of the 300 micron slit, the spectral lines become very much wider (ca. 100-200 grain widths) and therefore the transmission measurement of such a line becomes more representative. With this slit-width the ion-current enables exposures, equivalent to a detection level of 0,1 ppm, to be taken in a few minutes.

A feature of the low voltage discharge source is that often the population in the beam of doubly charged ions of any one isotope exceeds that of its singly charged counterpart. This feature can be put to advantage, for by restricting the visible mass range to 110 atomic mass units all the elements can be seen clearly and the line width is again increased, giving a larger area of image for transmission measurement.

The line profile has to be rectangular for optimum precision, but once the optics are set for optimum focus little or no adjustment is required to maintain this position.

Table I contains the instrument settings for the analysis of gold samples.

TABLE I

INSTRUMENT SETTINGS FOR GOLD ANALYSIS

	Reading
Source head position	1,825
Object slit	300μ
Entrance slit	$1\,800\ \mu$
Kugelcondensator voltage (V_A)	$1\,550$ V
Accelerating voltage (V_B)	22,5 kV
Ratio V_B/V_A (Uncalibrated)	470
Magnet current	300
Magnet setting	5/40/00
Magnet entrance slit	FULLY OPEN

EXCITATION CONDITIONS

The low voltage discharge system of ion excitation consists of a high voltage unidirectional initiator pulse (60 Kv) which is followed immediately by a low voltage (60 V), low current (3-10 A) discharge. The discharge current continues to flow at the pre-set current value until the electrical energy stored in the resistor/capacitance chain is drained when the discharge is extinguished.

The network is recharged during the "off" time of the system (> 10 ms/pulse) and a new initiator pulse triggers the event once again. The initiator pulse rate may be set to any value between 1 and 100 pulses/sec.

It was found that at 30 pulses/sec a good ion-beam could be maintained for up to 2-3 hours with very little electrode adjustment and this value was adopted. The magnitude of the current flowing during the discharge also affects the output of the source as indicated in Fig. 3 where the low voltage discharge current is shown with the corresponding source output. From the figure it can be seen that between 4 and 9 amperes the output is independent of discharge current. A value of 4.8 amperes was selected.

The samples being good metallic conductors with low work functions, a very low initiator pulse energy was required. Values available were 0,125, 0,31 and 0,625 Joules/pulse and the lowest initiator energy was selected and proved satisfactory.

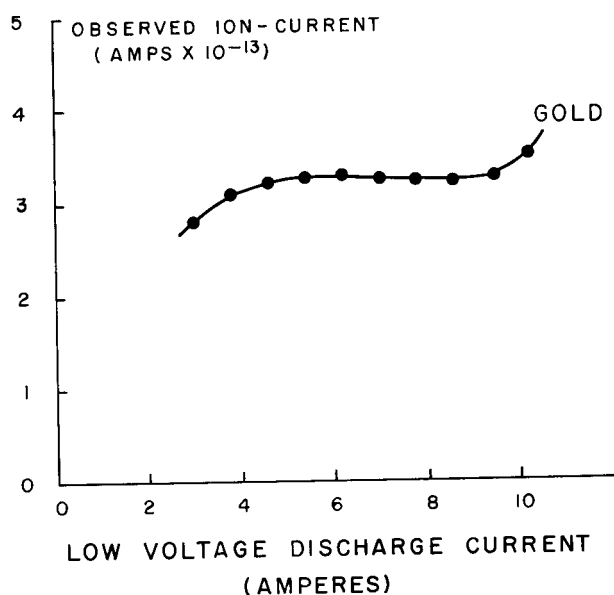A summary of instrumental conditions is presented in Table II.

Fig 3

TABLE II

EXCITATION CONDITIONS FOR THE ANALYSIS OF RAW BULLION

Spark Initiator	0,125 Joules
Spark Voltage	60 kV
Repetition Rate	30 p.p.s.
Low Voltage Discharge Current	6,2 A
Voltage	452 V

SAMPLES

Routine sampling was carried out by Rand Refinery personnel on the varied bullions entering the Refinery. Twenty-nine samples were selected to cover as wide a geographical range as possible. The samples included ten

samples of cyanide process gold, eight samples of amalgamation process gold and one known mixed sample. Ten samples of unidentified processing were also included in the survey.

Realising that gold originating from different reefs might have different elemental compositions, it was felt that with the wide range of samples selected any anomalous samples would be clearly differentiated from their respective gold processing type characteristics and that differences between the gold recovery systems would clearly be outlined. A complete list of the samples extracted, geographical locations and processing detail is given in Table III.

TABLE III

MINE, LOCATION AND PROCESS USED FOR SAMPLES TAKEN BY REFINERY

Sample No.	Mine	Grid reference	Process
1	Western Deep Levels	27242629	Cyanide
2	Buffelsfontein	26522656	—
3	Hartebeesfontein	26522656	—
4	Vaal Reefs	26482657	Mill*
5	Western Reefs	26432657	Cyanide
6	President Brand	26462802	Cyanide
7	Bracken	29072630	—
8	Kinross	29082628	—
9	East Daggafontein	28352617	Cyanide
10	Free State Geduld	26442755	Mill
11	Western Holdings	26432800	Cyanide
12	Loraine	26372746	Mixed
13	Harmony	26512805	Cyanide
14	Durban Roodepoort	27542610	Cyanide
15	Western Areas	27402620	—
16	East Daggafontein	28352617	—
17	Blyvooruitzicht	27222624	Cyanide
18	Elsburg	27392614	Mill
19	West Rand Cons.	27452607	Mill
20	West Driefontein	27262623	Mill
21	Virginia	26542805	Mill
22	Venterspost	27362616	Mill
23	Venterspost	27362616	Cyanide
24	The South African Land	28222616	Mill
25	Bracken	29072630	—
26	Kinross	29082628	—
27	Kinross	29082628	—
28	Kinross	29082628	—
29	Kinross	29082628	—

*Mill process to be read as synonymous to amalgamation process.

SAMPLE PREPARATION

Due to the fact that only small volumes of material are consumed during one analysis ($\sim$2-5 mg) the degree of homogeneity required is very high. To obtain this homogeneity it was essential to extract samples from the molten gold. Similarly, the technique is so sensitive that the introduction of impurities during sampling or during the subsequent electrode forming process was a serious possibility. A method developed in co-operation with the Rand Refinery enabled samples to be taken from the molten material in the required form with a minimum of contamination.

A pre-heated graphite tube of high purity and the required internal diameter (1 mm) was plunged into the molten gold. The end of the tube was then sealed and the tube extracted and the hot end quenched. Rods

10-15 cm long of the correct diameter were exposed on breaking the end of the tube. The extremities of each gold rod were removed and the rod cut into lengths of 1-1.5 cm.

These were then etched in aqua regia for 2-3 minutes to remove traces of impurity from the ends and faces. As the discharge takes place from the ends of the rods care was taken to pre-spark the electrodes long enough to expose virgin material and not to record the analysis of the etched material in case preferential etching had occurred. The electrodes were weighed before and after sparking. From the loss in weight, which was usually of the order of 10 mg, a transmission factor for the spectrograph can be calculated which will be essential when studying the electrolytic gold by electrical detection means for elements which it is anticipated will all be less than 1 ppm.

EXPERIMENTAL

The gold electrodes were mounted in the source region of the spectrograph and the source evacuated. After ten minutes the pressure in the source was normally well below 10^{-6} Torr. At this time the pre-sparking was started and the pre-spark continued for about 10 minutes at the selected excitation conditions.

During this time minor adjustments to the electrode position could be made until the ion-beam was apparently (from readings on the four beam collector plates) in exactly the same position as its predecessor. Only minor adjustments can be made as major adjustments result in changed focus conditions and also changed relative sensitivities. The electrodes should not be moved closer to or away from the entrance slit but their height above the entrance slit and position in the horizontal plane can be altered. After this time thirty exposures were recorded on each photoplate in the available positions. So that the concentration of each ion-species could be assessed, the exposures were recorded in increasing coulombic value until the required detection limit was reached. The limits set for gold analyses were 0,1 ppm at this stage and the thirty exposures were recorded in those ranges which enabled 0,06 ppm to 1 000 ppm to be read from the plate. It was considered that this range represented that in which most of the important impurity concentrations would occur.

For each sample two sets of electrodes were used and the two photoplates developed simultaneously in modified ID 19 developer for 6 minutes and then fixed in the usual manner. Each pair of photoplates was compared and an average concentration for 19 impurities calculated. The results were calculated using the normal mass spectral functions.[2] The results of the experiments are tabulated (see Tables IV, IVA, IVB).

PRECISION OF THE TECHNIQUE

The precision which can be obtained on perfect samples approaches 1 per cent. Statistical analysis of the lead isotopes in gold bullion indicated that values between 1 and 2 per cent may be expected in most cases. The average value which has been quoted in this report

TABLE IV
ANALYSIS OF EIGHT MILL SAMPLES AND ONE MIXED SAMPLE

Atomic No.		11/M/4 Vaal Reefs	2/M/10 Free State Geduld	37/M/18 Elsburg	36/M/19 West Rand Consolidated	4/M/20 West Driefontein	27/M/21 Virginia	24/M/22 Venterspost	31/M/24 South African land	20/CXM/12 Loraine
83	Bismuth	16	5.3	800	1 100	50	300	1.0%	200	212
82	Lead	2.1%	737	1 200	1 800	2 000*	1.1%	4.2%	1.9%	1.8%
80	Mercury	0.1%	10	150	200	40	150	650	850	100
78	Platinum	8	8	10	15	7	10	10	10	2
77	Iridium	0.8	1.5	3	5	2	8	5	10	0.5
76	Osmium	0.7	0.5	1	<0.1	<0.1	2	<0.1	<0.1	<0.2
75	Rhenium	0.14	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
51	Antimony	125	10	100	200	50	200	200	200	62
50	Tin	19	0.6	20	1 000	10	60	60	60	19
48	Cadmium	350	5	2.5	20	0.7	7	7	20	115
46	Palladium	11	14	10	10	10	40	10	7	11
44	Ruthenium	0.26	0.75	<0.1	<0.1	<0.1	4	<0.1	<0.1	<0.1
34	Selenium	8	0.8	4	8	0.5	8	20	8	80
33	Arsenic	570	75	>2 000	2 000	1 000	>>2 000	4 000	1 700	>750
28	Nickel	300	60	2 500	5 000	500	>6 000	3 000	500	450
27	Cobalt	0.6	0.3	700	250	150	1 500	1 500	550	120
25	Manganese	3.3	2.8	30	200	3	100	14	10	28
24	Chromium	0.4	0.4	15	15	5	10	10	10	0.5
23	Vanadium	0.13	0.08	0.3	0.3	1	1	0.3	0.5	<0.08

*Inhomogeneous.

TABLE IV A
ANALYSIS OF TEN CYANIDE SAMPLES

Atomic No.		5/C/1 Western Deep Levels	18/C/5 Western Reefs	3/C/6 President Brand	32/C/9 East Daggafontein	1/C/11 Western Holdings	7/C/13 Harmony	29/C/14 Durban Roodepoort	16/C/15 Western Areas	6/C/17 Blyvooruitzicht	24/C/23 Venterspost
83	Bismuth	0.1	<0.1	<0.1	0.05	<0.1	2	6	0.1	0.4	100
82	Lead	740	380	1 050	3 160	630	4 200	6 300	421	2.5%	2.4%
80	Mercury	7	1	32	10	100	5	1	9	<1	<1
78	Platinum	<0.3	<0.3	<0.3	<0.3	3	<0.3	4	<0.3	1	<0.1
77	Iridium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.5	0.5	5	0.6
76	Osmium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	4	<0.2	2	<0.1
75	Rhenium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5	<0.1	0.5	<0.1
51	Antimony	<0.06	<0.06	<0.06	2.5	<0.06	2.5	25	<0.06	2.5	3.7
50	Tin	<0.09	<0.09	<0.09	0.9	<0.09	<0.09	9	<0.09	3	10
48	Cadmium	5.2	17	5.2	57	14	100	115	14	250	800
46	Palladium	86	6	6	11	6	11	11	4	10	2
44	Ruthenium	0.5	<0.05	<0.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.01	<0.1
34	Selenium	0.8	6	8	24	8	160	60	0.8	250	4 700
33	Arsenic	4.5	4	3	3	0.8	150	150	6	40	200
28	Nickel		4.5	4.5	240	3	60	45	0.3	120	1 700
27	Cobalt	0.15	0.15	0.15	0.15	0.09	0.15	0.45	1.7	0.2	3
25	Manganese	1.7	3.4	3.4	4.2	1.7	6	42	0.5	30	30
24	Chromium	0.25	0.5	0.25	0.25	0.4	0.5	0.4		10	10
23	Vanadium	≤0.1	≤0.1	≤0.1	≤0.1	<0.03	≤0.1	0.1	<0.03	1	0.1

TABLE IV B
ANALYSIS OF TEN UNMARKED SAMPLES

Element	Atomic No.	8/NM/2 Buffelsfontein	15/NM/3 Hartebeesfontein	28/NM/7 Bracken	25/NM/8 Kinross	25/NM/26 Kinross	25/NM/27 Kinross	25/NM/28 Kinross	25/NM/29 Kinross	32/NM/16 East Daggafontein	28/NM/25 Bracken
Bismuth	83	0.1	0.1	<0.1	2	4	2	5	10	<0.1	<0.1
Lead	82	632	3 800	740	740	1 500	1 500	1 500	1 500	1 300	3 200
Mercury	80	10	1	5	45	400	400	35	35	<1	<1
Platinum	78	<0.3	<0.3	6	8	60	60	40	30	<0.1	20
Iridium	77	<0.1	<0.1	0.8	2	12	12	12	12	<0.1	8
Osmium	76	<0.2	<0.2	0.2	0.7	7	7	7	7	<0.1	<0.1
Rhenium	75	<0.1	<0.1	0.1	0.15	2	2	2	<1	<0.1	<0.1
Antimony	51	<0.06	0.6	<0.06	3.1	1	0.5	2	2	<0.1	<0.1
Tin	50	<0.1	<0.1	<0.1	0.3	0.7	<0.1	3	2	0.7	0.7
Cadmium	48	20	20	17	17	40	40	40	40	20	10
Palladium	46	6	13	6	6	3	2	10	10	6	10
Ruthenium	44	<0.05	<0.05	<0.05	0.8	4	2	6	4	<0.1	<0.1
Selenium	34	0.4	24	8	8	20	20	40	40	150	2
Arsenic	33	1	0.7	3	4	11	5	10	5	6	4
Nickel	28	4.5	30	72	60	120	120	120	120	10	20
Cobalt	27	0.15	3	0.45	0.15	3	0.3	3	1	0.6	0.1
Manganese	25	8.5	3	3.5	3	10	3	30	30	2	6
Chromium	24	0.3	0.3	0.6	0.6	10	10	10	10	3	10
Vanadium	23	<0.1	0.1	<0.1	<0.1	0.3	0.5	1	1	0.1	0.2

for all analyses has been found to be within 2-3 per cent of both values as obtained from the plates in most cases. Only in the case of very heterogeneous distribution (e.g., platinum group metals) does this precision worsen appreciably.

DISCUSSION OF THE RESULTS

From the nature of the differences in the two reduction processes, associated differences are to be anticipated in the trace element contents of the raw bullions entering the refinery. These differences may originate in two ways:

1. Differences characteristic of the type of recovery process employed;
2. Differences characteristic of the ore body mined at that particular location.

The differences are discussed in terms of physical and chemical relationships which may exist between the gold phase and the trace element impurities. In some cases periodic group relationships are established.

In order to simplify the identification of process differentiation a histogram presentation of the results (graphs 1-11) is given. It may be assumed that where process differentiation exists the general level of impurity of any element in one process group will differ radically from its counterpart. The results are plotted with concentration on an ordinate logarithmic scale where the mine and process type form the abscissa. Reference is drawn to the several anomalies observed in this classification and explanations where available are proposed.

Bismuth, Antimony and Arsenic — Group 5A elements
(Graphs 1, 2, 3)

From results presented in Graphs 1, 2 and 3 it is clear that in the amalgamation process the residual Group 5A metal content is much higher than in cyanide produced gold. It is known that in the Witwatersrand basin a considerable deposit of iron pyrites is associated with the gold phase. In conjunction with the pyrite smaller amounts of the isomorphous arsenopyrite are to be anticipated and it is presumed that for arsenic smaller concentrations of antimony and bismuth will be found in the same phase. In the case of the bismuth, however, it is suspected that bismuthinite (Bi_2S_3)[3] or bismite (Bi_2O_3) will be associated with the silver to account for the exceptionally high levels of bismuth recorded for some gold mines. The presence of the separate mineral stibnite (Sb_2S_3)[4] cannot be precluded although the levels of antimony suggest this is very low or preferentially removed in processing which is considered unlikely.

As the overall solubility of arsenic in gold is small it is unlikely that the arsenic is in the gold phase at this stage. More likely is the presence of arsenates or arsenides as separated minerals which follow the gold in the amalgamation process. These would not be removed either during amalgamation, where their solubility is favourable, or during smelting where the decreased vapour pressure due to arsenide (cf. arsenic) would prevent sublimation. Similar remarks apply in the case of antimony and bismuth.
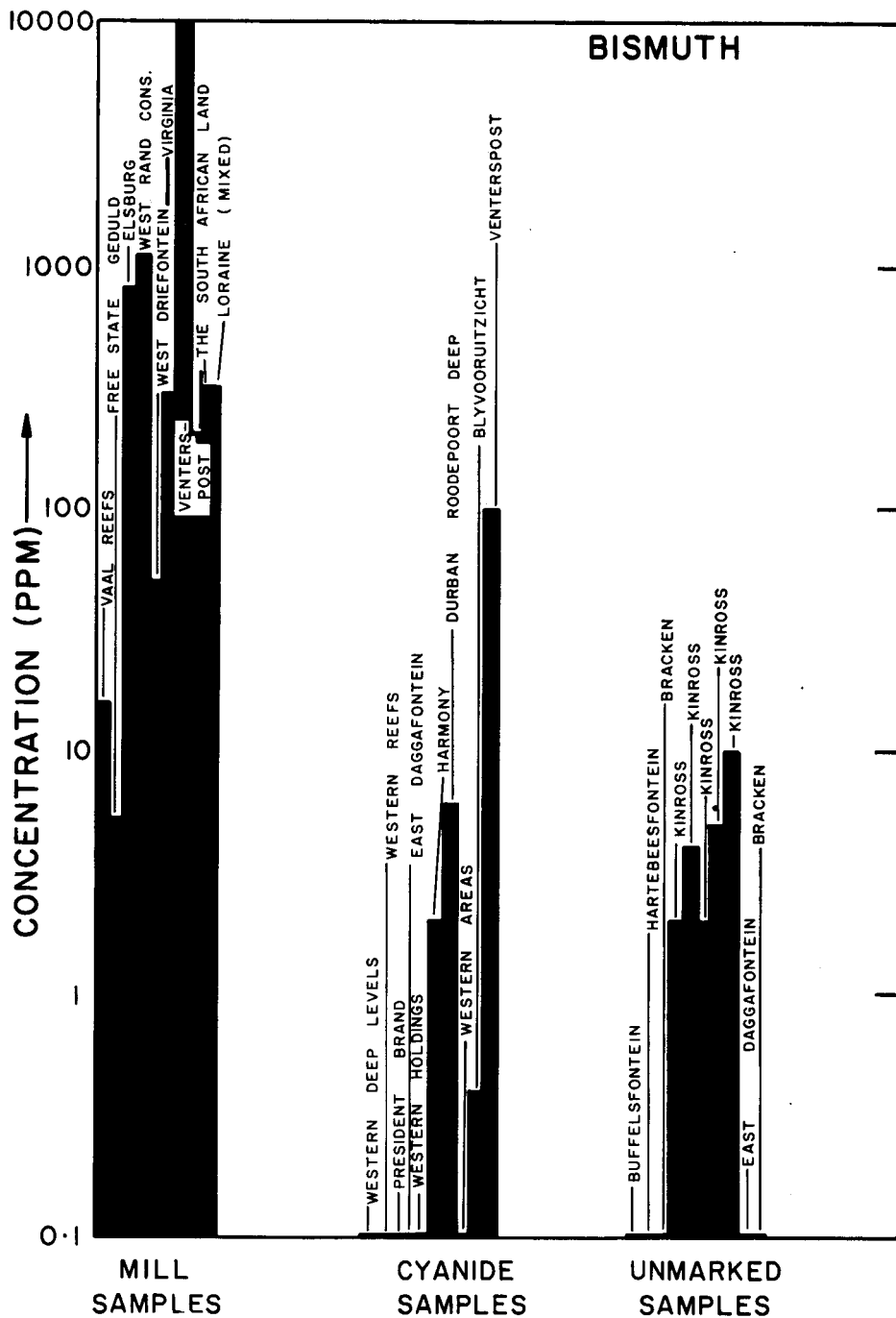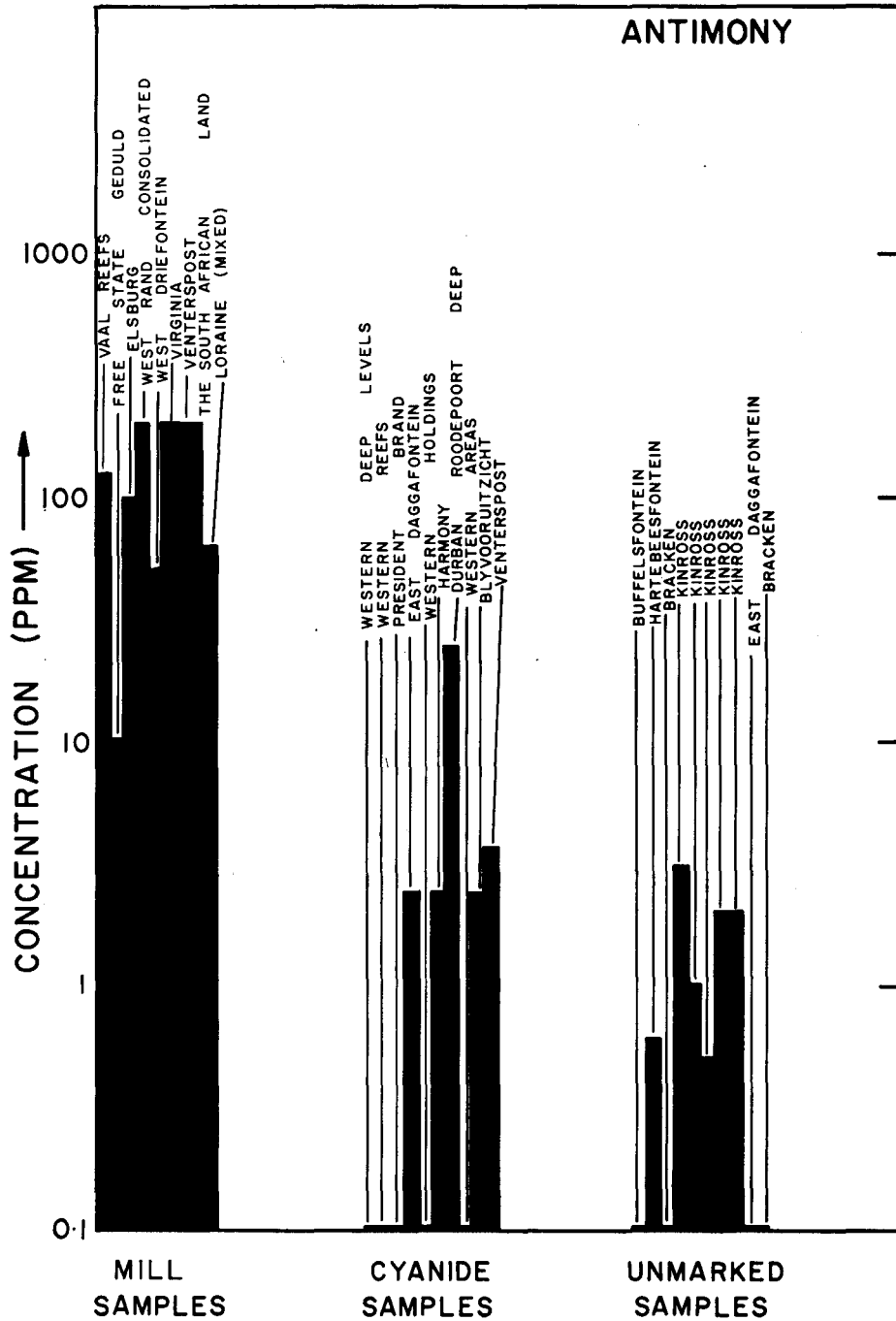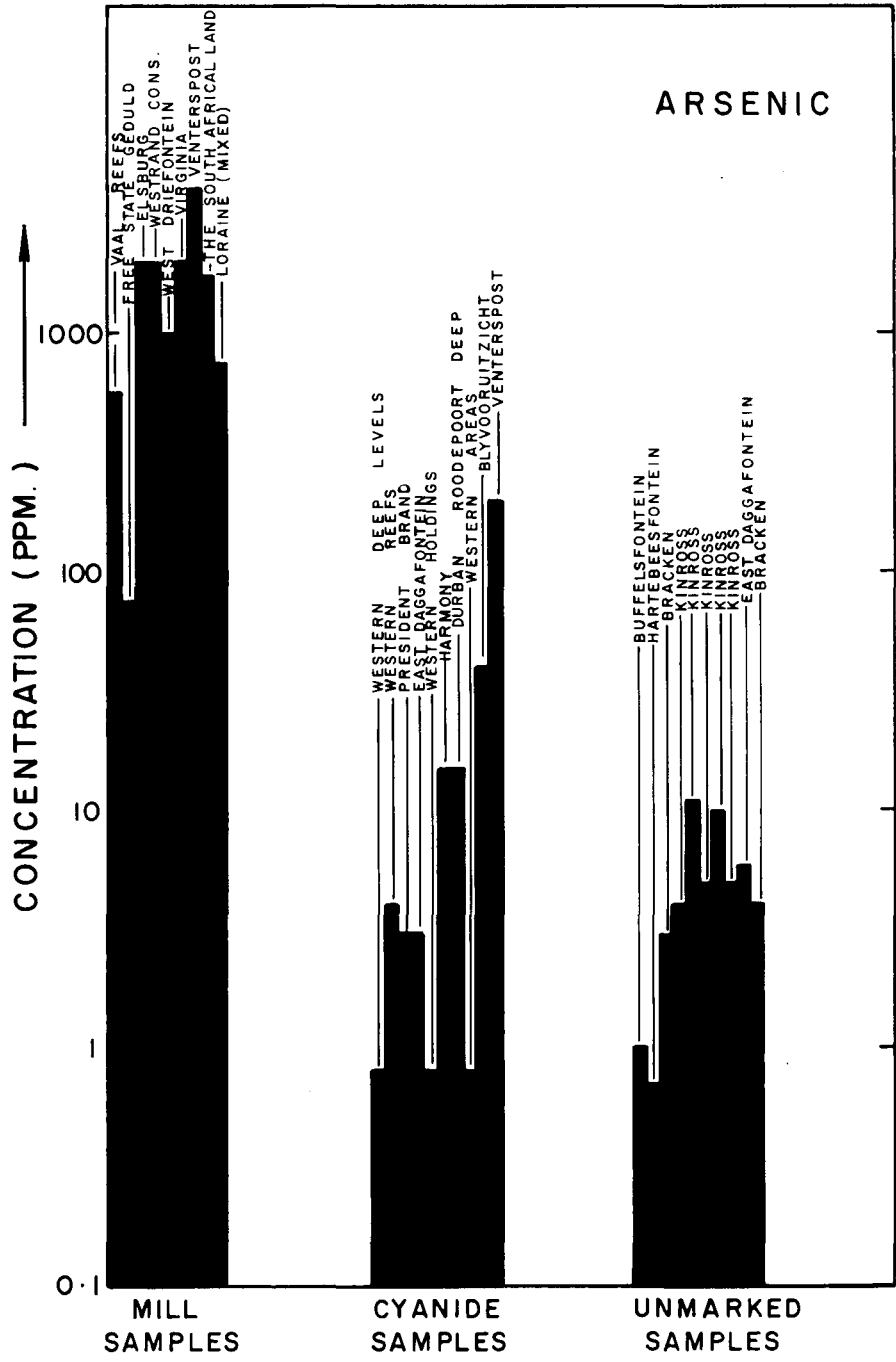
Graph I

In the cyanide stream the arsenic phase is not soluble and hence lost.

An exception in this category was the amalgamation process sample from Free State Geduld. Two separate samples were taken at a time interval of approximately three months. On each occasion the sample from this mine indicated very low trace element contamination. (Subsequent chemical analysis has shown that the gold, silver and copper concentrations constitute 99.85 per cent of the sample which is unusually high for this type of material). A sample of mill concentrate was taken and the analysis of it determined. The sample
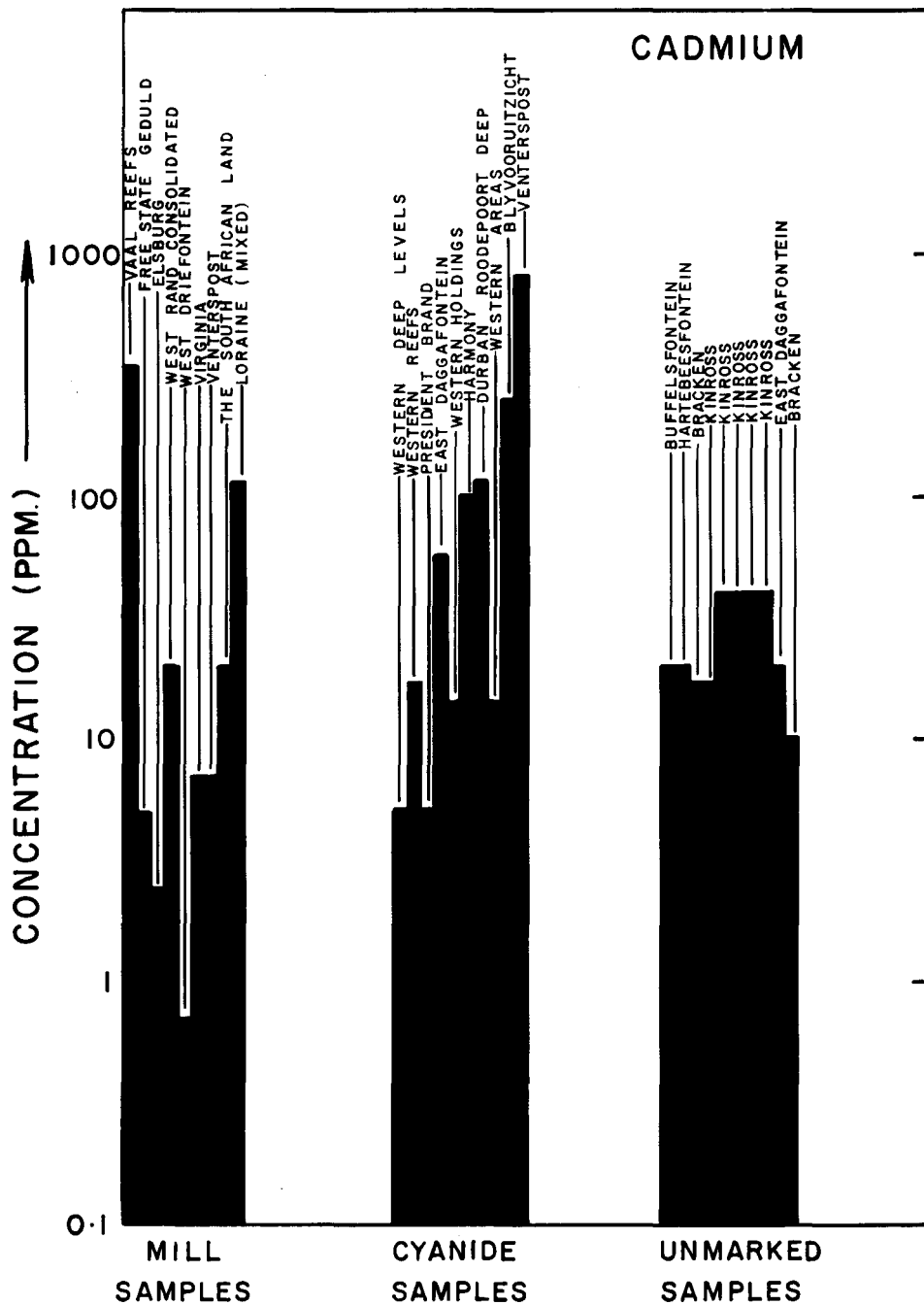
Graph 2
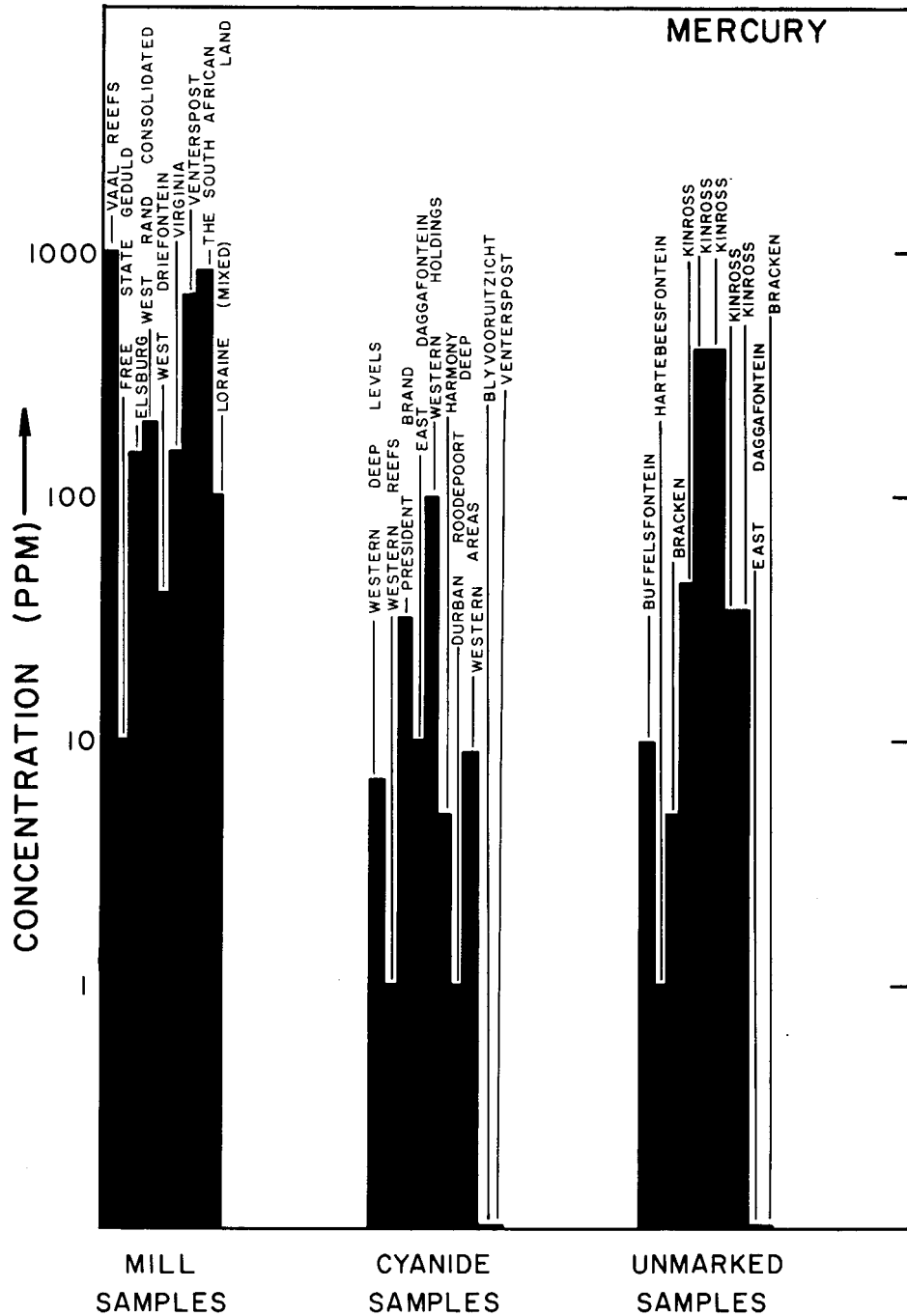
ARSENIC

Graph 3

Graph 4

showed a very high pyrite content (>90 per cent) but the arsenic level was low. It was thus presumed that the ore body mined was fortunately relatively pure (free from many mineral phases) and coupled with the fact that the ore is high grade (high gold content) the gold may be expected to be purer than from lower grade ores. This is in agreement with information already available.
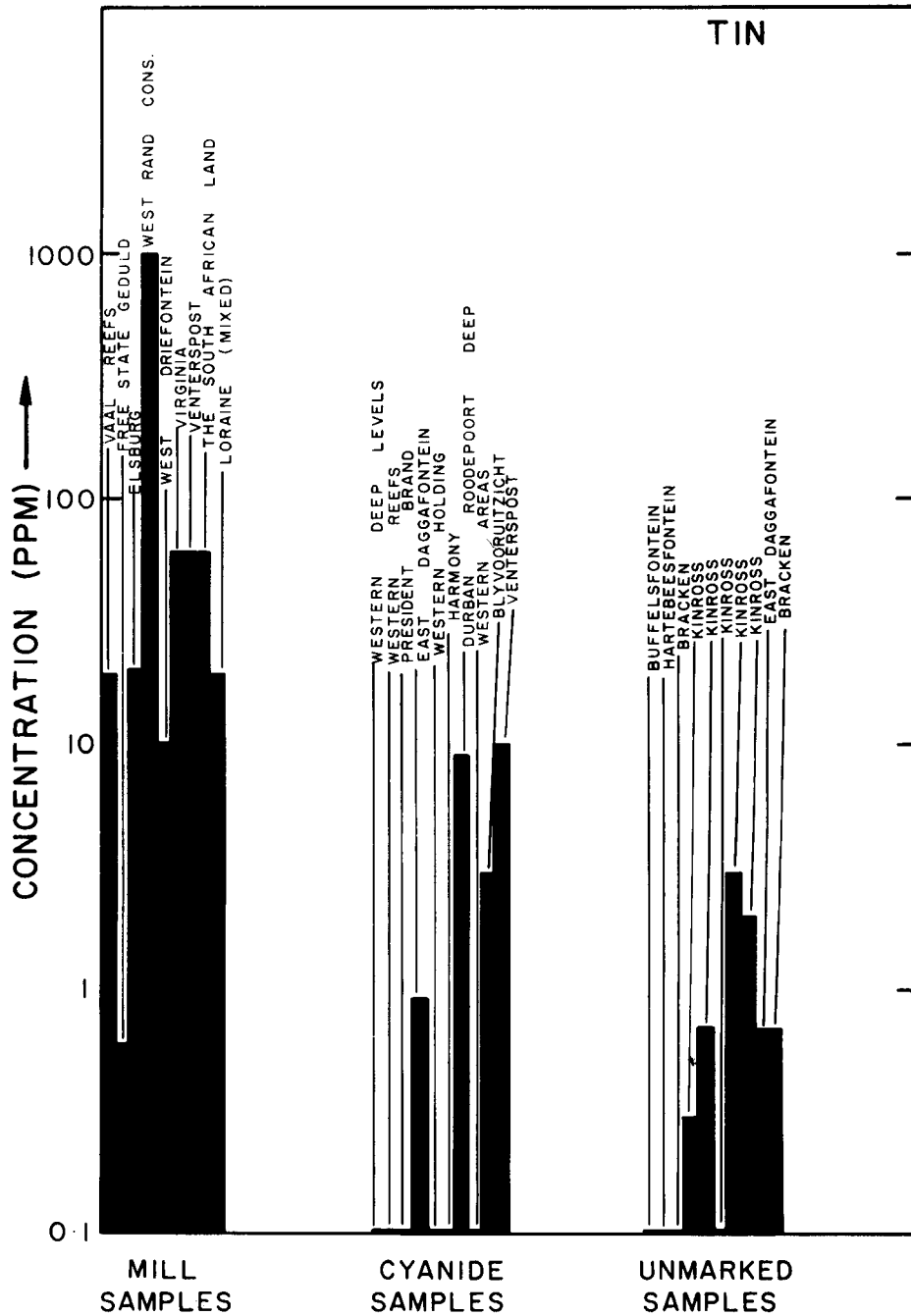
Graph 5

Mercury and Cadmium — Group 2B elements
(Graphs 4 and 5)

The group 2B elements mercury and cadmium show peculiar anomalies and no clear differentiation between processes can be established. An interesting feature which is being further investigated is the very high mercury content of some samples. The literature suggests no peritectic complex which would account for a decreased vapour pressure of mercury and hence its remaining in the gold phase during retorting and smelting.
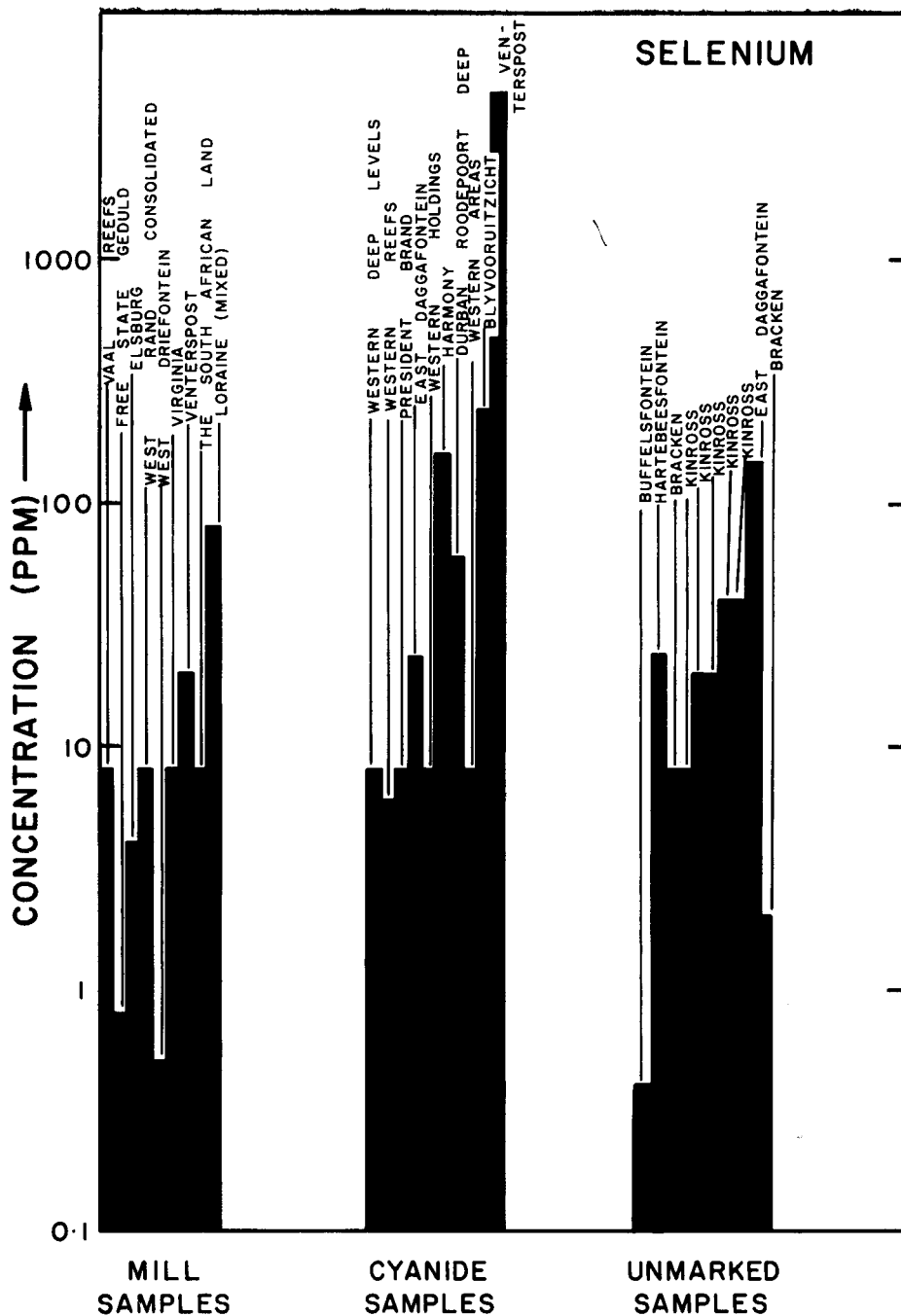
Graph 6

Tin (Graph 6)

The absence of a stable tin cyanide complex would preclude the transportation of this element through the cyanide process and it should be removed from the ore at this stage. It will, however, form solid solutions with gold and has several reported peritectic points in its equilibrium diagram. Tin will therefore be expected in

the amalgamation process gold when present in the ore-body.

Inspection of the results confirms that tin, if present in the ore body, is not removed by the amalgam process whereas it is removed in the cyanide stream. Only three out of the ten samples of cyanide produced gold exceeds one ppm whereas only the Free State Geduld sample of amalgamation process produced gold contains less than 10 ppm.
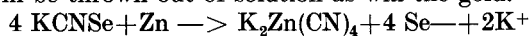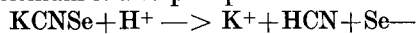
SELENIUM

Graph axis labels: CONCENTRATION (PPM) — 1000, 100, 10, 1, 0·1

MILL SAMPLES labels: REEFS, GEDULD, VAAL, FREE STATE, ELSBURG, WEST RAND, WEST DRIEFONTEIN CONSOLIDATED, VIRGINIA, VENTERSPOST, THE SOUTH AFRICAN LAND, LORAINE (MIXED)

CYANIDE SAMPLES labels: WESTERN DEEP LEVELS, WESTERN REEFS, PRESIDENT BRAND, EAST DAGGAFONTEIN, WESTERN HOLDINGS, HARMONY, DURBAN ROODEPOORT DEEP, WESTERN AREAS, BLYVOORUITZICHT, VENTERSPOST

UNMARKED SAMPLES labels: BUFFELSFONTEIN, HARTEBEESFONTEIN, BRACKEN, KINROSS, KINROSS, KINROSS, KINROSS, KINROSS EAST, DAGGAFONTEIN, BRACKEN

Graph 7

Selenium (Graph 7)

Selenium and its salts dissolve in alkaline potassium cyanide to form the soluble potassium selenocyanate
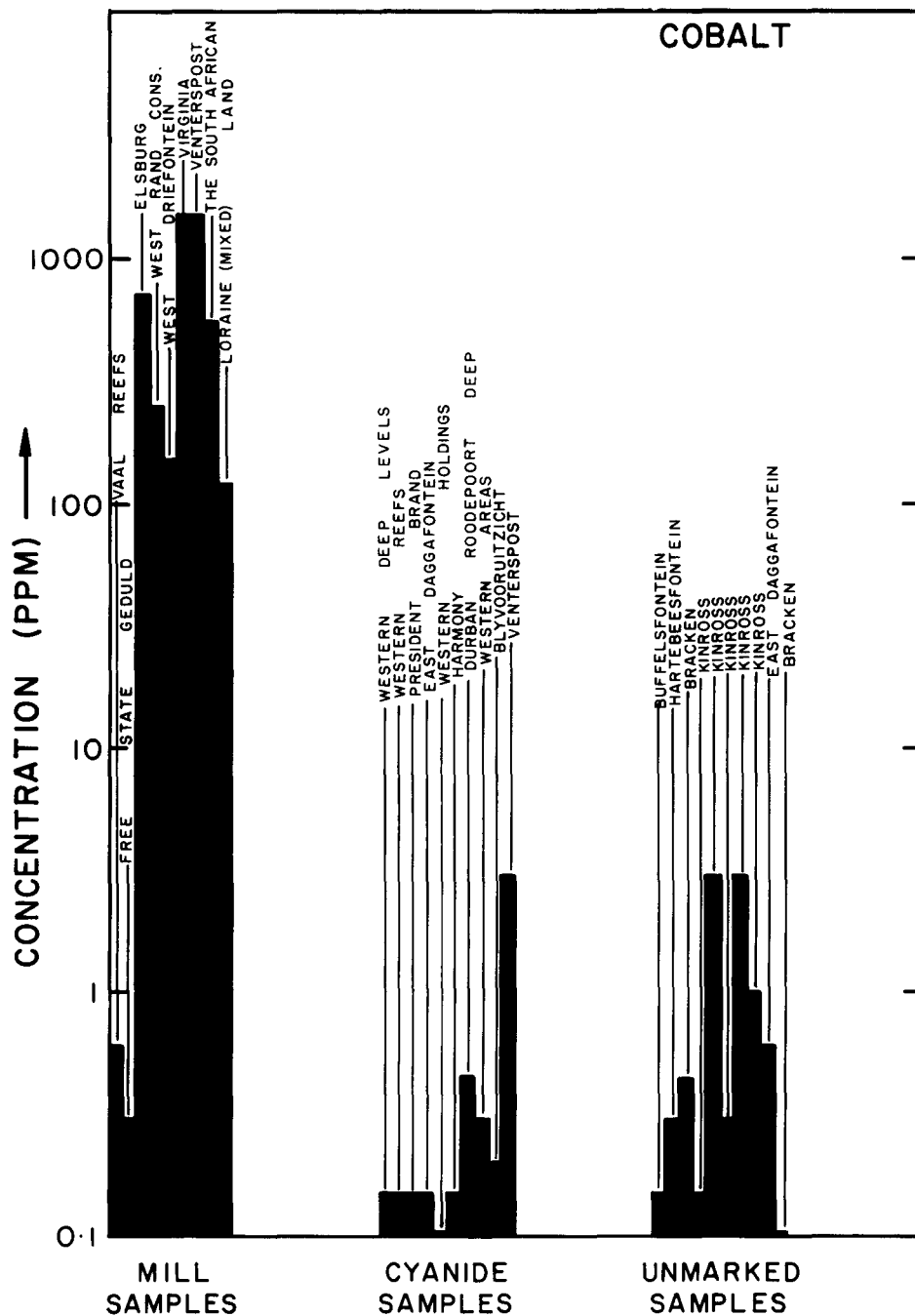
$$KCN + Se \longrightarrow KCNSe^{[5]}.$$
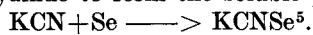
The selenium therefore will follow the gold within the cyanide process. On addition of zinc metal, selenium will be thrown out of solution as will the gold.

$$4\ KCNSe + Zn \longrightarrow K_2Zn(CN)_4 + 4\ Se{-} + 2K^+$$

Selenium is also precipitated in acid solution

$$KCNSe + H^+ \longrightarrow K^+ + HCN + Se{-}$$

Thus the selenium will be with the gold phase up to the calcination and smelting period. As can be seen some selenium remains behind in the gold. The boiling point of selenium (684 °C) is low and hence it can be presumed that the selenium will be present as a ternary selenide,[6, 7] complexed with the silver, copper and gold. This complex will have a very low vapour pressure at 1 200 °C (the smelting temperature). The source of the selenium may have been an association with the pyrite. However, during the geochemical ages in which the gold

COBALT

CONCENTRATION (PPM)

1000 — 100 — 10 — 1 — 0·1

MILL SAMPLES: FREE STATE GEDULD VAAL REEFS — ELSBURG CONS. — RAND — WEST DRIEFONTEIN — VIRGINIA — VENTERSPOST — THE SOUTH AFRICAN LAND — WEST — LORAINE (MIXED)

CYANIDE SAMPLES: WESTERN — WESTERN — PRESIDENT — EAST DAGGAFONTEIN — WESTERN — HARMONY — DURBAN — DEEP LEVELS — REEFS — BRAND — HOLDINGS — DEEP — ROODEPOORT AREAS — WESTERN — BLYVOORUITZICHT — VENTERSPOST

UNMARKED SAMPLES: BUFFELSFONTEIN — HARTEBEESFONTEIN — BRACKEN — KINROSS — KINROSS — KINROSS — KINROSS — EAST DAGGAFONTEIN — BRACKEN

Graph 8

has been present in the conglomerate, a revision of its environment with a possible complex selenide forming within the gold phase might be anticipated.

An analysis of the results tends to reveal that the selenium is lower in concentration in amalgamation process gold. This would tend to indicate that the selenium transfer process is prohibited (for Venterspost Amal. — 20 ppm, Cyanide — 4 700 ppm). However, a small amount of selenium did transfer since during amalgamation the pyritic fraction is separated from the gold phase.

Cobalt and Nickel (Graphs 8 and 9)

These metals may be introduced during the extensive milling to which the ore is subjected or they may be present as some co-deposited mineral phase. Nickel alloys are used occasionally but cobalt alloys are not. The fact that both are in high abundance in the amalgamation process produced gold would suggest that these are present as co-deposited minerals.

In the cyanide stream most of the cobalt is removed from the gold whereas more of the nickel remains in the gold phase.

The cobalt salts dissolve in alkaline potassium cyanide to form the extremely stable cobalticyanide complex:

$$3O_2 + 6H_2O + 24\ KCN + 4\ Co \longrightarrow 4\ K_3Co(CN)_6 + 12\ KOH\text{[8]}.$$
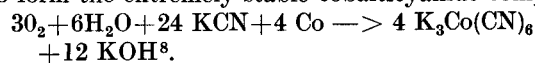
Under the cyanidation conditions the cobalt in the slurry is therefore expected to join the gold phase in solution.
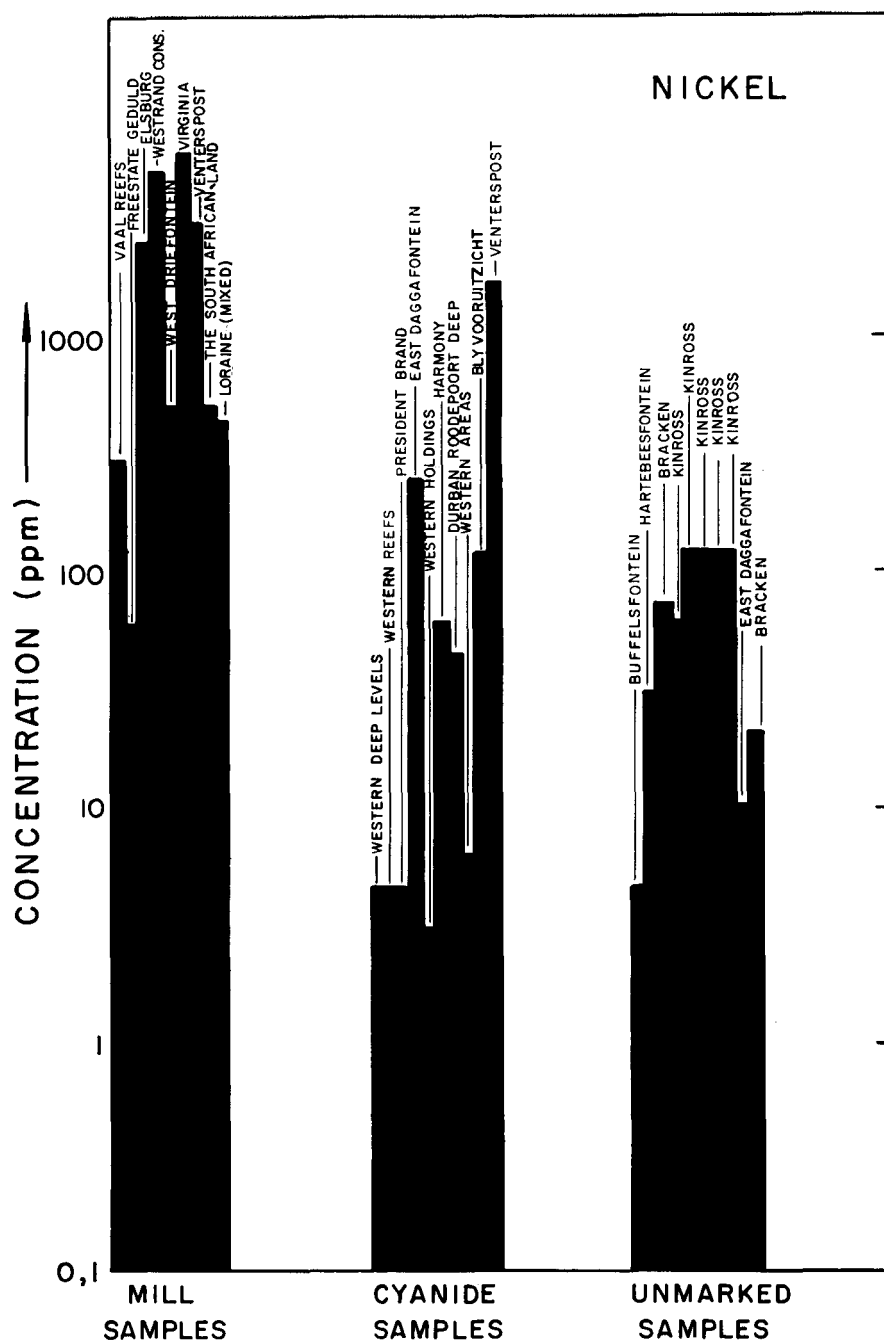
Graph 9

The cobalticyanide ion is extremely stable, being perfectly octahedral,[9] and is therefore not subject to cationic attack by zinc. Thus when zinc is used to precipitate the gold, the cobalt will remain in solution and be lost in the barren solution.

The nickel salts also dissolve in alkaline potassium cyanide to form potassium nickelocyanide

$$O_2+4H_2O+8KCN+2Ni \longrightarrow 2K_2Ni(CN)_4\ H_2O$$
$$+4KOH^{10}$$
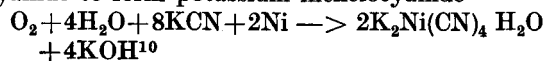
Thus under the cyanidation conditions nickel will join the gold phase in solution. However, as distinct from the cobalticyanide ion, the nickelocyanide, being square planar,[11] will decompose under the influence of cationic

attack. A simple cationic exchange will take place if the attacking cation is zinc:

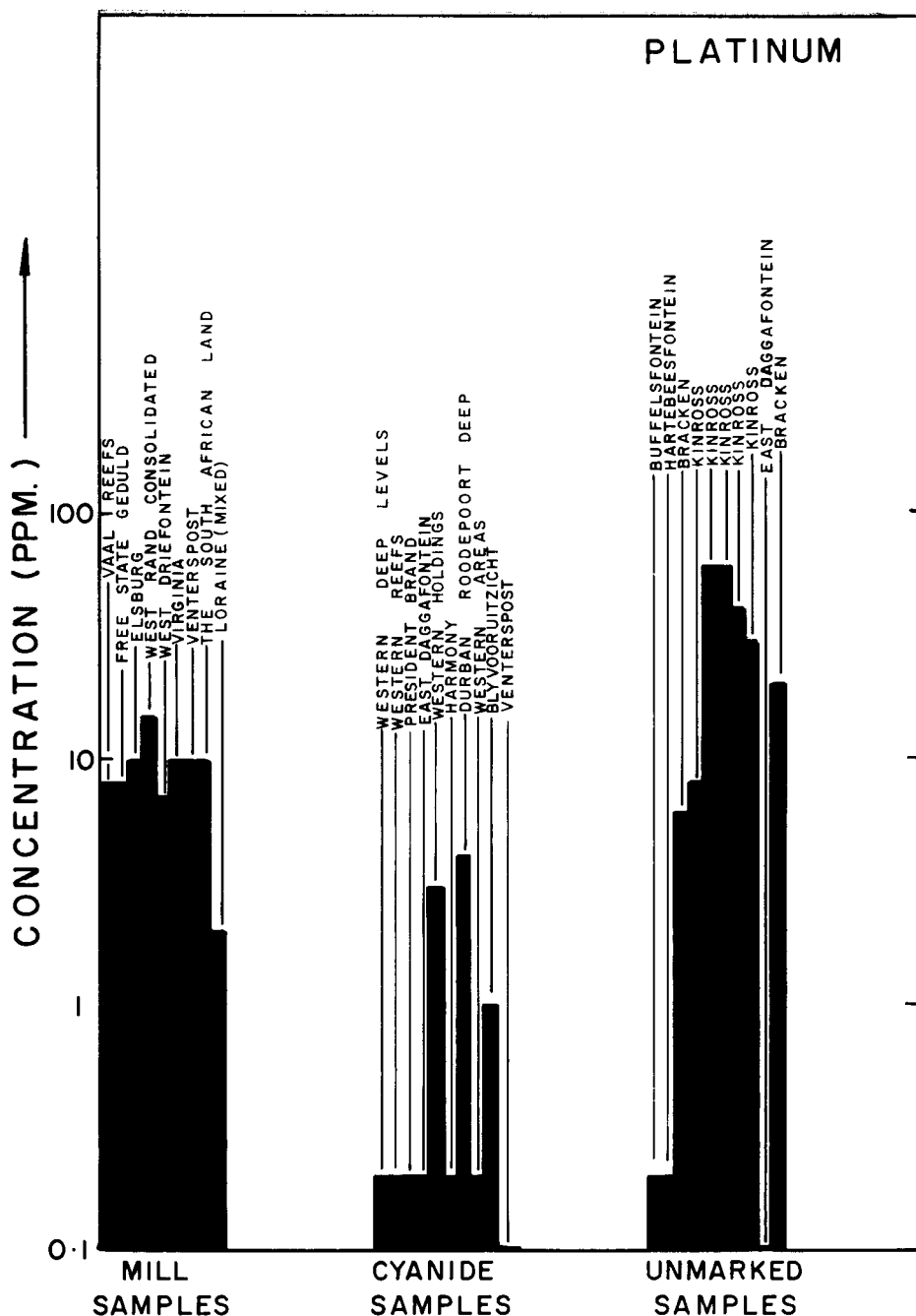$$Zn+K_2Ni(CN)_4.H_2O \longrightarrow K_2Zn(CN)_4+Ni+H_2O$$
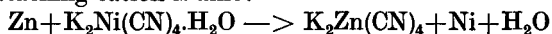
The nickel cation will be absorbed by the gold precipitating in its immediate environment. Thus the observed difference in the Group 8 elements cobalt and nickel can be directly attributed to the difference in stability of their cyano complexes.

The platinum group metals (Graphs 10 and 11)

The group Pt, Os, Ir

Although only the platinum content of the gold has been indicated graphically, all three elements display similar characteristics. From the graph it can be seen

PLATINUM

CONCENTRATION (PPM.)

100

10

1

0·1

VAAL REEFS
FREE STATE GEDULD
ELSBURG
WEST RAND CONSOLIDATED
WEST DRIEFONTEIN
VIRGINIA
VENTERSPOST
THE SOUTH AFRICAN LAND
LORAINE (MIXED)

WESTERN DEEP LEVELS
WESTERN REEFS
PRESIDENT BRAND
EAST DAGGAFONTEIN
WESTERN HOLDINGS
HARMONY
DURBAN ROODEPOORT DEEP
BLYVOORUITZICHT AREAS
VENTERSPOST

BUFFELSFONTEIN
HARTEBEESFONTEIN
BRACKEN
KINROSS
KINROSS
KINROSS
KINROSS
EAST DAGGAFONTEIN
BRACKEN

MILL
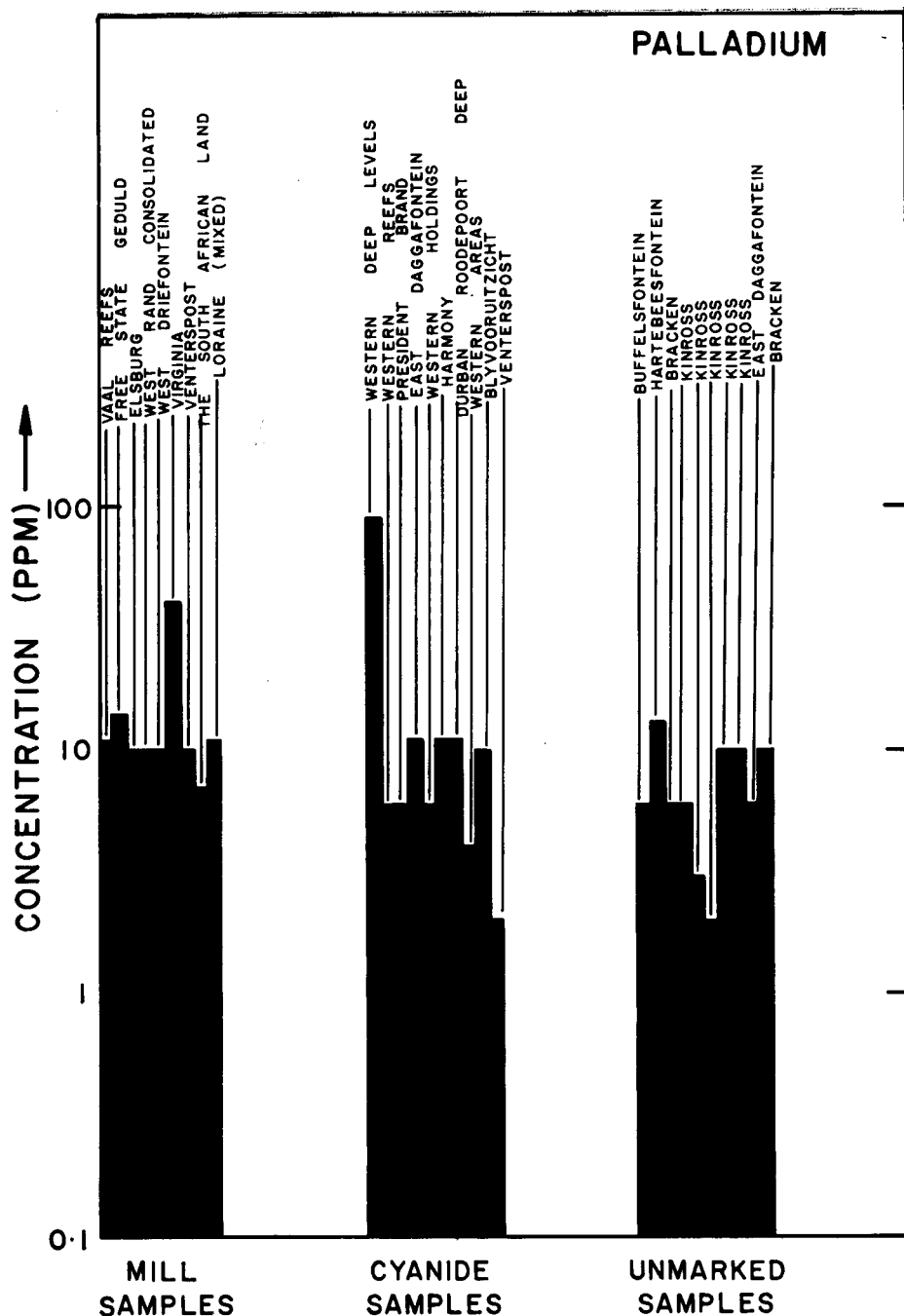SAMPLES

CYANIDE
SAMPLES

UNMARKED
SAMPLES

Graph 10

that in all mill samples platinum is found at trace level. This level appears fairly consistent over the amalgamation process samples, dropping considerably in the Loraine samples, which is known to be a mixture of amalgamation process produced and cyanide produced gold. In the cyanide samples the level is found to be less than 0,3 ppm although a value of 0,2 ppm has been shown as the probable value. Only in three cases does the level of platinum exceed this "nominal" blank value. Some degree of contamination of these golds may have occurred although it is possible that platinum metals not removed by gravity concentration have been transported through the cyanide stream. In order for this to be possible, the complex cyanoplatinite has to be formed.

A postulated reaction may be

$$3H_2O+4KCN+Pt^{++} \longrightarrow K_2Pt(CN)_4.3H_2O+2K^+$$ [12]

The conditions for this reaction are considered unfavourable but in this context it cannot at this time be totally disregarded. The cyanoplatinite ion will be subject to cationic exchange, with zinc replacing the platinum. The platinum would then be dissolved in the gold and remain there during further processing. Rather significant, however, is the fact that although some carry-over of the platinum metals from the gravity concentrator to the cyanide process stream most probably occurs in all cases, it is only in three cases that platinum is observed in the final gold. It is therefore more likely that some degree of contamination has taken place.

PALLADIUM

CONCENTRATION (PPM) →

MILL SAMPLES: VAAL REEFS, FREE STATE GEDULD, ELSBURG, WEST RAND CONSOLIDATED, WEST DRIEFONTEIN, VIRGINIA, VENTERSPOST, THE SOUTH AFRICAN LAND, LORAINE (MIXED)

CYANIDE SAMPLES: WESTERN DEEP LEVELS, WESTERN REEFS, PRESIDENT BRAND, EAST DAGGAFONTEIN, WESTERN HOLDINGS, HARMONY, DURBAN ROODEPOORT DEEP, WESTERN AREAS, BLYVOORUITZICHT, VENTERSPOST

UNMARKED SAMPLES: BUFFELSFONTEIN, HARTEBEESFONTEIN, BRACKEN, KINROSS, KINROSS, KINROSS, KINROSS, KINROSS, EAST DAGGAFONTEIN, BRACKEN

Graph 11

In the amalgamation process stream platinum is known to alloy with mercury and hence will be present in the amalgam at the retorting stage when it will remain in the gold phase homogeneously dissolved.

Palladium

The level of palladium in the final gold phase does not appear to depend on the process by which the gold was extracted. It is anticipated that the palladium will originally be in the same phase as the gold in the ore due to the extreme solubility of palladium in gold.

During the amalgamation process the palladium will adopt precisely the same phase as the gold and hence no loss of palladium is to be anticipated. It is seen that a reasonably consistent value of 10 ppm is exhibited by all

golds made by the amalgamation process of extraction. This would tend to suggest an average Pd/Au content in South African ore of 0,001 per cent.

The same value, within experimental error, is shown by most of the cyanide produced golds. This would tend to suggest the transport of the palladium through the cyanide stream without loss. This being the case, the formation of the palladocyanide at the cyanidation stage is required.

$$Pd + 4KCN \longrightarrow K_2Pd(CN)_4 + 2K^+ \ [13]$$

This is then destroyed on addition of zinc and the palladium reprecipitated with the gold. Only in two cases, Virginia and Western Deep Levels, was the palladium content distinctly abnormal. In these cases the

explanation of this phenomenon must be in a richer Pd/Au ratio in the ore.

CONCLUSION

The trace elements present in raw bullion frequently indicate the recovery process that has been employed and possibly the degree of care that has been taken during processing. They also indicate the peculiarities of the individual ores that are being mined in the various localities within the Witwatersrand basin. With the increasing interest being paid to impurities in gold and the possible existence of other useful elements in the gold reefs more research should be devoted to these differences and the reasons for them. With the aid of spark source mass spectrography with its sensitivity, comprehensive elemental coverage, and simplicity, this work can now be envisaged. Up to the present, however, many of the differences between individual bullions bearing similar process histories remain inexplicable and work is proceeding to elucidate the reasons for these differences.

REFERENCES

1. DRUYVENSTEIN, M. J. Z. *Physik*, 64, 781 (1930).
2. SCHÜY, K. D. and FRANZEN, J. Z. *anal. Chem.*, 225, 260 (1967).
3. PALACHE, C., BERMAN, H. and FRONDEL, C. 'Dana's system of Mineralogy', Vol. I, J. Wiley & Sons, New York, 7th ed., d. 134 (1958).
4. Ibid, p. 133.
5. MELLOR, J. W. 'Comprehensive Treatise on Inorganic and Theoretical Chemistry', Vol. X, Longmans, Green and Company, London, New York, Toronto, p. 750 (1946).
6. Ibid, p. 765-802.
7. PALACHE, C., BERMAN, H. and FRONDEL, C. 'Dana's system of Mineralogy', Vol. I, J. Wiley & Sons, New York, 7th ed., p. 183 (1958).
8. FORD-SMITH, M. 'The Chemistry of Complex Cyanides', H.M.S.O., London, p. 24 (1964).
9. Ibid, p. 24.
10. Ibid, p. 31.
11. Ibid, p. 32.
12. Ibid, p. 61.
13. Ibid, p. 46.