(1)

GOLD COMMISSIONER
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TITLE PAGE

A PROSPECTING REPORT

Including the general purpose of the prospecting and related mineral testing with particular emphasis on prospecting of a portion of Minute Creek lying and being within

CLAIM T 3 TENURE NUMBER 364 387
VICTORIA MINING DIVISION

NTS 092CO59

Legal corner of claim T3 is at Long. 124 deg. 17 min 42 sec. West
Lat 48 deg. 30 min. 52 sec.North

Owner **TRIANGLE VENTURES LTD FMC 127 267**

Operator **TRIANGLE VENTURES LTD**

Consultants **Dr. Alan Shaver, Dr. Eric Hoffman, Dr. Chen, Mr. George Mason**
These were consulted for individual aspects.

Author **Ian M. Sherwin,**

President TRIANGLE VENTURES LTD
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Date **8 October 1999**

GEOLOGICAL SURVEY BRANCH
ASSESSMENT REPORT

26,052

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(3)
INTRODUCTION

General geographic and phsyiographic position, access to the claims and index map

Claim T3 lies astride the main West Coast Highway from Victoria to Port Renfrew and is approximately 10 kilometers by road easterly of Port Renfrew and is best described as being at Minute Creek, Renfrew Land District, Victoria Mining division.

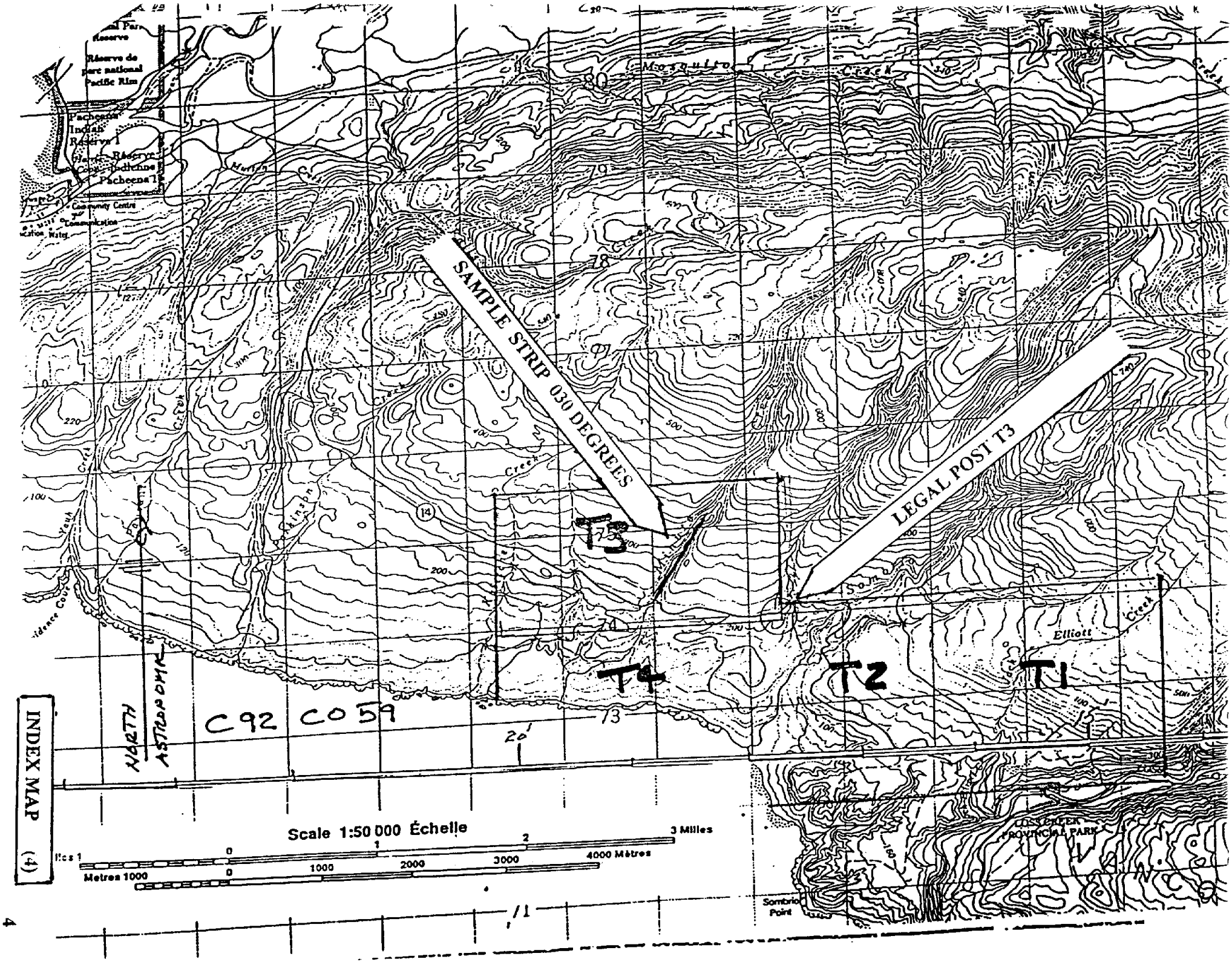
If a line were produced north and south passing through the centre line of the West Coast Highway and its intersection of the centre line of Minute Creek it would almost exactly divide the T3 claim into equal east and west portions.
It is commencing at this intersection point thence proceeding 030 degrees(north 30 degrees east) that the herein described sampling was done. This intersection point lies approximately 400 metres north of the south line of T3. The legal post of T3 lies approximately 1500 metres easterly of this intersection point. (both approximations made by scaling from both airphotos and provincial 1/50000 geographic base maps)

The exact position of the legal post for T3 is 111 metres 090 degrees(astronomic south) of the centre line of the West Coast Highway at a point 150 metres westerly along the centre line of the west coast highway from it's intersection of the centre line of the most westerly branch of the Sombrio River. The legal post is a the end of a short abandoned logging spur. In addition to bearing trees and blazing it is witnessed with a 1 1/4 iron pipe set into the ground at a point 15 centimetres 00 or astronomic north of the centre loci of the post.

T3 has been almost entirely logged by clear cutting including the canyon of the Minute Creek and is laced with abandoned industrial logging roads some now partially washed out and growing up with alder. They provide excellent future industrial access for drill sites, bulk sampling etc.

Upon the inland or northerly side of T3 the land rises progressively and on the sea side the land drops off sharply such that taken together any working open pit quarry faces would have natural drainage which could be safely contained with no fishery, or residential or agricultural aquifer involvement. Drainage of any clarified and purified water from mine operations would enter the open Pacific Ocean at one of the rare places where in the event of human or equipment failure there is a natural net seaward movement of ocean water (It is by reason of this natural disposal that the Capital Region District is permitted to continuously discharge highly toxic leachate into the same Strait of Juan de Fuca at a far less favoured place)

With industrial electric power existing through the property combined with road and sea access the potential for a very large very low cost gravity assisted open pit exists if even a very low multi metal yield is proven.


Réserve de parc national Pacific Rim
Pacheena Indian Reserve 1
Pacheena 1
Community Centre
Communication
Mosquito Creek
Hunter Creek
Mainspn Creek
SAMPLE STRIP 030 DEGREES
LEGAL POST T3
T3
T4
T2
T1
Elliott Creek
C92 C059
NORTH ASTRONOMIC
Scale 1:50 000 Échelle
3 Milles
4000 Mètres
Metres 1000
Sombrio Point
LOS CREEK PROVINCIAL PARK

INDEX MAP (4)

Property definition, containing history of the property, current owner, operator, brief economic assessment of property etc .

The legal survey post of T3 lies 2000 metres north of what was described shortly after the turn of the century in contemporary government reports, as the largest placer mining operation ever attempted on Vancouver Island. After some five million tons was mined by hydraulic methods the operation came to a close by reason of recovery problems with the primitive equipment of the time.

The placer deposit has been estimated at 350 million tons and has been held and worked on by TRIANGLE VENTURES LTD for over twenty years. By reason of the size and the extremely low cost operating potential of this deposit. a large body of metallurgical research and recovery work involving technologists from around the world has been done by TRIANGLE in regard to establishing a low cost multi metals and materials recovery project upon this deposit.

Regrettably and without even the Mines Department being informed, a park was imposed in such fashion as to totally destroy the sea access and resultant low cost operational characteristics of the deposit and repeated pleadings and suggestion to the Parks Ministry as to how this might be ameliorated were brushed aside.

In response to this ruinous taking TRIANGLE VENTURES LTD being possessed of over twenty years research in the metallurgy of this deposit then elected to apply this knowledge to the adjacent hard rock logged off lands which had no park potential whatever with the object that if successful a large hard rock open pit might well help support the ruinous additional costs imposed on the placer deposit as well as provide an access to the sea.

It had been long suspected that the schist belt lying to the north of the Sombrio deposits and the Sombrio deposits had a related genesis and the Earth Sciences project "Lithoprobe" had indicated that the Leech fault was indeed a terrane contact of massive proportions and had traced this to within a few kilometers of the upper mantel of the earth .

Grab samples taken by TRIANGLE at opportune exposures, rather than by grid sampling, had when treated by a bromine/chlorine leach followed by selective resins, elutriation with HCL/ Acetone and the resultant bead fire assayed yielded .048 gold. Not something to get excited by itself, however samples from the Sombrio sands 2000 metres south treated By Dr. Poole in South Africa for Dr. Shaver (Chairman Chemistry and now dean of Sciences Mcgill) a world authority on Platinum group metals had returned platinum and rhodium values several time the gold values. Dr. Pooles method of borate fusion fire assay is included as page 22 Attention was therefore directed to the several square kilometers of adjacent schists.

Historically the Mines staff have always been competent and helpful to the mining industry however today the actions by other departments of government are at best ignorant of and at worst completely hostile to the mining industry and for this reason the question was how to do this exploration with minimum of boat rocking.

In order to do this with minimum ground footprint this exploration was done by ground penetration radar coupled with a proprietary computer algorithm to yield a coloured presentation which is included herein in black and white only to conform to the regulations under which this report is submitted as page 18. No part of this exploration work the cost of which including its mobilization ran in excess of some twenty five thousand dollars is included in these work claims since it was done prior to the staking of T3 and is therefore not an allowable expence under the regulations. It is included only to confirm and support the reasons, purpose and value for the particular nature of the sampling done later.

The result of this ground penetration radar work was the discovery of what was suspected to be a massive plate fragment located within what was to become T3 which was immediately staked. Subsequently owing to the heavy logging slash, two aircraft were then chartered to attempt by low level flying and colour photography to locate local offsets and exposures for identification on the ground.
Vide. Minute trench oblique photo(originally in colour) as page 17

It became apparent that Minute Creek which flows in a cross fault in the middle of the property provided a natural rock trench 100 metres deep which owing to the normal torrents of water in this 100 inch plus rainfall area and the tumbling boulders pushed by these torrents, presented a polished bottom section 1000 metres long bisecting the plate segment. The name Minute Creek is claimed by locals to come from a story that when the rain hits (which is most of the time), it is a roaring torrent in a minute. This is a gross exaggeration but I can attest that the creek can rise at a surprising rate and should be treated with respect.

The summer of 1998 however was a rare dry summer when this natural polished bottom was almost dry and could be accessed and for this reason it was decided to during this window of opportunity, get samples about which there was no doubt as to their precise locations. Since assaying properly for platinum group metals and rare earths is extremely costly it was decided that two directors who were the major investors in TRIANGLE with many many years of relevant field experience would run the lines make critical observations and would take the samples in order that certainty would prevail when the sampling area became again inaccessible by reason of the normal almost continuous rainfall.
(TRIANGLE is a closely held local private company and the directors cum field men were the president and treasurer)

This long explanation may be unnecessary however it arose from concern over the interpretation of the Mineral Tenure Act regulations regarding work page 2 item f which TRIANGLE presumes was originally intended as an example of process rather than realistic cost today for assays for copper lead zink and silver which are shown as a total of three dollars. Indeed some common metal assays are very cheap (I used to pay $5 fifty years ago) however they can be wildly unreliable for minute complexes of platinum group metals

By contrast today a reliable professional assay for platinum alone is $400 and rhodium can be twice that much partly because complexes of very minute traces have value. Nor does cost stop there for depending on the high temperature metallic bonds the method of assay which will work for one type of ore will not work for another. As support for this statement a paper by Dr. Kallman brought to my attention by Dr. Shaver of Mcgill, himself an authority on platinum group metals as accurately defining the problem is enclosed as pages 33 to 54 inclusive.
In practice it has been shown that even methods such as neutron activation will not solve this puzzle unless the material is first carefully refined to simplify the assay in support of which statement a paper by Dr. Hoffman is enclosed as pages 23 to32 inclusive. This background detail is submitted to confirm the reason why by reason of expertise gathered over twenty years involvement with this project and the large stakes involved TRIANGLE was particularly concerned with doing it once and doing it right. Casual labour was not a prudent option nor is any help that cannot be counted on for continuous hands on participation since this pioneering work requires a continuous seamless nexus between the laboratory and the field.

A BRIEF ECONOMIC ASSESSMENT of the property must take note of the fact that the platinum group metals (including the isotopes of some) are of very great dollar value. Rhodium the rarest of the platinum groups not only has great dollar value but great strategic and social value.

The United States Bureau of Mines in a published report postulated a job loss of 570,000 in the auto industry and a loss of sixty billion dollars to the United States GNP over five years if supplies of rhodium failed.

An economic assessment must therefore recognize that any proof of economic rhodium would open the door to a wide range of senior industrial financing of a most responsible kind, always assuming security of mineral title which is vital.

The mineralized plate segment inferred from the ground penetration radar is of such size that if proven all to be economic, could host an open pit of between three billion to six billion tons of 2000 lbs.

The work done was the first small careful steps toward that proof.

Summary of work done

Guided by the interpretations of the ground penetration radar and oblique air photos taken along the therin indicated fault lines 18 Claim units were partly prospected on T3 and 2 on T4 however the greater proportion of the work was on T3 and that mainly in the area of Minute creek as indicated in the log of Prospecting Traverse of Minute Creek a matter of 100,000 square metres (100 metres by 1000 metres) The structural deformaties suggested by the ground penitration radar analysis were, during prospecting, supported by the observation of abundant and complex quartz presumed by the author to be later intrusions. (Minute Creek has a long local reputations for nuggets probably associated with this)

47 Samples as per log of prospecting traverse were taken examined and stored pending the completion of a special laboratory and arrival of Dr. Bruce Perry a platinum specialist to conduct this work. This work is on hold owing to concerns over Indian title(government is proposing to offer these lands as Indian settlement)

5-200 lbs. bulk samples representative of above were ground to 100 mesh and treated in a proprietary WISETECH magnetic separation system. A covenant of secrecy was signed by the author in regard to the details of this apparatus however no significant free gold was observed optically . Samples were retained for platinum group testing which is on hold as per Indian uncertainty above.

An optical microscope observation by another knowlegable party of what was thought to be rhodium in "pimples" in the rock which might if true, yield a short cut for prospecting led to 4 very small samples of the pimple material being submitted for laser ablation under Dr. Z. Chen of the University of Victoria. It was the parole observation of Dr. Chen that rhodium tends to occur in nugget form and therefore the the four extremely small laser scans 300 microns in diameter might miss them . No rhodium was detected. titanium and vanadium values typical of the area were indicated in these small samples. These scans are included as pages 55 to 74

A 2 kilo sample containing pimple material was milled , then submitted to Dr. Eric Hoffman (Author of the paper appendix pages 23-32) for borate fusion followed by neutron activation. This result showed less than one part per billion

If this area was the source of the rhodium at Sombrio it was not supported by the albeit limited work to date.

Hand panning however showed gold nuggets in Minute Creek (one half of which are hackled suggesting local origin) see photo included as page 12 and detailed note page 11.

LOG OF PROSPECTING TRAVERSE OF MINUTE CREEK

The prospecting purposes of this traverse were as follows

1. To confirm or otherwise the continuity and uniformity of altered sediments

2. To log the banding of the sediments as a possible indicator of alteration.

3. To log and estimate the actual tonnage of visable material at each log station in order identify points at which further samples could be taken if need be by rappeling from above when high water made other access impossible.

4. To log any any unusual features, nodules or "pimples" that might betray localized mineralization. (A third party with experience in rhodium thought at least one pimple appeared to contain rhodium under the microscope)

5. To log and take dependable samples that were truly representative of the the rock that might ultimately be taken, if need be, as a large volume low value open pit.

6. To observe uniformity of wall rock for drilling.

7. Most importantly to secure dependable samples before the normal rains came which renders this type of sampling impossible such that samples could be processed carefully in the laboratory for platinum group metals as well representative samples could be taken for concentration tests of prorietory appratus both of which were in process.

A typed copy of the logs is enclosed as pages 10 to 15 inclusive
A plan of this sample traverse is enclosed as page 16

TYPED COPY OF FIELD NOTES

Sample number are given in metres bearing 030 of a point which is the intersect of the centre line of the West Coast highway and the centre line of Minute Creek within T3 Victoria Mining Division.

LINE RUN AND SAMPLES TAKEN 15 AUGUST 1998

00 metres is approx. 124 deg 18 min 45 sec West long.
48 30 50 North Lat.

024 24 metres bearing 030 of minute creek. sample from one ton boulder 20 such boulders in a 10 metre radius

044 Small float 100 lbs many pimples rhodium? 20 - 100lb boulders 10 mete radius

071 Small float pimples 100 lbs 10 -100 lb in 10 meter radius 2 by 5 metre outcrop east side strike N 85E Dip 45 north pimple material in place 25 tons. this material continues perhaps for 30 metres on ridge buried on west side . separate sample taken on outcrop marked 071 outcrop

101 Sample taken outcrop rock continuous as per 071metres same dip and strike pimples not as prominent but outcrop at least 30 tons(of 2000 lbs) looks like rock exposure both sides to say station 150 same dip and strike

117 Sample 4 inch milkey quartz in outcrop 5 metres exposed on west side in 40 ton outcrop. Milkey with vugs.

132 No sample pimpled rock continues in bedrock west side 50 tons in sight in a 10 metre radius.

138 No sample lot of mica and quartz in banding 20 tons in sit same dip strike S65E

157 No sample rock still exposed both sides of creek pimple and quartz.

157 157 looks like good access from south side down a draw or slide perhaps this slide cetre is at 170 metres at top

170 Start of large granite float 5 tons?

178 Large lenticular quartz float begins . specimen 1/2 ton12 inches thick

192 Strike now W70E dip 45West

211 Large quartz vein east side 10 inches wide exposed for 6 feet strike N20 W cross vien 6 inches wide at 90 angle to above exposed for 10 feet

206 Strike now N90 E dip still 45 north. quartz interleaving now abundant mineralized thruought? It would appear continual quartz banding probaly in excess of 20 per foot say 1/4 inch thick. This sediment layered rock is not, but has the appearanceof edge wood grain mineralized. great rock exposures both sides.

237 Slide on west side at 237 First big offset.(10metres)
Can almost see bridge (point of commencement)

243 In offset canyon. Great folding diagram of east side exposure in original notes exposure 5 by 15 metres approx. Lots of deformed quartz stringers many 1 to 2 inches wide others more numerous 20 to the inch 1/4 inch thick

250 In offset canyon , banding as much as 20quartz viens to inch.

260 Sample west side offset canyon, quartz extremly hard, cant break it maybe fifty leaves per inch.

270 West side offset canyon very hard milkey quartz 50 leaves (layers) to the inch

292 Coming out of offset canyon sample of creek gravel from snipers location

292 Recreational hand panning "snipers" showed gold nuggets retrieved form two shovelfulls. The nuggets were 10 millimeters in size. One was of traditional nugget configuration however the other was "hackeled" suggesting local origin. The Sniper said this was a typical division between the two types and is interestingly consistant with the TRIANGLE observations at 2000 metres south at Sombrio. A photo of the author and location as well as a photo of the nuggets in the pan compared with a Canadian twenty five cent piece which is 24 MM in diameter is here inserted.

308 Sample strike N 75E Dip 45N slightly north of offset canyon (30 metre) still intense quartz banding pimples galore in east side rock exposure 150 tons in sight

328 Same material same dip and strike

390 Same material still highly banded. First milk stone found, same dip same strike same rock both sides northerly and southerly for 100 metres

402 same highly folded

425 large quartz vein

542 Southerly end of 2nd big offset canyon Big slide second offset S75E
Possible route down through slide . A rope would be useful for safety and samples.

End of sample strip 15 August 1998

LINE RUN AND SAMPLES TAKEN 20 AUGUST 1998

20 August 1998 This is a re-run to double check sample positions taken 15 August and to extend samples further northerly on a course 030

00 Metres is the same point of commencement being intersection of centre line of West Coast Highway and centre line of Minute Creek Victoria Mining Division

043 large flat pimple rock float centre stream

048 more pimple rock , lots of pimple rock float

090 huge pimple rock float float 2 by 3 by1/2 metres
East side wall rock is pimple rock 50 tons in sight

101 Masssive float boulder and rock wall all pimple rock 20 plus per inch

119 quartz on west wall and pimple rock

226 massive boulder pimple rock 2 by 2 by 1 metres east side about 50 metres south of first small (10 metre?) offset. Opposite small slide on west side
226 A samples of crystals on surface of boulder 226 shape columnar, colour black redish when pounded into powder.

236 Directly oposite first offset slide(small slide really rock face 100 feet high)

270 In first offset canyon highly folded

420 pimple rock almost all way (from station270) lots of quartz, few large glacier boulders?

541 metres this is at end of sample line run 15 august 1998 this was found by re measurement at 542 meters or a one metre error. In each run chain was carefully checked at the new station and seen to be clear of obstructions to the last station. However no allowance was made for slope which was almost negligable being at constant hight above water level. (estimated elevation rise approx 10 metres)

541 is opposite large hemlock stump 15 inches diameter and 8 ft high with "sniped" or beveled top which is 5 metres above canyon floor on a point of rock on East side and opposite slide

541 continued . All pimple rock,more pimples,more quartz, more layers per inch layers of 4 inch thick siltstones in west sidewall

601 Quartz in stream bedrock 2 inches wide . part of a series 20 metres north of offset but might be part of material at 541 probably south side of offset.
Five or six 2 inch viens run width of 10 feet in stream bedrock exposed for 20 feet strike S 70 E dip S36 N. On wall rock south 20 ft opposite also quartz 50 leaves or viens per inch. Almost impossible to break highly altered and apparently highly compressed.

601 continued slope of of bank (logged for possible skyline access)
Bottom to east rim 42 deg (90%)
Bottom to West Rim 26 deg (50%)

613 Extremely hard banded rock 50 plus layers or quartz viens per inch

628 Many many bands of quartz 1/2 to to 2 inches wide between 601 and 608 maybe 5 percent in large veins much more in small veins.

697 One metre diameter Hemlock stump 2 metres tall 5 metres on east side of stream and above pool. Quartz continues but not as large.

712 Pimple rock material bedrock east side , bedrock on both sides

759 Still lots of quartz mica amalgram , very hard rock

831 Deep pool , waterfall . In flood times probably 2 metres high narrow gorge 3 metres wide direction N30 E (030)
Bedrock strike N 85 E dip 37 North

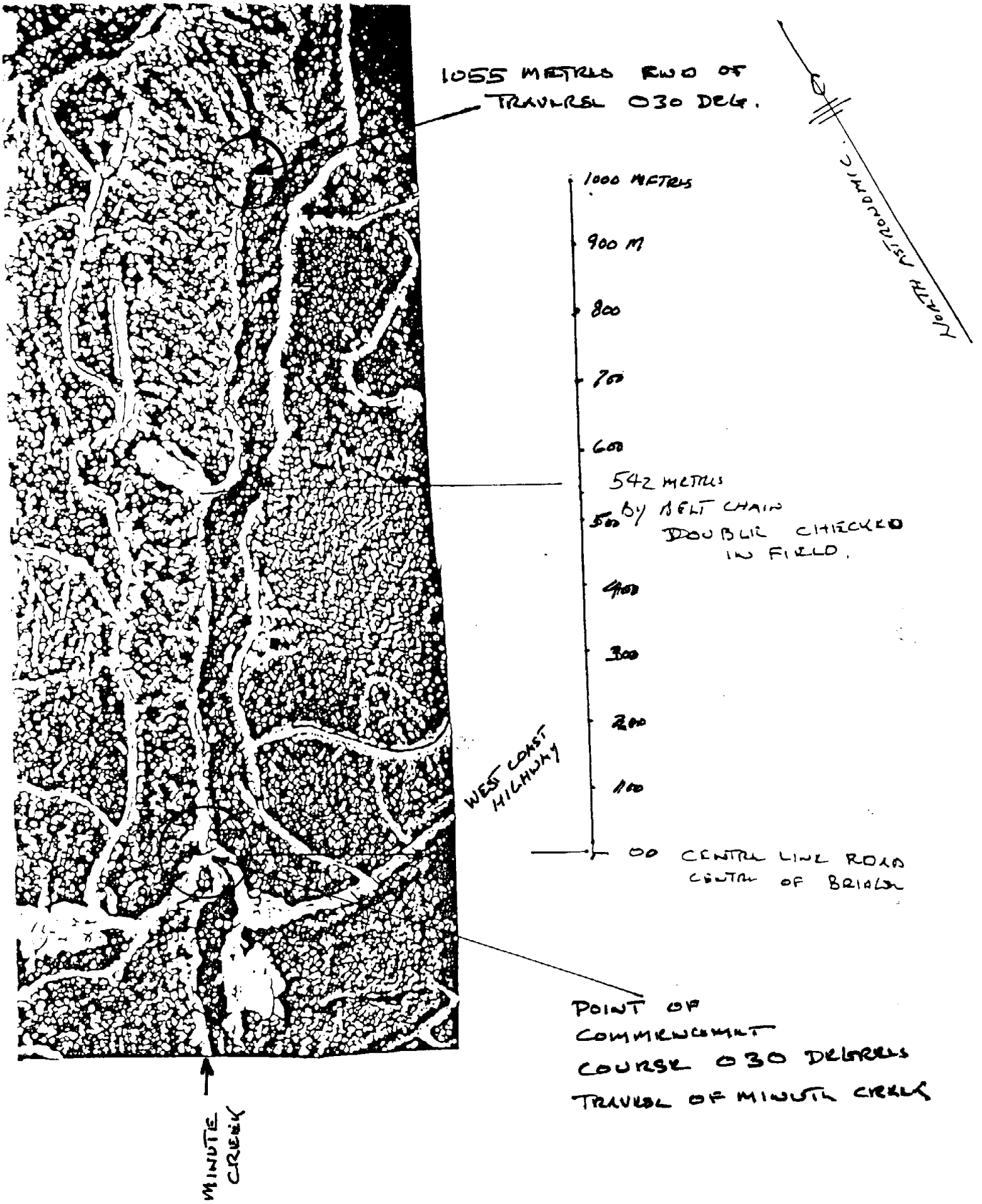
Wall rock on east side heavily folded and banded lost of post fold quatz milkey with vugs

Line between 831 and 1055 is N30 E or 030

1055 metres END of SAMPLE LINE TRAVERSE

at this point creek bed takes an approximately 70 degree bend eastward (090) for a short unmeasured distance estimated to be 100 metres before reassuming a track roughly 030 degrees which the valley of Minute follows from the point of commencement of this line to the point at which minute creek enters T3

This offset was not examined

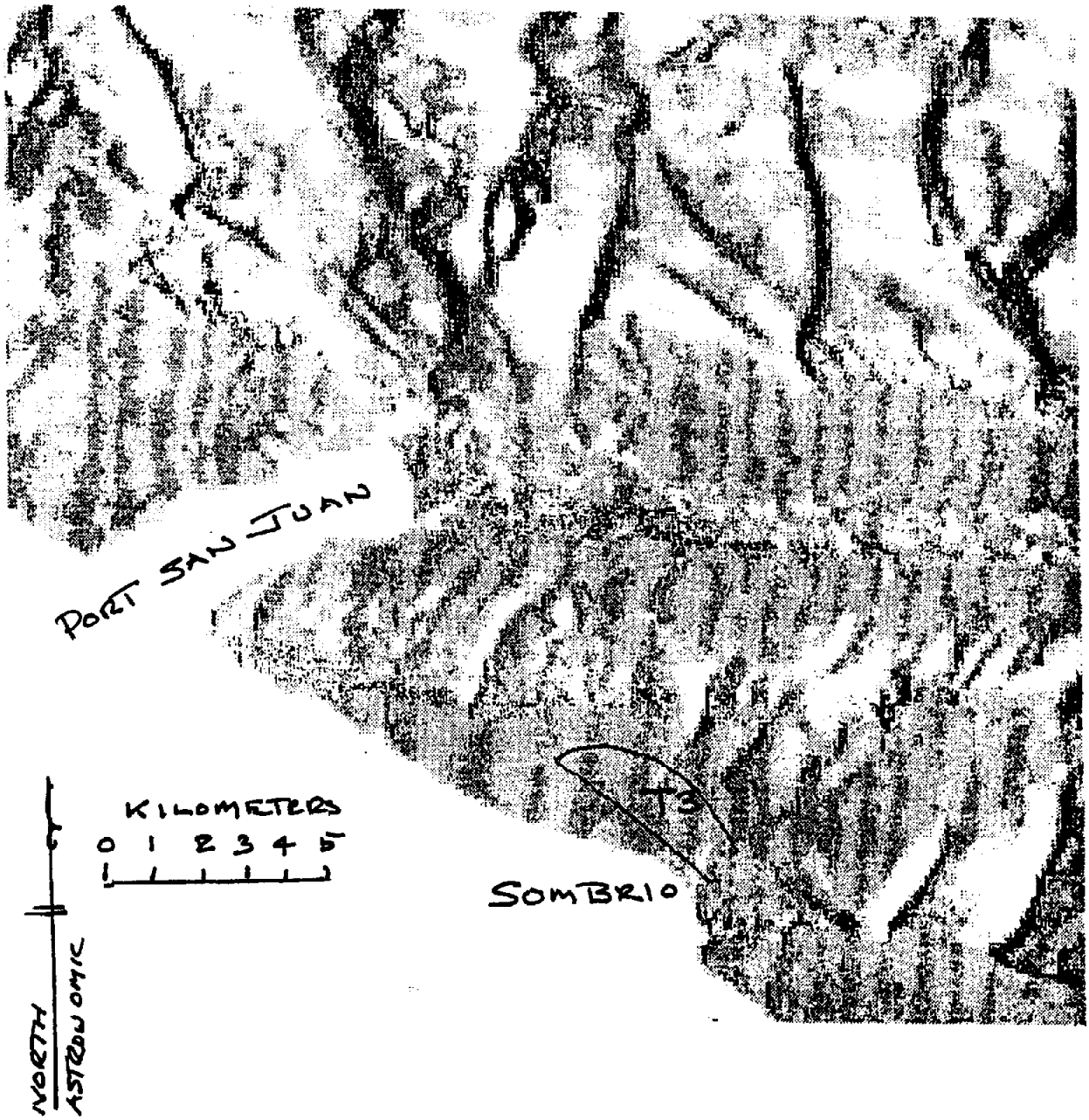


The line of samples are taken at water level and by reason of the small rise of only 40 metres in 1000 metres parallax is not graphically measurable given the flying altitude and focal length.

OBLIQUE AIR VIEW

From a point approximately 500 metres north of the north line of T3 looking down Minute Creek on a bearing of approximately 210 degrees astronomic.
Point of commencement can be made out in distance on West Coast Highway bridge

SOMBRIO - T3 GROUND PENETRATION RADAR SCAN.



STATEMENT OF PROSPECTORS QUALIFICATIONS

Prospector and author of this report is Ian M. Sherwin
Founder in 1977 and president of TRIANGLE VENTURES LTD.

The prospectors qualifications are

1. Late 40's early 50's member of the Canadian Society of Forest Engineers and the Appraisal Institute of Canada

2. Fifty years technical field involvement in natural resource development, field observations and basic field surveying, prospecting etc., photogrammetry, Land form analysis, water course analysis, heavy materials handling and environmental impacts. (FMC holder since 1949. A mineral property owner since at least 1951)

3. The author of original research in soil microbiology, including the development of technical papers related to the application of this research which resulted in the grants of patents in Canada, Great Britain, The United States, South Africa and other countries.

4 The invention of a system to enhance the survival of salmon fingerlings in hydro electric developments.

5. Many years involvement in technical processes related to mineral exploration and industrial mineral development and all this requires of a prospector.

6. field studies 1962- 5 in paragenic relationships of hydro-thermal deposits. in regard to a Manganese property which I owned, my mentor in these Dr. Hewett postulated the formation of "blue smokers"many years before they were discovered.

7. Long - term intense interest in chemistry, physics and electronics and their practical applications in resource exploration in the field.

Ian M. Sherwin

8 October 1999

ITEMIZED COST STATEMENT

Rations for work described on page 1		
Rations for 12 man days at $20 per day		**$240**
Transportation for work described on page 1		
Four by four vehicle 6 journey of 100 miles return at a milage of		
50 cents per mile		**$300**
Air photograhy of T3		
Two Charter flights Cesna 175	**inv 2360**	**$511.12**
Assays Dr. Hoffman		
Borate fusion process,	**inv 16193**	**$470.67**
shipping samples		**37.59**
Laser Ablation and Scanning Electron Microprobe analysis of samples		
University of Victoria Dr. Chen invoice 1N98 1023		**$500.00**
Assays		
Activation labs inv. 16359		**53.50**
Chemex labs		**59.06**
Air fare for		
George Mason Geophysist to examine and sample		
Plate segment exposed by low water minute Cr. T3		**447.53**
WISETECH magnetic separations		
International Separations Systems Inc.	**inv. 23 1108**	**5,500 .00**
Being in total the sum of Eight thousand one hundred nineteen		**$ 8119.47**
Detail from following page 21		**$ 3600.00**
	Total	**$11,719 47**

I herebye certify that I Ian M. Sherwin as a bare minimum caused, did or paid for the above work upon T3 as described.

Ian M. Sherwin FMC 124 506

President TRIANGLE VENTURES LTD FMC 127 267

MINE WORK T3 1998 page 1

15 August 1998

Chain and Compass traverse trending north ~~85~~ 30 east along Minute Fault.
000 metres at Hwy centre line hand samples taken and logged dip and strike taken at 024,044,071,101,117,132,157,170,178,192,211222,237,241,250,250,260,270'270,292,308,328,390,402, 425, 542 metres. Average sample weight 5 lbs rock
I. Sherwin and F. Matthes. each worked a long day of 16 hours
Nominal rate for work of two men of this expertise and class of work $ 600

20 August 98

Repeat Chain and compass traverse trending north ~~85~~ 30 east of minute fault to both double check above chainages and to extend sampling northerly. Also to thicken up sampling. 000 metres at HWT centre line, samples taken and logged at 043,048,090, 090,101,119,226,236, 270,420,541,601,613,628,697,712,759,829,831metres average sample weight 5 lbs rock. dip and stike taken and logged
I Sherwin and F. Matthes each worked a long day of 12 hours
Nominal rate for work of two men of this expertise and class of work $600

12 Sept 1998

200 lbs opf bulk hand sample taken between 000 and 100 metres for milling and processing by Wise apparatus. Examination of quartz vein at 211 metres entire minute cut photographed with particular attention to sample sites. potential drilling sites and access scouted.
I Sherwin and F. Matthes each worked a long day of at least 12 hours
Nominal rate for work of two men of this expertise and class of work $600

6,7,8 October 98

Chain and compass traverses of trails and roads, reconnaissance of access including tape marking of trails. Referencing sample locations to legal posts. Identifying road work,drill sites and other work that will require permits, assessing means of causing least or if possible no disturbance to second growth, surface values, hydrology etc.
I. Sherwin and F. Matthes three 12 hour days
Nominal rate for two men of this expertise and class of work(3 days) $1,800

I hereby certify that I. Sherwin and F. Matthes as a bare minimum did the above work upon the said T3 as described and that the said I. Sherwin and F. Matthes have each over thirty years experience in this technical type of work and did an do hire people for this class of work from time to time in this area and that the sums described are consistent with the rates for this type of expertise, reliability and work and being in total the sum of three thousand six hundred dollars $3,600.
May we beg that the above work upon T3 be accepted as field work.

Ian. M. Sherwin FMC 124 506 President TRIANGLE VENTURES LTD
F. Matthes FMC 141 444 Treasurer FMC 127 267

12 APRIL 99

FIRE ASSAY : NICKEL SULPHIDE COLLECTION

1. Flux components for Nickel - Sulphide collection.

$NiCO_3$	-	32,0g
Na_2CO_3	-	45,0g
$Na_2B_4O_7$	-	90,0g
S	- approx	12,5g (depends on ore - reducing or not/see formula in 3)
SiO_2	-	10,0g (depends on ore - silica content).
$CuSO_45H_2O$	-	2,0g (has little effect really - but will stop erratic gold collection).
$FeSO_47H_2O$	-	4,0g

2. The above mixture is useful at (PGM) concentrate levels of say 10 ppm to 10-20%, figures above this tend to be inaccurate and do not produce good replicates.

3. Sulphide to sample ratio is approximately 1:1.

4. Reduction formula - Sulphur required = $\frac{\text{Ore oxidation}}{\text{Amount ore 1g S oxidizes}}$ = S

5. Assay run for a hour at 1100°c.

6. NiS button is cleaned then crushed.

7. NiS is leached with 300mℓ conc. HCl, to leave PGM residue (i.e. wash out Base Metals).

8. Residue is dissolved in approximately 150mℓ Aqua Regia.

9. Solution presented to ICP or AA in normal way.

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THE DETERMINATION OF ALL THE PLATINUM GROUP ELEMENTS AND GOLD IN ROCKS AND ORE BY NEUTRON ACTIVATION ANALYSIS AFTER PRECONCENTRATION BY A NICKEL SULPHIDE FIRE-ASSAY TECHNIQUE ON LARGE SAMPLES

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SUMMARY

The noble metals are inhomogeneously distributed in sulphide ores and their host rocks. It is therefore necessary to analyse large sample sizes to obtain representative analyses. A nickel sulphide fire assay technique has been adapted to extract the noble metals from a large sample size (50 g) into a nickel sulphide button. Subsequently the fire assay button is dissolved in hydrochloric acid and the solution is filtered. The noble metal residue retained on the filter paper is analysed quantitatively by i.n.a.a. techniques. This method is rapid, relatively inexpensive and has better sensitivities for all the noble metals than other analytical techniques.

The noble metals are inhomogeneously distributed [1—6] in rocks and ores, forming discrete noble metal minerals and possibly occurring in solid solution in rock-forming minerals, chromites and sulphides. The levels (ppb) at which the noble metals occur in most rocks and ores are generally well below the detection limits of most analytical techniques [4]; neutron activation with γ-spectrometry gives sensitivities under ideal conditions that are several orders of magnitude better than those obtainable by other approaches. The limiting factors in n.a.a. are the small sample size (typically less than 500 mg) and the complexity and cost of isolating the individual elements from the interfering matrix so that the best sensitivities may be realized. N.a.a. provides a powerful analytical method at relatively low cost if large sample sizes can be treated rapidly.

A nickel sulphide fire-assay technique quantitatively collects all the platinum group metals (PGM) and gold from a large sized sample. The bead is dissolved in 12 M HCl; the residue is collected on filter paper and irradiated. The noble metals on the filter paper can be determined by instrumental neutron activation analysis (i.n.a.a.).

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Previous noble metal analyses by n.a.a.

It has rarely been possible to determine the noble metals by i.n.a.a. at the sub-μg levels at which they occur in rocks and ores. Crocket [7] stated that radiochemical neutron activation analysis (r.n.a.a.) methods were necessary for terrestrial rocks; however, some elements, particularly Au and Ir, could be determined instrumentally in some meteorites and ores.

Various r.n.a.a. procedures have been developed for the determination of most of the noble metals (excluding Rh) in rocks and ores. Crocket et al. [8] developed a procedure for Ru, Pd, Os, Ir, Pt and Au by fusion of a small (100—200 mg) irradiated sample with non-radioactive carriers of those elements; Nadkarni and Morrison [9] determined Au, Ru, Pd, Os, Ir and Pt in geological materials by r.n.a.a. procedures on 300—500 mg samples with Strafion NMR (Polycycle-NBL-17) ion-exchange resin; Caramella-Crespi et al. [10] determined Pd, Pt, Ir, Au and Ag by r.n.a.a. techniques after selective adsorption of these metals on molybdenum dibromide; and Millard and Bartel [2] used a mini-lead fire-assay procedure after sample irradiation (0.5—1-g sample) to separate Pd, Pt, Au, Ru, Os and Ir from their matrix.

Turkstra et al. [11] determined Rh, Pd, Pt, Au, Ir and Ag in ores, mattes and lead assay beads by i.n.a.a. procedures. Only Ir, Pt and Au could be determined directly in South African platinum ores, whereas Rh, Pd, Ag, Ir, Pt, and Au could possibly be determined in mattes containing very high PGM contents (15—500 ppm). Lead fire-assay beads prepared from South African platinum-bearing ores could be used to determine Rh, Pd, Ag, Ir, Pt and Au if these samples contained very high PGM concentrations. Ru and Os were not detectable by any of these methods.

Fire-assay procedures

The classical fire-assay technique uses lead as the collector for the noble metals. Beamish [12] found that there was "non-quantitative collection of the more insoluble platinum metals in the classical fire-assay". The insoluble noble metals were iridium, osmium and ruthenium. Robert et al. [13] reported that the lead fire-assay procedure did collect the noble metals quantitatively; however, subsequent cupellation for the separation of the lead resulted in large losses of osmium, ruthenium and iridium. Samples which contained sulphur had to be roasted and if more than 0.5% nickel was present it had to be removed with an HCl leach. For nickel sulphide ores these preliminary processes were necessary but undesirable as possible losses of the noble metal could occur.

Robert et al. [13] found that for all the noble metals a nickel sulphide fire-assay procedure was equal or superior to collection of the noble metals by the lead method; with the nickel sulphide procedure samples containing any amounts of nickel and sulphur do not require any pretreatment and a lower fusion temperature (1000°C in comparison with 1000—1200°C) reduces the possibility of losses of some of the more volatile PGM, particularly osmium. (High purity nickel produced through a carbonyl process

was supplied by Inco Metals Company Ltd. This material contains only 0.1 ppb Au and Ir; < 1 ppb Pt, Pd, Os, Ru and Rh.)

Subsequent to the fire-assay procedure, Robert et al. [13] dissolved the nickel sulphide fire-assay bead in 12 M HCl, filtered the solution and dissolved the noble metal residue in hydrochloric acid and peroxide. Robert et al. [14] studied the effects of sample matrix elements on the efficiency of the fire-assay procedure. The noble metals were determined colorimetrically or by atomic absorption spectroscopy. The preparation of three fire-assay beads (if Os < 10 ppm) was necessary and the sensitivities realized were poorer than those possible by n.a.a. techniques.

EXPERIMENTAL

Apparatus

During the fusion procedure a large home-made muffle furnace capable of reaching 1000°C was used. For the filtration procedure a Gelman Instrument Company vacuum filter apparatus (cat. no. xx1004720) was used.

Irradiations were performed (SLOWPOKE II reactor, University of Toronto) with a thermal neutron flux of 1.0×10^{11} n cm^{-2} s^{-1}. Pd and Rh were counted on a horizontally mounted Ge(Li) detector which has a resolution of 1.93 keV (FWHM), a peak-to-compton ratio of 32:1 for the 1332-keV peak of ^{60}Co, and a relative efficiency of 6.7%. The detector was connected to a Canberra Instruments 8180 4096-channel analyser. Pd, Pt, Ir, Os, Ru and Au radioisotopes were counted with a Princeton Gamma-Tech Ge(Li) detector with an active crystal volume of 65 cm^3, connected to a Tracor Northern TN-1700, 4096-channel analyser. This system has a resolution of 1.75 keV (FWHM), a peak-to-compton ratio of 43.1:1 for the 1332-keV peak of ^{60}Co, and a relative efficiency of 12.4%.

Reagents

All reagents must be tested to make sure that they are free of noble metals. Commercially available nickel products may contain substantial amounts of noble metals. Blank fire-assay charges were analysed whenever new reagent batches were introduced to ensure absence of noble metals. The following reagents were used in the fusion procedure: fused, ground sodium borate (Fisher Scientific S-252); calcined dry, purified sodium carbonate (Fisher Scientific S-261); silica floated powder, ca. 240 mesh (Fisher Scientific S-153); sublimed sulphur (J. T. Baker Chemical Co., 5-4088); nickel carbonyl powder (Inco Metals Co. Ltd.); 30-g fire-assay crucible (Canlab 8522-30C). During the dissolution stage 12 M HCl (J. T. Baker Chemical Co., 3-9535) and Metricel GA-1 (pore size 5.0 μm, 47 mm) filter papers (Gelman Filtration Products, #60003) were used.

Sample preparation

Fusion. Nickel sulphide fire-assay buttons were prepared from 30—50-g

samples, according to the fusion procedure of Robert et al. [13] with slight modifications. Instead of mixing the reagents and sample on glazed paper it was more satisfactory and convenient to mix them directly in the crucible; nickel powder, prepared by the nickel carbonyl process, was used instead of nickel oxide; after fusion the crucible contents were allowed to solidify in situ instead of pouring the crucible contents into an iron mold.

Dissolution and filtering. The bead was crushed in a hardened steel piston-type device to obtain a particle size of ca. 1 mm. The crushed pellet was heated with 400 ml of 12 M HCl in a covered beaker on a hotplate until the sample dissolved completely. When cooled, the solution was filtered under vacuum and washed with ca. 400 ml of distilled water. The black residue on the filter paper was folded into a triangular shape and sealed in plastic ready for the irradiation and counting procedure.

I.n.a.a.

The noble metal content was determined by a procedure involving two to three countings. Rhodium and palladium were determined during the first count, palladium if required (low levels, below ca. 50 ppb are not detected in the first count) during a second counting and the balance of the noble metals in a third count.

Rhodium and palladium. The samples were irradiated serially for 5 min and then allowed to decay for 60 s so that very short-lived radioisotopes, e.g. ^{77m}Se ($t_{\frac{1}{2}}$ = 17.5 s), could decay. Samples and standards were counted for 200 s for the ^{109m}Pd and ^{104m}Rh γ-rays. Nuclear data for the radioisotopes are given in Table 1. Peak areas, corrected for background, were compared for samples and standards.

Palladium, platinum, osmium, ruthenium, iridium and gold. Up to forty

TABLE 1

Nuclear data (Data from Bureau of Radiological Health and the Training Institute Environmental Control Administration [18])

Element	Induced nuclear reaction	Isotope counted	% Isotopic abundance target isotope (θ)	Cross-section (barn)	Half-life of nuclide produced ($t_{\frac{1}{2}}$)	γ-ray used (keV)
Rhodium	^{103}Rh (n, γ) ^{104m}Rh	^{104m}Rh	100.0	800	4.41 min	51
Palladium	^{108}Pd (n, γ) ^{109}Pd	^{109}Pd	26.7	12	13.5 h	88
	^{108}Pd (n, γ) ^{109m}Pd	^{109m}Pd	26.7	0.2	4.69 min	186
Platinum	^{198}Pt (n, γ) ^{199}Pt (β^-) ^{199}Au	^{199}Au	7.2	4	3.15 d	158
Iridium	^{191}Ir (n, γ) ^{192}Ir	^{192}Ir	38.5	750	74.2 d	317 468
Osmium	^{190}Os (n, γ) ^{191}Os	^{191}Os	26.4	3.9	14.6 d	129
Ruthenium	^{102}Ru (n, γ) ^{103}Ru	^{103}Ru	31.5	1.4	38.9 d	497
Gold	^{197}Au (n, γ) ^{198}Au	^{198}Au	100.0	98.8	64.8 h	412

samples, ore standard, internal standard and flux monitors were sealed in a 27-cm^3 plastic irradiation container which was irradiated for 16 h. Samples were allowed to decay for ca. 4 h from the end of the irradiation and were counted for ^{109}Pd for 500—2500 s depending on the palladium content.

The samples were allowed to decay for a further 7—9 d depending on the rhenium content of the sample. The 155-keV ^{185}Re γ-peak interfered with the 158-keV ^{199}Au photopeak. The samples were recounted for ^{199}Au (for platinum content), ^{191}Os, ^{103}Ru, ^{192}Ir and ^{198}Au. Integrated peak areas, corrected for background, were entered into a computer program, which took into account sample weights, yield through the crushing procedure, irradiation time, counting time, and duration of count. Radioisotopes were corrected for decay and the activity was compared with standards of known concentration.

Various problems have been encountered [8, 15, 16] in neutron activation techniques for the noble metals, e.g. the fission production of ^{103}Ru and ^{109}Pd by the reactions ^{235}U (n, f) ^{103}Ru and ^{235}U (n, f) ^{109}Pd, particularly in rocks containing uranium at levels in excess of the noble metals. Gijbels [16] found that this problem was not serious in rocks with low uranium contents, as would be found in basic to ultrabasic rocks and nickel sulphide ores.

Millard and Bartel [2] reported that 75-keV lead x-rays produced by γ-rays from the sample, bombarding the shielding surrounding their Ge(Li) detector, interfered with the 77-keV ^{197}Pt peak. The ^{197}Pt isotope was not used in this work, but it was noted that the 88-keV ^{109}Pd peak suffered from interference from 88-keV lead x-rays. This problem was effectively eliminated by lining the interior of the counting chamber with copper and cadmium sheeting to absorb the lead x-rays; similar results were then obtained for palladium from the 88-keV ^{109}Pd and the 186-keV ^{109m}Pd peaks.

Platinum was counted by means of the 158-keV ^{199}Au γ-ray produced by the reaction ^{198}Pt (n, γ) ^{199}Pt (β^-) ^{199}Au. However, ^{199}Au may theoretically be produced by the reaction ^{197}Au (n, γ) ^{198}Au (n, γ) ^{199}Au.

Filter papers, impregnated with various amounts of gold, were irradiated under the conditions used for samples and standards to test that ^{199}Au was not produced from ^{197}Au by the latter reaction. After a decay period similar to that used for the samples, the test filter papers were counted. Production of 158-keV ^{199}Au from ^{197}Au was negligible.

RESULTS AND DISCUSSION

The proposed procedure was followed for the internal ore standard L.S. 4 [1]; the results presented in Table 2 show better than 13% reproducibility for the 11 individual fire-assay pellets analysed. Certain pellets were split into two portions prior to the dissolution stage and were analysed separately; the reproducibility for different portions of the pellet (e.g., Pt value of H1-18 and H2-18) is poorer, signifying that the fire-assay beads may not be completely homogeneous.

TABLE 2

Reproducibility of analytical data for noble metals in the internal standard L.S. 4

Run	Found (ppb)						
	Rh	Pd	Pt	Ir	Os	Ru	Au
A-4	116	272	285	71	35	132	30
B-2	128	300	339	74	35	125	42
C1-9	134	323	267	80	32	165	43
C2-9	135	320	277	83	32	175	44
(Av.	135 ± 1	322 ± 2	272 ± 7	82 ± 2	32 ± 0	170 ± 10	43 ± 1)
D-10	134	338	312	82	33	173	44
E1-13	130	285	300	76	33	150	41
E2-13	135	275	279	78	31	156	42
(Av.	133 ± 4	280 ± 7	290 ± 20	77 ± 1	32 ± 4	153 ± 4	41 ± 1)
F1-15	130	283	282	74	32	158	42
F2-15	139	291	298	73	34	148	43
(Av.	135 ± 6	288 ± 7	290 ± 10	74 ± 1	33 ± 1	153 ± 7	43 ± 1)
H1-18	143	337	341	80	31	169	37
H2-18	146	331	234	65	31	141	31
(Av.	145 ± 2	334 ± 4	290 ± 80	70 ± 10	31 ± 0	150 ± 20	34 ± 4)
I1-16	132	366	307	76	29	136	46
I2-16	136	332	280	75	28	126	46
(Av.	134 ± 3	350 ± 20	290 ± 20	75 ± 1	29 ± 1	131 ± 7	46 ± 0)
J1-17	141	376	275	76	30	147	46
J2-17	135	327	236	68	26	135	37
(Av.	138 ± 4	350 ± 40	260 ± 30	72 ± 6	28 ± 3	141 ± 8	42 ± 6)
SN-1	141	321	248	—	—	—	36
SN-2	—	—	270	75	—	152	57
Averages	135 ± 7	320 ± 40	290 ± 30	75 ± 5	30 ± 3	150 ± 20	42 ± 6

The accuracy of the method was tested on PTC, the Canadian certified noble metal ore standard; the results are presented in Table 3. For Rh, Pd, Pt, and Au the average values are well within the 95% confidence limits of the recommended values specified by McAdam et al. [17] and the values for Os, Ru, Ir are within the 95% confidence limits of the estimated mean.

The accuracy and precision shown are superior to those reported for most analytical procedures for the noble metals. The detection limits obtained by this method (Table 4) are superior to analytical procedures that do not utilize n.a.a.

The recovery of the noble metals was tested by adding irradiated noble metals to a variety of sample types and carrying out the fusion and dissolution procedures. Loss of the noble metals through these procedures occurs mainly during the fusion procedure in which the average total losses were less than 6% for Pd, Pt, Ir, Os, Ru, and Au. Individual losses for Au did run as high as 8%. These results are summarized in Table 5. Losses of Rh through the procedure could not be tested by radiotracer techniques because of the short half-life of ^{104m}Rh (4.41 min). The experimentally determined and recommended values for Rh are very similar (Table 3).

TABLE 3

Analyses of noble metals-bearing concentrate, PTC, and comparison with the recommended values for Rh, Pd, Pt and Au, and the estimated mean values for Os, Ru and Ir

Run	Found (ppm)						
	Rh	Pd	Pt	Au	Os	Ru	Ir
1a	0.62	13.2	3.1	0.55	0.36	0.63	0.21
1b	0.58	12.9	2.8	0.55	0.31	0.54	0.19
(Av.	0.60	13.0	2.9	0.55	0.33	0.59	0.20)
2a	0.62	12.9	3.3	0.57	0.32	0.58	0.21
2b	0.61	12.1	2.8	0.57	0.31	0.49	0.19
2c	0.64	13.0	3.4	0.64	0.34	0.62	0.21
(Av.	0.62	12.7	3.1	0.59	0.32	0.56	0.20)
3a	0.62	12.6	3.1	0.57	0.37	0.60	0.21
3b	0.59	13.3	3.3	0.58	0.38	0.63	0.20
3c	0.63	12.1	2.8	0.58	0.39	0.59	0.21
(Av.	0.61	12.7	3.0	0.58	0.38	0.61	0.20)
5a	0.64	12.6	2.6	0.58	0.31	nd	0.20
5b	0.64	13.0	2.9	0.61	0.37	nd	0.20
5c	0.62	12.7	2.7	0.78	0.35	nd	0.20
5d	0.64	12.6	2.2	0.60	0.28	nd	0.16
(Av.	0.64	12.7	2.6	0.64	0.33		0.19)
Averages (this study)							
	0.62	12.8	2.9	0.59	0.34	0.59	0.20
Earlier values [17]							
	0.62[a]	12.7[a]	3.0[a]	0.65[a]	0.24[b]	0.65[b]	0.17[b]
95% confidence intervals [17]							
Low	0.55	12.0	2.8	0.55	—	0.34	0.00
High	0.69	13.0	3.2	0.72	—	0.93	0.34
Number of labs. reporting results					1	3	3

[a]Recommended values [17]. [b]Estimated mean [17].

Detection limits by n.a.a. are superior to other methods with the possible exception of electrothermal a.a.s. which is, however, still very much unproven for the real analysis of the noble metals at present. In any case, a fire assay, followed by more lengthy chemical treatments than necessary for the above procedure would be essential for these types of samples prior to a.a.s.

The determination of all the noble metals in rocks and ores by n.a.a. has not been reported previously. Although preconcentration of the noble metals by lead fire-assay techniques prior to activation was tried by Turkstra et al. [11], the analyses did not include Os or Ru and the data were poor for Pt, Pd, and Rh.

TABLE 4

Noble metal detection limits and counting details (Ge(Li) detector number 1 at the SLOWPOKE II reactor facility, University of Toronto, was used for Rh and Pd. All other elements were analysed with the Ge(Li) detector at the Erindale College, neutron activation laboratory)

Element	Detection limits[a] (ppb)	Time counted (s)
Rh	1	200
Pd	50	200
	5	500–2500
Pt	5	700–5000
Ir	0.1	700–5000
Ru	3	700–5000
Os	2	700–5000
Au	0.1	700–5000

[a]Detection limits achieved at the maximum time counted. (Detection limit is defined as the smallest concentration which gives a net peak count of twice the standard deviation of the background.)

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TABLE 5

Recovery of the noble metals from the nickel sulphide fire-assay fusion and dissolution procedures

Sample	Type	Loss (%)[a]						Fusion or dissolution[b]
		Pd	Pt	Ir	Os	Ru	Au	
L.S. 4	Massive sul.	3	3	2	1	1	4	(1)
		—	—	—	—	—	1	(2)
		3	3	2	1	1	5	Total
L.S. 17	Diss. Sul.	4	5	2	2	1	7	(1)
		—	—	—	—	—	1	(2)
		4	5	2	2	1	8	Total
L.S. 35	Host rock (gabbroic)	1	6	1	5	3	5	(1)
		—	—	—	—	—	1	(2)
		1	6	1	5	3	6	Total
L.S. 40	Stringer ore	6	2	2	4	4	6	(1)
		—	—	tr	—	—	1	(2)
		6	2	2	4	4	7	Total
F417917	Host rock (ultramafic)	4	4	—	3	5	4	(1)
		—	—	—	—	—	1	(2)
		4	4	—	3	5	5	Total
F418355	Massive Sul.	5	5	1	3	5	6	(1)
		—	—	—	—	—	1	(2)
		5	5	1	3	5	7	Total
F418341	Vein ore	3	5	2	3	—	4	(1)
		—	—	—	—	—	1	(2)
		3	5	2	3	—	5	Total
L.S. 1	Diss. Sul.	2	2	4	2	—	4	(1)
		—	—	—	—	—	—	(2)
		2	2	4	2	—	4	Total
Average total losses		<4	<4	<2	<3	<3	<6	

[a]— Indicates not detected; tr indicates only traces detected; [b]Fusion stage loss (1); dissolution stage loss (2).

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A SURVEY OF THE DETERMINATION OF THE PLATINUM GROUP ELEMENTS

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Summary—The platinum-group metals (PGMs), Ru, Rh, Pd, Os, Ir and Pt, are widely used as catalysts in petroleum and chemical processes. They find wide applications in automotive exhaust-gas control converters and are of immense importance to the electronics industry. They are found in many items of jewellery and serve to an increasing extent as a form of investment. The PGMs are extracted in minute quantities from a limited number of ores, found mainly in S. Africa and the USSR. They are concentrated and separated from each other by elaborate chemical processes. Because of their great intrinsic value (Pt $650 per oz; Rh $1400 per oz), the recycling of the PGMs from literally hundreds of different forms of scrap is an essential factor in the overall management of the PGM economy. In this survey emphasis is placed on the need to tailor the analytical method according to (*a*) the environment in which the PGMs occur, (*b*) the individual PGM concentrations, and (*c*) the desired sensitivity and precision. The factors which determine the choice of chemical, physicochemical and/or instrumental approaches are discussed. They are further commented on in extensive presentations of dissolution and separation techniques and methods for the final measurement of individual PGMs. Appendices are provided which present the compositions and sources of the products most frequently encountered in PGM analysis, along with information on methods of decomposition, separations required, type of separation, and final determination.

SAMPLING[1-4]

The sampling of homogeneous substances containing precious metals is comparatively simple. Minerals, ores and concentration products should be in powdered form, preferably finer than 200-mesh. They can be sampled by conventional techniques with such sampling equipment as thiefs, riffles and screens. Sampling may be manual or automatic. Homogeneous metals and alloys can be sampled by taking swarf, chips, millings, or sawings.

The sampling of heterogeneous substances is more complicated. Electronic scrap can be alloyed with copper, nickel, or sometimes lead, to produce homogeneous alloys which can be sampled by the conventional sampling procedures mentioned above; alternatively the material can be melted with aluminium, leading to a friable alloy which can be crushed to a powder suitable for normal sampling methods. Some heterogeneous substances can be burned to a powder. Solutions containing precious metals can be evaporated or treated with zinc or aluminium, and the residues ignited prior to sampling. Powdered material containing precious metals is often referred to as "sweeps".

DECOMPOSITION

Low-grade material

Geochemical exploration samples, ores, residues and sweeps.[2,6,7,9-12] These substances contain one or more of the platinum-group metals (PGMs), often in acid-insoluble form. To remove the matrix elements and isolate the PGMs, it is often advantageous to employ some form of fire-assay concentration. It must, however, be borne in mind that the traditional fire-assay methods involving the lead collection system are suitable for isolating gold and silver, less so for isolating platinum and palladium, and only to a very limited extent for isolating rhodium, ruthenium, iridium and osmium. This is largely due to the high melting points of the PGMs and their inability to form alloys with gold and silver that are suitable for subsequent chemical treatment. Therefore, a brief outline of the fire-assay procedure should suffice.

An assay ton* (29.166 g), or a fraction thereof, of sample is taken for analysis and mixed with a suitable flux containing a large proportion of lead monoxide and various proportions of compounds such as sodium carbonate, potassium carbonate, borax, silica, potassium nitrate, or organic substances, such as starch or flour. The ratio of the various components depends on whether the sample (*a*) contains an excess of basic components, in which case more silica is added, (*b*) contains an excess of acidic components (additional carbonate or borax is then required), (*c*) is high in copper (more PbO is then used), (*d*) tends to oxidize the flux components, requiring addition of organic reducing substances, (*e*) reduces too much PbO to lead, in which case potassium nitrate is added as an oxidizing agent.

Optimum conditions, as indicated by the fluidity of the melt and the weight of lead button desired, are ensured by a judicious balancing of the weights of sample and the various flux reagents. The PGMs, together with silver and gold, are collected in the resulting lead button. The matrix elements react with

*One mg per assay ton is equivalent to 1 troy oz per ton.

the flux components to form a slag which is subsequently discarded, unless additionally reworked for the recovery of trace amounts of precious metals retained in it.

If the lead button obtained is of proper weight (30–60 g) and comparatively clean, the scorification step may be omitted. However, when the lead button weighs more than 60 g or is known or suspected to retain base metals, it should be transferred to a fireclay dish called a scorifier. More lead is added, and a little silica, and the mixture is melted in an oxidizing atmosphere for about 30 min at about 900°. Much of the lead then oxidizes to form a glassy slag which further extracts impurities. The lead button is next placed on a preheated cupel prepared from bone ash or magnesite. On heating in a muffle furnace at a temperature of about 800–850° in an oxidizing environment, the resulting lead oxide is absorbed into the cupel or is volatilized. A bead of precious metals remains. This cupellation step is only feasible when the bead contains an adequate amount of silver, either present in the original sample or added to the sample-fusion charge, to collect the PGMs. Osmium is largely volatilized during the cupellation step. For further treatments of the silver bead, see below. For a chemical treatment of the lead button, see the section on separations, below.

Other fire-assay collection media have been suggested for determining small amounts of platinum-group elements. They involve the use of iron–nickel–copper alloys and tin.[2,12,13] Because of the lower fusion temperature required, copper alone has also been suggested as a collector of the precious metals.[14–17] However, none of the methods above has yet found general acceptance. On the other hand, the collection of PGMs into nickel sulphide (fusion of the sample with a mixture of borax, sodium carbonate, nickel carbonate and sulphur) is being used to an increasing extent.[18–20] This approach has many advantages over the conventional lead-based fire-assay systems. A new technique involving the collection of PGMs into copper sulphide has recently been described,[21] and has several advantages over the nickel sulphide technique. First of all, in the copper sulphide method gold is also quantitatively collected. Another advantage is the possibility of dissolving the copper sulphide in hydrobromic acid, thus allowing the separation of the PGMs from large amounts of silver and lead. In both the nickel sulphide and copper sulphide collection schemes the matrix elements are removed by acid treatments and the precious metals contained in the acid-insoluble residue are eventually determined instrumentally or, where justified, gravimetrically.

Automotive exhaust and petroleum reforming catalysts.[22–27] For the most exacting requirements, the samples are decomposed by an acid treatment with sulphuric acid alone or mixed with phosphoric acid. The final determination is either spectrophotometric or by some other instrumental technique. In the opinion of the writer, fire-assay procedures are less suitable for decomposing catalysts, whether automotive or reforming, since the normal fire-assay fluxes cannot successfully cope with the large alumina content of these catalysts.[28] Other investigators, however, claim quantitative recoveries of platinum metals by fire-assay procedures.[27,29,30]

Metals and alloys containing small amounts of PGMs. Fire-assay procedures are often applicable but in many instances a chemical attack can be used to greater advantage. Typical are copper metal and alloys containing the PGMs originating in electronic scrap. This type of sample can be dissolved in dilute nitric acid and the solution evaporated with sulphuric acid. Sometimes, the sample can be directly decomposed with sulphuric acid. A subsequent treatment with formic acid will aid in the precipitation of platinum and palladium. An additional precipitation of a small amount of copper as sulphide, with either hydrogen sulphide or sodium thiosulphate, ensures complete recovery of even trace amounts of platinum and palladium.[31] In the case of rhodium, this precipitation is quantitative only if the rhodium is first converted into chloride complexes by boiling with hydrochloric acid. This approach is not applicable to ruthenium, since this element is largely volatilized during the heating with sulphuric acid. In addition, the method cannot be applied to iridium, since iridium sulphate is sufficiently stable to resist quantitative precipitation with formic acid, hydrogen sulphide or thiosulphate. More efficient is the dissolution of copper base alloys in fuming perchloric acid and subsequent precipitation of all the PGMs with formic acid from a dilute perchloric acid medium.[31]

Intermediate concentrations of PGMs in powdered form (individual elements up to 25%)

In many instances, the PGMs are soluble in *aqua regia*. If a small residue remains, it may be solubilized by fusion with sodium peroxide, or the precious metals in it may be recovered by one of the fire-assay procedures. It must, however, be remembered that rhodium, iridium and ruthenium do not alloy with silver. On the other hand, small amounts of rhodium and iridium can be collected into gold. Upon treatment with *aqua regia*, gold and rhodium dissolve while iridium remains insoluble.[32,33]

High concentration of PGMs

Platinum-base alloys, Pt 80%, containing 0–5% of Pd, Rh, Ru, Ir, Au or Ag. These alloys are usually soluble in *aqua regia*. Any insoluble silver chloride must be filtered off and re-treated for the recovery of occluded PGMs. The separation of these elements from each other and their final measurements will be described later.

Platinum-base alloys containing more than 10% of Ir or Rh. These alloys are insoluble in *aqua regia* at atmospheric pressure but can be dissolved in it at elevated temperatures in high-pressure systems.[34]

More convenient is preliminary fusion of the sample with zinc and dissolution of the melt in hydrochloric acid.[7] A black powder remains, containing the platinum metals in elemental form, ready for an attack by acids or by other appropriate means, prior to distillation (Os and Ru), chlorination (Rh, Ir), or chemical separations such as by bromate hydrolysis (Pt, from Ir and Rh).

Also of considerable value is a fusion of the sample with lead. The resulting lead alloy can be dissolved in dilute nitric acid, leaving a residue containing PGMs. A small amount of rhodium must, however, be recovered from the nitric acid filtrate. If the lead alloy is decomposed with perchloric acid all PGMs and also silver and gold, can be precipitated as metals by the use of formic acid.[31,35]

Pt–Rh and Pt–Ir alloys, if in finely divided form, can also be solubilized by mixing the sample with 10 times its weight of sodium chloride and heating at 800° in a stream of chlorine.[7]

Palladium-base alloys. These usually contain silver and often varying amounts of platinum, gold and ruthenium. Dental alloys may also contain non-precious metals such as tin, indium, gallium, zinc or copper. These alloys can sometimes be decomposed with nitric acid, but more often require the use of *aqua regia*. Any undissolved ruthenium must be fused with sodium peroxide, dissolved and added to the main sample solution. The separation and determination of the PGMs in palladium-base alloys will be described later.

Pure PGMs

Platinum and palladium are soluble in *aqua regia*; rhodium is solubilized by fusion with sodium pyrosulphate; ruthenium is strongly attacked by hypochlorites; Ru, Rh, Os and Ir are rendered soluble by fusion with sodium peroxide and dissolution of the cooled melt in hydrochloric acid.

SEPARATIONS

Separation from matrix elements

Separations involving fire-assay products. The lead button obtained as described above is treated with dilute nitric acid. After filtration, the insoluble residue contains all the gold, ruthenium and iridium, most of the platinum, but only part of the palladium and rhodium. The insoluble residue is therefore best suited for the determination of ruthenium, iridium and, where required, of gold. The determination of the other platinum group elements by the lead button–nitric acid dissolution method is complex. Thus, when a lead button containing Au, Ag, Pt, Pd, Rh, Ir, Ru and/or Os is dissolved in dilute nitric acid, most of the osmium is volatilized. Silver and part of the palladium and rhodium are dissolved together with the lead. If the silver content of the sample is significant, some platinum will also dissolve. When the insoluble residue is treated with *aqua regia*, gold, platinum, residual palladium and part of the rhodium dissolve, while iridium, ruthenium and residual rhodium remain insoluble. Recently an alternative treatment of the lead button was described,[35] based on the dissolution of the lead button in perchloric acid with the addition of acetic acid. Subsequently, the PGMs were precipitated with formic acid. More recent tests indicate that the acetic acid can be entirely omitted, and if the lead button contains only small amounts of PGMs the dissolution can be speeded up by the addition of about 0.25 g of arsenious oxide. The method can be extended to major concentrations of all the PGMs.[31] Most surprisingly, no Ru is lost during the heating step with perchloric acid, since the Ru apparently remains as an Ru–Pb alloy.

If the lead button has been subjected to cupellation (see fire-assay methods, above), the silver bead containing PGMs is treated with dilute nitric acid to dissolve the silver and most of the palladium. Platinum will also dissolve if the sample contains at least an equivalent amount of gold. The silver bead naturally must be large enough to hold any rhodium, ruthenium, and iridium mechanically (minimum ratio of Ag to PGM 1000:1). These three elements, together with gold, remain insoluble in dilute nitric acid and can be determined instrumentally after fusion of the insoluble residue with sodium peroxide and acidification of the leached melt with hydrochloric acid. In another recently introduced fire-assay technique, cupellation is interrupted when the weight of the lead button has been reduced to less than 1 mg. This lead bead is then analysed for the PGMs by standard optical emission spectrometry techniques.[36] Platinum and palladium can also be determined instrumentally after removal of the silver by precipitation as the chloride. If present in sufficient quantities, platinum and palladium can be determined gravimetrically after precipitation with ammonium chloride (Pt) or dimethylglyoxime (Pd). Also of interest is the selective extraction of the palladium dimethylglyoxime complex with chloroform.[37]

Other separation schemes. These are justified only if other elements interfere with the final determination of individual platinum group elements. With modern instrumentation it is often possible to make final measurements without the necessity for any separations. In other instances, limited separation schemes may suffice. Thus, the PGM content of a solution can be determined efficiently by plasma techniques without the removal of modest concentrations of alkali metals (*e.g.*, from sodium peroxide fusions) or copper (from dissolution of Cu_2S).[21] Similarly, small amounts of copper or nickel do not interfere with the precipitation of platinum by ammonium chloride or the precipitation of palladium by dimethylglyoxime (DMG). On the other hand, the gravimetric determination of a PGM presupposes the absence of all other elements when the final weighing form is the PGM itself. Of the many ion-exchange

methods suggested in the past, only the separation of PGMs from base metals by cation-exchangers (such as Dowex-1) is used to any extent.[11] Thus, in weakly acid medium, base metals are retained, while the PGMs, owing to the strength of their chloride complexes, pass into the effluent. Unfortunately, there is slight retention of palladium, probably as palladium(IV). One other cation-exchange procedure deserves to be mentioned. Strelow[38] recently described a method for the separation of all the PGMs from large amounts of base metals, with the strongly acidic cation-exchange resin Ag5QW × 4. This method is based on the formation of stable PGM–thiourea complexes which are sorbed by the resin.

Various possibilities of applying solvent extraction techniques to separations of PGMs from base metals and from each other have been discussed by Freiser.[39] Another technique which has not yet been fully investigated is based on cellulose chromatography.[11,40]

Only a few other separation schemes can be cited here. Platinum and palladium in trace amounts can be collected by freshly precipitated tellurium.[25,26] Palladium can be separated from large amounts of silver and/or lead by its precipitation from dilute nitric acid solution with dimethylglyoxime.[31] Small amounts of $Pd(DMG)_2$ can be extracted with chloroform.[11] All the PGMs can be separated from the matrix elements by precipitating the former with hypophosphite and a mercurous salt in a slightly acid medium[41] or with hydrazine hydrate or aluminium in an alkaline medium.[31] Sodium nitrite can also be used; it is one of the most effective reagents for complexing the PGMs and precipitating gold and base metals.[2,42]

Separation of PGMs from silver and gold

The separation from silver is achieved by precipitation of silver chloride. It must, however, be remembered that the precipitate has a tendency to occlude PGMs, particularly palladium, so it must be purified. This can be done by fire-assay or by converting AgCl into soluble $AgClO_4$ by fuming with perchloric acid. There are many schemes for separating the PGMs from gold, amongst which precipitation of the latter with oxalic acid appears to be the most quantitative.[2] There are also ion-exchange resins suitable for the separation of PGMs from gold.[43]

Separation of the PGMs from each other

As in the case of the separation of the PGMs from base metals, there is an increasing tendency to avoid at any cost chemical separation of the precious metals from each other. Since there exist comparatively few mutual interferences of the precious metals in their determination by atomic-absorption spectrometry (AAS) or plasma techniques, the belief is widespread that, with good instrumentation, time and money could be saved by eliminating chemical separations altogether by relying strictly on instrumental measurements. Nothing could be further from reality. First of all, the precision obtainable by AAS or plasma techniques is rarely better than 1% and may be as poor as 5–10%, particularly when the sample and standard solutions cannot be closely matched. Also, in most instrumental methods the sensitivity varies to a great extent from one PGM to another. For instance, the sensitivity for rhodium by both AAS and by PES (plasma emission spectrometry) is very high, whereas that of AAS for iridium is wholly unsatisfactory and that of plasma emission just about acceptable. This will be discussed further below in the section on instrumental methods. It is for this reason that the chemical separations, which admittedly are considerably slower and which also require a thorough knowledge of the chemistry of the precious metals, cannot be entirely avoided.

Separation of platinum and palladium. If platinum is the predominant element, the usual procedure consists of precipitating the platinum with ammonium chloride and determining the palladium in the filtrate by precipitation with dimethylglyoxime. The platinum usually retains a little palladium and must therefore be reprecipitated. A small amount of platinum is soluble in the ammonium chloride medium and must be determined by AAS or plasma techniques, usually after destruction of the ammonium chloride with nitric acid.

If palladium is the predominant element, or the sample contains at least 100 mg of palladium, prior precipitation of the palladium with dimethylglyoxime is more effective. Platinum is determined in the palladium filtrate after the alcohol has been boiled off and the organic matter destroyed by evaporation with nitric and perchloric acids. Subsequently, the platinum is precipitated with ammonium chloride or other agents such as hydrazine or hydrogen sulphide. The separation of platinum from palladium can also be achieved in conjunction with the bromate hydrolysis scheme described later.

Separation of platinum from iridium and/or rhodium. This is a modification suggested by German analysts[44] of a method originally introduced by Gilchrist.[45,46] Rhodium and iridium are separated from platinum by the interaction of sodium bromide with sodium bromate in a very dilute hydrochloric acid solution. The reaction takes up protons and liberates bromine, until a pH of 6.5 is reached. At this pH rhodium and iridium are quantitatively precipitated, while palladium and platinum stay in solution. In the original Gilchrist version the palladium accompanied the rhodium and iridium, because the pH was adjusted to 7. The pH adjustment is automatic in the German version, whereas the adjustment in the original method requires considerable skill. To achieve a quantitative separation it is advisable to reprecipitate the rhodium plus iridium. Platinum is recovered from the combined filtrates by precipitation with zinc and the addition of hydrochloric acid. The platinum sponge is filtered off and dissolved in *aqua regia* and

the metals are eventually precipitated with ammonium chloride. The hydrated oxides of rhodium and iridium are dissolved in acid and the metals determined instrumentally.

Separation of rhodium from iridium. This is one of the most difficult analytical tasks. No entirely satisfactory method is available. Copper, silver and antimony powders have been suggested by some and rejected by others.[2,7,47-50] The precipitation of rhodium with titanium trichloride, originally proposed by Gilchrist,[45] though tedious and lengthy, is probably as good as any other method. This then is one area where modern instrumentation can come to the rescue of the chemically inclined precious-metals analyst.

Separation of ruthenium and osmium from the other PGMs. Ru and Os in their octavalent state form volatile compounds which give clean separations from the other PGMs. The oxidation to this state can best be achieved in an alkaline medium. This can be done by fusing the finely divided sample with sodium peroxide in a zirconium crucible. Beamish describes a number of distillation procedures. For the simultaneous removal of both metals, oxidation with sodium bromate, bromic acid, perchloric acid, chlorine, bismuthate, permanganate, ceric oxide, lead dioxide or peroxydisulphate can be used.[2] For selective distillation of osmium tetroxide, nitric acid has been recommended.[2] The present writer prefers the distillation of the osmium from a hydrochloric acid medium with sodium chlorate and absorption of the resulting OsO_4 in a sodium hydroxide solution containing some ethanol as reductant. Use of a 1–2*M* hydrochloric acid medium prevents the loss of any ruthenium during the distillation of the osmium. After removal of the osmium, an excess of sulphuric acid is added to the sample solution, which is then evaporated until light fumes appear. A small amount of perchloric acid introduced into the distillation flask will then effect instantanteous oxidation of the ruthenium to the tetroxide, which distils. The RuO_4 is passed into a train consisting of several flasks containing 6*M* or 4*M* hydrochloric acid, which will reduce the RuO_4 to non-volatile $RuCl_3$. Other PGMs can be recovered in the sample solution after the distillation of the Os and Ru.

DETERMINATION OF THE PLATINUM GROUP ELEMENTS

The question whether an element should be determined chemically or by an instrumental technique is a fundamental one for which there is no easy answer. Ideally, the goal is to obtain an analytical result as fast as possible, as precisely and accurately as possible, with equipment which is as cheap as possible, and with personnel requiring the minimum amount of training and/or supervision. Obviously, there have to be choices and compromises. Generally speaking, chemical methods are more precise, instrumental methods more rapid. Errors in gravimetric measurements are usually of the same absolute magnitude, those in instrumental measurements are usually of the same relative magnitude. Thus, a 1-mg error in a gravimetric procedure causes a relative error of only 1 part per thousand if 1 g of the element determined is present. The error is 1 part per hundred (1%), if 100 mg of the element determined is present, and 1 part in ten (10%), if only 10 mg of the element is present. Since the concentration of an element in solution which can be determined instrumentally is more or less constant, the analytical errors are constant and relate to the concentration of the element in the original sample. A typical 1–2% relative error in measurements is intolerable if the concentration of a PGM in the sample is 50% or more. The same error may be tolerable when the concentration of an element is less than 10%. Since the relative error in a typical gravimetric procedure for the same concentration range is 1%, a generalization can be made that instrumental methods should be used optimally in the 10% range or lower, while gravimetric measurements, if applicable, are best suited for the >10% range. The errors inherent in spectrophotometric methods are similar to those of instrumental methods requiring the preparation of solutions, namely AAS and PES (plasma emission spectrometry) techniques. Spectrophotometric methods have the additional disadvantage that in most instances they require the removal of virtually all other elements, particularly other precious metals.

Determination of platinum group elements by chemical methods

Platinum. Earlier researchers disapproved of the ammonium chloride precipitation of platinum because of (*a*) the slight solubility of $(NH_4)_2PtCl_6$ and (*b*) the occlusion of small amounts of other PGMs in the precipitate.[2,45] These objections, however, are no longer valid, since solubility losses and impurity gains can be monitored effectively by modern instrumentation, and corrections applied. The precipitate is ignited to the metal, which is a convenient weighing form. The method is well suited for amounts of platinum greater than 100 mg, particularly for the determination of platinum in platinum-base alloys. Another effective precipitation agent for platinum is formic acic. It should be used in 4.5*M* sulphuric acid medium. The platinum sponge obtained can be directly ignited and weighed, as long as the solution contains no other PGM. Other precipitating agents are hydrogen sulphide, zinc, magnesium and hydrazine. As a rule, the platinum sponge thus obtained is either purified, or dissolved, and the platinum finally precipitated as $(NH_4)_2PtCl_6$. Other precipitants have been described by Beamish and van Loon.[50]

Small amounts of platinum (1–75 mg) can be determined with good precision by the spectrophotometric stannous chloride method.[51,52] This

method is particularly suited to the determination of platinum in reforming and automotive catalysts, since large amounts of alumina and acids, such as hydrochloric, sulphuric and phosphoric, do not interfere. If the final determination is based on the differential spectrophotometric principle, precisions of 0.5% relative can be achieved.[53] Palladium interferes in the determination and must be removed by a dimethylglyoxime–chloroform extraction. The small but significant effect of rhodium and the slight effect of iridium can be compensated for by preparing platinum standard solutions containing matching amounts of the interfering elements. Other reagents suitable for the spectrophotometric measurement have been described by Beamish,[2] Beamish and van Loon,[50] and more recently by Gorda *et al.*[54] Diaminobenzoic acid, originally proposed in 1971,[55] has recently been proposed for the determination of platinum in automotive catalysts.[56] For the determination of 0.1–100 mg of platinum by instrumental methods, see below. Prior separation or concentration schemes may or may not be required.

Palladium. Dimethylglyoxime (DMG) has been used for more than 70 years as a precipitating agent for amounts of palladium ranging from a few mg to 1000 mg.[57] Its value lies in its specificity and the fact that the Pd–DMG product is of definite composition, and hence can be used as the weighing form. There is no interference from the other PGMs, but more than milligram amounts of gold do interfere. Normally, a 1% solution of the reagent in ethanol or methanol is used. An aqueous solution of the sodium salt of DMG is used if alcohol interferes in subsequent treatments of the Pd–DMG filtrate. A great many other dioximes have been suggested over the years. None, however, has been shown to be superior to DMG.[2] Two reagents used in the past, nitrosonaphthol[58] and potassium iodide[59] are now largely replaced by the dioximes. Beamish lists a number of other reagents suitable for gravimetric purposes;[2] their use, however, is limited to special situations and can hardly be justified in view of the recent developments in the instrumental field.

There are a number of possibilities for determining trace amounts of palladium spectrophotometrically.[2] The present writer prefers furildioxime. Its complex with palladium can be extracted with chloroform and measured directly, without back-extraction.[31] For milligram amounts of palladium, the palladium iodide complex looks attractive.[60] Recent developments in spectrophotometric methods for palladium are discussed by Chang and Zhou.[61]

Rhodium. The anhydrous trichloride, $RhCl_3$, obtained by chlorination, can be converted into metallic rhodium by ignition, first in air and then under hydrogen, producing an excellent weighing form. Iridium, which also forms an acid-insoluble trichloride, interferes. In the absence of other H_2S-group elements, hydrogen sulphide is also an excellent precipitant for rhodium. If rhodium has been separated from platinum and palladium by the bromate hydrolysis technique, the precipitate, after thorough washing with ammonium chloride solution, can also be converted into the metal by ignition first in air and then under hydrogen.[7] The metal, however, must be treated with hot dilute hydrochloric acid for removal of residual alkali metal. Again, iridium interferes. It was mentioned above that the separation of the two elements is difficult. It is therefore now a common practice to determine the sum of the two elements gravimetrically, then the lesser component instrumentally. Several other precipitating agents are available.[2,50]

For trace amounts of rhodium, spectrophotometric methods using either stannous chloride[62] or bromide[63] are available. Both methods tolerate small amounts of iridium, but no other PGM. Again, Beamish lists several other reagents which may be of interest.[2] Since the sensitivity for rhodium is one of the highest in both emission and absorption spectrometry, most precious-metals analysts now opt for an instrumental approach.

Iridium. Chlorination to give the anhydrous trichloride and subsequent conversion into the metal can be applied in the same way as for rhodium. Similarly, the product obtained by bromate hydrolysis can be converted into the metal. There is a scarcity of specific precipitating agents for iridium in an acid medium. Reducing agents which easily precipitate the other PGMs are useless for iridium, since small but significant amounts of the iridium are merely reduced to a lower oxidation state.

For trace amounts of iridium there are several spectrophotometric procedures which, unfortunately, are not particularly attractive.[2] They may be of limited interest to those who do not have plasma equipment. The most selective method is based on the production of a purple colour by heating with a mixture of perchloric, sulphuric, phosphoric and nitric acids.[64] The detection limit, however, is only 20 μg per ml of mixed acid.[2] A procedure for determination of iridium in the presence of moderate amounts of platinum (as in Pt–Ir catalysts) is based on the reddish colour developed in hydrochloric or sulphuric acid medium on addition of sodium hypochlorite,[7,65] but rhodium interferes. The instrumental approach involving plasma techniques is far superior (see below).

Ruthenium and osmium. These two elements have many characteristics in common, *e.g.*, they can be separated from matrix elements and other PGMs by distillation of the tetroxides. For the gravimetric determination of both elements precipitation with hydrogen sulphide is feasible, or both elements can be precipitated by hydrolysis at a pH of about 6–6.5.[7] The ruthenium products can be filtered off on paper, but the osmium products must be collected in a Gooch crucible on a pad of asbestos, or on a Munroe-type platinum crucible, before ignition in a stream of hydrogen.

For trace amounts of both elements the spectrophotometric determination based on the thiourea complexes appears attractive. The ruthenium colour is blue[66] and that of osmium is red.[2,67] Other spectrophotometric reagents have been mentioned by Beamish.[2] Owing to the position of Fe and Ru in the Periodic Table it should be of interest that most reagents suitable for spectrophotometric determinations of iron(II) also form coloured compounds with ruthenium.

Determination of the platinum group elements by instrumental methods

The instrumental methods introduced during the last 20 years have undoubtedly revolutionized the repertoire of the precious-metals analytical chemist. In 1966, Lewis mentioned atomic-absorption spectrometry, introduced by Walsh,[18] on the last page of Beamish's classical monograph.[2] In the same monograph Beamish gave a brief outline of potential applications of neutron activation and mass spectroscopy and prophetically predicted "each of these methods may contribute much to the analytical field. As with all analytical methods, they are subject to limitations." At that time, spectrochemical and X-ray fluorescence (XRF) methods were to some extent already used in precious-metals laboratories and therefore were more prominently featured in Beamish's monograph.

The question whether a PGM should be determined by a chemical procedure or by an instrumental technique has already been touched on above. There is no single correct answer to this question. The expression "it all depends", although usually considered a cliché, is most appropriate here. Let us then consider the various factors which may influence the chemist in deciding whether to use a chemical or an instrumental approach, or possibly both.

Type and concentration of elements to be determined. For the trace to low range (0.01% or less) the PGMs are preferably determined instrumentally or, where applicable, by spectrophotometry (generally considered a chemical technique). For the low to medium range (1–10%), there are many instances where a chemical approach may be justified, *e.g.*, the gravimetric determination of palladium with dimethylglyoxime, the gravimetric determination of rhodium and/or iridium after chlorination, the gravimetric determination of osmium or ruthenium after distillation. In this range an instrumental error of 2% relative is reflected in an uncertainty of 0.02–0.2% absolute in the final PGM result. In the high range (10–100%), chemical methods generally have the advantage over instrumental methods, primarily because of their superior precision. Even so, if matrix matching is possible and statistical data indicate that a precision of 1% can be achieved, many analysts may prefer instrumental measurement of the PGMs, particularly if lengthy separations can be avoided.

Equipment available. Instruments are expensive. DCP, ICP and XRF instruments cost $75,000 or more, AAS equipment somewhat less. For the occasional user, the purchase of such instruments, therefore, can scarcely be justified. If the work load of the laboratory, however, consists of often recurring analytical requirements, the acquisition of appropriate instrumentation should be seriously considered. The case for the introduction of instrumentation becomes even more compelling, if more than one PGM must be determined in the same sample. Also of primary importance is the question whether the preparation of the sample solution is simple and the instrumental measurements relatively free from matrix interferences.

Personnel available. The use of instrumentation requires personnel of a higher calibre than that commonly found in a fire-assay laboratory. Though many of the operations with instruments have been simplified and even automated, there has to be someone in the organization who is capable of trouble-shooting when the equipment misbehaves and someone who is capable of determining which parameters of a method are essential. A sound knowledge of the analytical chemistry of precious metals, as well as that of base metals, is a prerequisite for ensuring optimum use of an instrument as the final measuring device.

Standards. It should be remembered that all instrumental methods, unlike most chemical methods, merely compare the concentration of an element in the sample with that in a reference material of known composition. The instrumental method used may tolerate small, moderate, or even large deviations between the concentrations of matrix elements in standards and samples. If the time required to prepare matching standards becomes excessive, a chemical procedure may be more attractive.

The most important instrumental techniques

X-Ray fluorescence.[70,71] XRF was developed from X-ray emission (XRE), in which the sample is directly exposed to radiation with an energy greater than the excitation threshold of the element under study. The method is based on measurement of the secondary X-rays emitted by the constituents of a sample excited by primary X-rays. The inner electron shells of the atom lose one or more electrons, which are then replaced by the outer shell electrons. There is an accompanying loss of energy by the replacement electrons, which is emitted as radiation. The resulting line spectrum is characteristic for each element. Though the intensity of the emitted lines of XRF is only a small fraction of that of XRE, recent advances in electronics have reduced much of the sensitivity advantage of XRE. The main advantage of XRF is its simplicity. Two different types of XRF instrument are available; energy-dispersive and wavelength-dispersive.

Considerable progress in the instrumentation, particularly with regard to the energy sources, the

precision of the dispersion systems and the electronic quality of the detection and measuring devices, allows rapid analysis for the PGMs with excellent precision. Multi-channel spectrometers facilitate the simultaneous determination of all the PGMs, and of gold, silver, and many base metals.

The main advantage of XRF over the various atomic emission or absorption techniques (OES, DCP, ICP, AAS) described below, is that it is non-destructive, allowing recovery of the original sample after the determination. Its main disadvantage is that for quantitative work standards with the same chemical composition and physical characteristics as the sample must be available or prepared. If solid samples are to be analysed, facilities are required for preparing a set or sets of PGM-bearing alloys with highly polished surfaces. One laboratory[71] routinely analyses platinum alloys containing 5–10% of palladium and/or rhodium, another[70] determines the PGMs in a tin button[72] obtained by the fire-assay technique mentioned earlier. A solution technique used by another organization[73] simplifies the preparation of standards, but at the expense of sensitivity. Microgram amounts of all precious metals have been determined by absorbent-pad-and-cellulose pellet techniques.[74] Computer programs have been designed to correct for the positive or negative effects of other PGMs or those of base metals on the result for the PGM being determined. As far as sensitivity is concerned, with wavelength-dispersive instruments, the radiation of the *K*-lines of Ru, Rh, Pd and Ag is 2–3 times more intense than that of the *L*-lines of Os, Ir, Pt and gold.

Optical emission spectroscopy (*OES*). This technique is particularly well suited for the determination of impurities in pure PGMs. In addition, when combined with preconcentration techniques based on chemical or fire-assay principles, it allows determination of platinum and palladium concentrations in complex matrices down to 0.03 μg/g or 0.001 oz/ton.[31] In this particular procedure 20 mg of gold is used as a collector and the Pt and Pd content of the gold is compared with that of gold standards containing known quantities of the two PGMs. With minor variations, the method can be applied to the determination of trace amounts of rhodium and iridium.

The direct current (dc) arc is the most useful spectral source. It is produced by passing a current of 2–30 A between two electrodes, one of which contains the sample. Although the high-voltage ac and interrupted dc arcs are useful for some applications, they have largely been replaced by newer techniques, such as AAS and PES. One attractive feature of OES with photographic recording is its capability of providing simultaneously qualitative and/or quantitative information on many elements (typically 20–40 or more).[75]

Spark-source mass-spectroscopy (*SSMS*). SSMS is a semiquantitative technique with ultrahigh sensitivity, which has detection limits in the low μg/g and ng/g ranges. When used instead of OES for final measurements, it allows determination of the PGM content of complex matrices at the 1 ng/g level.[31] In this technique the sample is sparked in a vacuum by a high-energy radiofrequency spark to produce positive ions of the sample elements. A double-focusing spectrometer separates the ions according to their "mass-to-charge" ratio, first in an electrostatic, then in a strong magnetic field. The ions thus separated are recorded photographically on an ion-sensitive photoplate or are measured by means of photomultipliers. Accelerator mass spectrometry has recently been used to determine the isotopic composition of osmium in terrestrial samples.[76]

Flame atomic emission and absorption spectrometry. In FAES and in FAAS the sample solution is subjected to a high-energy thermal environment provided by a flame, which evaporates the solvent and produces excited-state atoms, which return to the ground-state or other lower energy state and emit light. In FAES the emission spectrum is measured. This technique cannot be applied to PGMs because the flame is unable to provide the energy needed for excitation of the PGMs. In FAAS, some of the ground-state PGM atoms are excited by resonance absorption light of specific wavelength from a suitable source containing the analyte element. The fraction of light absorbed increases with the number of PGM atoms present, thus providing quantitative measurement of the amount of the PGM.

FAAS has largely replaced spectrophotometry as the work-horse in the precious-metals analytical laboratory. There are several reasons for this. (*a*) FAAS is virtually element-specific. Thus a PGM which cannot be determined spectrophotometrically at all in the presence of certain other PGMs or base metals, can often be determined with comparative ease by FAAS. (*b*) In many instances, there is no interference by moderate concentrations of base metals, and even where there is, it can be dealt with by the standard-addition technique. The limitations to the use of FAAS in precious-metals analysis mainly arise from the sensitivity, which is poor for some PGMs, particularly iridium. The relative concentrations of PGMs required to match the AAS response of a reference unit concentration of silver are: Pd 4, Rh 5, Ru 9, Os 100, Ir 150, Pt 38, Au 5. A relative value of 40 or more would indicate that the element should not be handled by FAAS (Os, Ir), unless present in substantial quantities or isolated from the matrix. It must also be remembered that FAAS is a solution technique and therefore requires that the element(s) can be dissolved with relative ease, and without introducing too much extraneous matter. This is obviously difficult, if not impossible, in the case of many samples containing the PGMs in a complex matrix.[11,50,77,78]

Electrothermal atomic-absorption spectrometry (*ETAAS*). This technique supplements FAAS, inasmuch as it offers greatly enhanced sensitivity. This can be explained as follows. In FAAS, the sample

passes through the observation zone so rapidly that the effective lifetime of the absorbing atom is very brief, only a few thousandths of a second. In ETAAS, on the other hand, the residence time of atoms in the light-beam is 100–1000 times longer, thereby providing correspondingly greater sensitivity. Unfortunately, the precision is much poorer because of the small volume of sample solution (5–50 μl) used and the difficulties encountered in reproducible sampling and control of the atomization conditions. In addition, since ETAAS also generally relies on the preparation of solutions of samples and standards, it is subject to the same dissolution limitations as FAAS. Attempts have been made to use solid samples, but with limited success. An interesting application of ETAAS for geochemical exploration work was recently described,[79] in which diantipyrylmethane was used for isolating the PGMs by extraction into chloroform.

Plasma emission spectrometry (PES). Plasma emission spectrometry is a variant of atomic emission spectrometry (AES), based on use of a plasma for excitation. It is based on the principle that in high-intensity electromagnetic fields gases become conductors and complex electric charge-transfer phenomena occur, called gas discharges. The result of a gas discharge is the production of an ionized gas at very high temperature, containing electrons, positive ions and neutral atoms and molecules, called a plasma.

Plasmas are increasingly used as a spectral excitation source for determining the PGMs. Generally, the sample is introduced in the form of a solution that is atomized by the carrier gas in various fashions. Two types of plasma are used: the direct current plasma (DCP) and the inductively-coupled plasma (ICP). Lasers are also used as an excitation source.

Instrumentation for both techniques has been developed rapidly during the last few years. Moderately priced instruments are readily available, based on the sequential principle (measurement of one PGM at a time). There are also more expensive instruments based on the use of multichannel detectors (ICP) or cassettes (DCP) allowing the simultaneous determination of all the PGMs, as well as of silver, gold and many base metals. There is even a fast sequential DCP instrument.[80–84]

Though FAAS has certain advantages over the arc and spark emission methods for PGM analysis, it is decidedly inferior to PES in sensitivity and linear dynamic range. Also, the PES methods tolerate the presence of moderate amounts of alkali-metal salts, and this will often permit use of fusion of a sample with alkaline fluxes such as sodium peroxide and sodium carbonate.

The linear dynamic ranges (μg/ml) of DCP for the eight precious metals at interference-free wavelengths are Ru 0.5–50, Rh 0.1–50, Pd 0.1–30, Ag 0.4–60, Os 0.5–100, Ir 0.5–5, Pt 0.3–75, Au 0.3–100. The corresponding ranges of ICP are similar, but depend to some extent on the instrumentation used and the availability of interference-free wavelengths.

Inductively-coupled plasma–mass spectrometry. This technique (ICP–MS) has recently been introduced, but not yet fully examined as to its suitability for PGM determinations.[85] However, effective means have been devised to extract ions from the plasma (which is at atmospheric pressure) and introduce them (at greatly reduced pressure) into a quadrupole mass spectrometer for mass resolution and detection. ICP–MS may be of interest to laboratories having no access to SSMS. Laser MS instruments have also been built, but are still in the experimental stage.

Inductively coupled plasma–atomic fluorescence spectrometry. This technique (ICP–AFS) has recently been advocated as an efficient tool for PGM analysis.[86] In atomic fluorescence, the plasma does not function as an excitation source but solely as an atomization cell to produce ground-state (or low-energy excited state) atoms. Excitation is mainly by resonance absorption of light from an external light-source, and the fluorescence emitted by return to a lower energy state is viewed at an angle to the excitation beam. The sensitivity of the method is said to be comparable to that of FES techniques. The cost of the equipment compares favourably with that of AAS.

Activation analysis. Gamma rays, charged particles, and particularly neutrons react with isotopes of the PGMs to produce radioactive nuclides. The characteristic radiation emitted by the nuclides produced can be used for detection and determination of the PGMs. In some instances, neutron-activation analysis is more sensitive than any other technique. Though instrumental NAA (INAA) can be applied effectively to gold and silver determinations, in the case of the PGMs some separation or concentration is necessary, either before or after the irradiation.[50,87]

Controlled-potential coulometry (CPC). In controlled-potential coulometry, the substance is electrolysed at a working electrode with the potential controlled or kept constant during the electrolysis by means of a potentiostat. The current is integrated with an electronic integrator or coulometer. A reference electrode and a two-electrode electrolysis cell are employed.

For the analyst, the manipulation of the technique resembles that of conventional titrations, except that the amount of "titrant" used is measured by means of current and the operations are inherently semi-automatic. This technique has been shown to be very effective for the determination of all the PGMs, as well as of gold and silver.[88] Unfortunately, it has not yet received the attention from precious-metal analysts that it richly deserves.

Other instrumental techniques that are of value to the PGM analyst for specific applications include polarography, differential pulse polarography, anodic stripping voltammetry, ion-selective electrode potentiometry and most recently, ion-chromatog-

raphy. The applicability of this latter technique to PGM analysis was recently discussed by Heberlin.[89]

CONCLUSIONS

Up to twenty years ago the chemical repertoire for the analysis of PGMs was largely limited to gravimetric methods (including fire-assay), enhanced to a limited extent by various spectrophotometric methods. The analysis of substances rich in PGMs always involved extensive and often tedious separation schemes to isolate the elements to be determined, before a final gravimetric method could be applied. In many respects, the introduction of instrumental methods of analysis has lessened the burden on precious-metals analysts, by reducing the need for extensive chemical separations. On the other hand, the availability of these techniques has led to tightened accuracy requirements and to the extension of the analytical repertoire to additional elements and to a variety of products not previously encountered.

Only a limited number of PGM materials can be analysed by purely instrumental techniques. Though in instrumental methods random errors can sometimes be limited to 1% relative, systematic errors are often significantly greater, unless standard samples of the same composition, both chemical and physical, are available and employed.

Although the 1% relative error (at best) of the instrumental approach may be acceptable when the content of an element is 10% or less, for higher concentrations of an element a 1% error is in most instances intolerable. Where a higher degree of precision is required or when the PGMs are present in trace amounts, the precious-metals analyst has to take recourse to chemical methods, some involving gravimetry, others preconcentration steps. It should be pointed out that chemical methods, whether based on some form of classical or neoclassical form of fire-assay or on wet chemical techniques, can often be extensively modified by instrumental measurement of the solubility of certain precipitates or of the contamination of final products. It is thus possible to streamline or revitalize many older procedures which previously had suffered from such defects. This clearly demonstrates, in the case of PGM analysis, the "Interdependence of Chemical and Instrumental Methods".[90]

APPENDIX

CONDENSED OUTLINE OF METHODS OF ANALYSIS APPLICABLE TO THE PLATINUM GROUP METALS

Table 1 lists the common designation and composition of important PGM-bearing substances. In the case of minerals, the formulae will often correspond only roughly to the actual result of an analysis.

Table 1 also provides each substance with a code number which is used to identify it in Table 2. In addition, Table 1 lists the constituents of each substance for which methods of analysis are included in Table 2. Although the determination of other elements may occasionally be required for various special purposes, only those for PGMs are included. Thus, the entry Pt–Re catalyst following the sample code 25 signifies that only methods suited to the determination of Pt will be found in Table 2.

As pointed out repeatedly in the text, the choice of a procedure for determining any particular element depends considerably on the environment in which this element occurs, the equipment available for its isolation and final determination, and also on the experience of the analyst. Different substances must be decomposed in different ways and necessitate the execution of different separations. Procedures which are suited to the determination of a PGM in a specific substance may not be applicable to its determination in a sample of different origin. This is particularly so in the case of sweeps, which have wide ranging base-metal compositions and precious metal contents ranging from below 1 ppm to 20–30%. In the case of referee analysis, the analyst is also frequently asked to determine just one or two PGMs, with the remaining PGMs not to be determined at all. No attempt is therefore made to provide methods covering all eventualities. The procedure which is best suited for the determination of a specific PGM may be identified by locating the code number in the second column of Table 2. The remaining columns of this table will then provide information concerning the decomposition of the sample, the nature and some details of the separations that must be made, and the final isolation and determination of the element sought. A reasonable estimate of the composition of most PGM-bearing substances can be obtained by a preliminary XRF scan.

Table 1. List of important PGM-bearing substances often analysed

No.	Name of PGM substance	Approximate composition	Associated compounds	Analyse for
1	Native platinum concentrate	Pt 75–85%; OsIr 1–4% raw ore about 7 ppm Pt	Au, Pd, Rh, Pd, Rh olivine mineral	Pt, Pd, Au, Ir, Rh
2	Osmiridium	Os:Ir:Ru:Pt 3.5:3:1.0:0.6	Native Pt	Os, Ir, Pt, Ru
3	Sperrylite	$PtAs_2$; Pt 50–55%	Ni–Cu sulphides	Pt, Rh
4	Cooperite	PtS; Pt 82%, Pd 2.5%	Minerals of of Merensky Reef	Pt, Rd, Rh
5	Braggite	Pt_2PdNiS_4	see No. 4	Pt, Pd, Rh
6	Stibiopalladinite	Pd_3Sb and Pd_7Sb_3	see No. 4	Pd, Pt
7	Laurite	RuS_2	see No. 4 sands of Borneo	Ru, Os
	PGM-metals or sponge	Ru, Rh, Pd, Os, Ir, or Pt		
8	99.999%		—	Purity
9	99.99%		—	Purity
10	99.9%		—	Purity
11	99%		—	Purity
	PGM salts			
12	Ru-salts, pure	$RuCl_3.3H_2O$	—	Ru
13	Rh-salts, pure	$RhCl_3$, $Rh(NO_3)_3.nH_2O$	—	Rh
14	Pd-salts, pure	$PdCl_2$, Pd ammines	—	Pd
15	Os-salts, pure	OsO_4	—	Os
16	Ir-salts, pure	$Na_2IrCl_6.6H_2O$	—	Ir
17	Pt-salts, pure	H_2PtCl_6, Pt ammines		Pt
	PGM solutions			
18	Solutions of substances 12–17			elements of substances 12–17
19	Ru-soln.	pure or impure	waste or recovery	Ru
20	Rh-soln.	pure or impure	waste or recovery	Rh
21	Pd-soln.	pure or impure	waste or recovery	Pd
22	Ir-soln.	pure or impure	waste or recovery	Ir
23	Pt-soln.	pure or impure	waste or recovery	Pt
	Catalysts			
24	Pt catalyst	Pt 0.3–0.8%	on alumina	Pt
25	Pt–Re catalyst	Pt 0.3–0.6%	on alumina	Pt
26	Pt–Pd catalyst	Pt 0.03–0.15% Pd 0.02–0.12%	on alumina	Pt, Pd
27	Pt–Rh catalyst	Pt 0.03–0.25% Rh 0.005–0.03%	on alumina	Pt, Rh

continued

Table 1—*continued*

No.	Name of PGM substance	Approximate composition	Associated compounds	Analyse for
28	Pt–Pd–Rh catalyst	Pt 0.03–0.20% Pd 0.03–0.15% Rh 0.005–0.05%	on alumina	Pt, Pd, Rh
29	Pt–Pd monolith	see No. 26	on cordierite	Pt, Pd
30	Pt–Rh monolith	see No. 27	on cordierite	Pt, Rh
31	Pt–Pd–Rh monolith	see No. 28	on cordierite	Pt, Pd, Rh
32	Pt–Ir pellets	Pt 0.30%–Ir 0.30%	on alumina	Pt, Ir
33	Pt catalyst	Pt 0.3–15%	on carbon	Pt
34	Pd catalyst	Pt 0.25–20%	on carbon	Pd
35	Pt–Pd catalyst	Pt 0.15–15% Pd 0.15–20%	on carbon	Pt, Pd
36	Ru catalyst	Ru 0.5–10%	on carbon	Ru
37	Ru catalyst	Ru 0.25–0.60%	on alumina	Ru
38	Ru residue	Ru 0.15–0.50%	on various organics	Ru
39	Rh catalyst	Rh 0.5–4%	on carbon	Rh
	Residues			
40	Rh residue	Rh 0.20–0.60%	on various organics	Rh
41	Anode slime Se > 5%	Ag 5–50%; Au 0.1–0.5%; Pt 3–10 ppm; Pd 10–100 ppm	often high Cu, Pb, Sn, Sb	Pt, Pd (Ag, Au)
42	Anode slime Se 20–30%	similar to No. 40	similar to No. 40	Pt, Pd (Ag, Au)
43	Electronic scrap	Ag, Au, Pt, Pd, Rh; any one 0.01–1%	powder left after ignition	Pt, Pd (Ag, Au)
44	Electronic scrap	Ag, Au, Pt, Pd, Rh; any one 0.0–1%	usually collected in copper	Pt, Pd (Ag, Au)
45	Ruthenium paste	Ru 3–10%; Ag 5–20% Pd 3–8%; Pt, Au low	high in Pb, Bi SiO_2; for making resistors	Ru, Ag, Pd Au, Pt
46	Ag–Pd paste	Ag:Pd 7:3	usually on barium titanate for making capacitors	Pd(Ag)
47	Copper anodes	Ag, Au, Pt, Pd	upon electrolysis anode slime remains; see 40, 41	Pt, Pd (Ag, Au)
	Alloys			
48	Pt–Rh	Rh 5–10%	balance is Pt	Pt, Rh
49	Pt–Ir	Ir 5–20%	balance is Ir	Pt, Ir
50	Pt–Pd	Pd 40–60%	HNO_3 production "gettering alloy"	Pt, Pd
51	Jewellery scrap	Pt 80–90%, Pd 0–10% Rh 0–10%, Ru 1–5% Ir 0.25–8%, Au 0–5% Ag 0.25–3%	various precious metals are melted with platinum to form solid soln.	Pt, Pd Ir, Rh Ir, Rh, Ru (Ag, Au)

continued

Table 1—*continued*

No.	Name of PGM substance	Approximate composition	Associated compounds	Analyse for
52	Dental alloy	Ag 10–50%, Pd 10–60% Pt 0–2%, Ru 0–0.5%	often contains Cu, Sn, In, Zn, Ga	Pd, Pt Ru(Ag)
53	Dental alloy	Ag 5–15%, Au 50–60% Pd 3–10%, Pt 3–7%	always contains Cu	Pd, Pt (Ag, Au)
54	Pt–Ni	Pt 20–45%	Ni is used to melt heterogeneous Pt material	Pt
55	Pt–Co	Pt 20–45%	Co serves the same purpose as nickel	Pt
56	Ir–Ni	Ir 20–35%	Ni is used to melt heterogeneous Ir scrap	Ir
57	PtPd–Rh concentrate	Pt 18–35%, Pd 7–15% Rh 0.8–3% Fe 20–50%, Pb 0.5–3%	Recovery of the PGMs from automative catalyst	Pt, Pd, Rh
	Examples of "sweeps" compositions			
58	Example No. 1	Rh 2.5%; Pd 0.015%; Pt 0.72% Ru 3.5%; also Au, Ag each	Majors: Pb, Bi, Cu	Pt, Pd, Rh (Ag, Au)
59	Example No. 2	Pd 2.5%; Pt 0.1%; Ag 0.25%	Majors: Al, Si, Zr Minors: Fe, Ni, Zn	Pt, Pd (Ag)
60	Example No. 3	Pd 10.5%; Ag 12.3%; Pt 0.12%; Au 0.27%	Majors: Ba, Ti Minors: Zr, Nb, Sr	Pt, Pd (Ag, Au)
61	Example No. 4	Au 2.8%; Ag 3.2% Pt 0.14%; Pd 1.3%	Majors: Cu, Pb, Al Minors: Fe, Zn, Zr	Pt, Pd (Ag, Au)
62	Example No. 5	Au 0.04%; Pt 0.07% Pd 3.25%; Rh 0.05% Ir 0.18%; Ru 0.10% Ag 1.25%	Majors: Si, Al, Cu, Pb, MgO. Minors: Fe, Ni, Cr, Ti, Sn Zn, Ba	Pt, Pd Rh, Ru, Ir, (Ag, Au)
63	Example No. 6	Pt 15%; Pd 1% Rh 0.15%	Majors: Fe, Ni Minors: Cr, Si	Pt, Pd Rh
64	Example No. 7	Pd 35%; Pt 2%; Rh 1.5%; Ru 0.04%; Ir 0.07%;	Majors: Si, Fe, Pb	Pd, Pt, Rh, Ru
65	Example No. 8	Rh 17%; Pt 0.20%; Pd 0.48%	Majors: Si, Al, Fe	Rh, Pd Pt
66	Example No. 9	Ru 12%; Ir 0.15%; Pt 0.05%; Pd 1.24%	Majors: Si, Pb, Bi Fe, Zn	Ru, Ir Pt, Pd
67	Example No. 10	Au 0.18%; Ag 2.4%; Pt 0.75%; Pd 3.4%	Majors: Al, Cu, Pb Si, Zn	Pd, Pt (Ag, Au)

Table 2. Procedures for the analysis of PGM substances (n.a. = not applicable; coll. = collector)

Element(s) determined	Material code (see Table 1)	Decomposition with	Separation required from	Type of separation	Final determination	References
Ru, Os, Ir, Pt	2	Zn, then Na_2O_2 fusion	all matrix elements	distillation	Os, Ir grav. Ru, Pt PES	2,7
Ru	8	n.a.	n.a.	n.a.	SSMS	91,92
Ru	9, 10, 11	n.a.	n.a.	n.a.	OES	75,93,94
Ru, Os	7	fire-assay Cu_2S, NiS	all matrix elements	Na_2O_2 fusion of acid-insol.	PES	18–22
Ru	12	convert into metal	n.a.	n.a.	grav. + OES	
Ru	18, 19, pure Ru < 100 mg	n.a.	n.a.	n.a.	PES	20
Ru	18, 19, pure Ru < 100 mg	pptn. with H_2S or hydrolysis at pH 6	n.a.	n.a.	grav.	7
Ru	19, impure Ru < 100 mg	n.a.	n.a.	n.a.	PES	20
Ru	19, impure Ru > 100 mg	(a) n.a. (b) n.a.	n.a. matrix and all PGMs	n.a. distillation	PES grav.	20 7
Ru	36, 38	ignition and Na_2O_2 fusion	n.a.	n.a.	PES	20
Ru	37	(a) Na_2O_2 fusion (b) fire-assay	n.a. Pb	n.a. fusion of HNO_3-insol. with Na_2O_2	PES PES	20 20
Ru, Pd, Pt (Ag, Au)	45	Pb, NiS, Cu_2S	HCl, HBr, $HClO_4$	distil Ru	PES	18–21,35
Ru, Rh, Pd, Ir (Ag, Au)	51	*aqua regia*	n.a.	fusion of residue with Na_2O_2	PES	20
Ru	62	see 62, Pd, Pt, Rh, Ru, Ir (Ag, Au)				
Ru, Ir, Pt, Pd	66	Na_2O_2 fusion	isolation of ruthenium	distillation	grav. or PES	7,20
Rh, Ir, Pd(Au)	1	*aqua regia*	insol.	filt., Na_2O_2 fusion of residue	AAS, PES	20
Rh, Pt, Pd	3, 4, 5 (a) ore (b) mineral	lead fire-assay *aqua regia*	matrix filtration	collection in gold Na_2O_2 fusion of residue	OES grav. or PES	2,7,50,75,93,94 2,20

	(b) mineral	*aqua regia*	filtration	Na_2O_2 fusion of residue	grav. or PES	2,20
Rh	8	n.a.	n.a.	n.a.	SSMS	91,92
Rh	9, 10, 11	n.a.	n.a.	n.a.	OES	75,93,94
Rh	13	conversion into metal	n.a.	n.a.	grav. + OES	2,7,75,93,94
Rh	18, 20, pure Rh < 100 mg	(a) direct (b) convert into metal	n.a. n.a.	n.a. n.a.	AAS, PES grav.	11,20 2,7
Rh	18, 20, pure Rh > 100 mg	convert into metal	n.a.	n.a.	grav. + OES	2,7,75,93,94
Rh	20, impure Rh < 100 mg	n.a.	n.a.	n.a.	AAS, PES	20
Rh	20, impure Rh > 100 mg	n.a.	all base metals and other PGMs	precipitate + chlorinate	grav.	7
Rh	27	see 27, Pt, Rh				
Rh	28	see 28, Pt, Pd, Rh				
Rh	30	see 30, Pt, Rh				
Rh	31	see 31, Pt, Pd, Rh				
Rh	39, 40	ignition Na_2O_2 fusion	n.a.	n.a.	AAS, PES	7,20
Rh	43, 44	see Pt, Pd, Rh (Ag, Au)				
Rh, Pt	48	(a) direct (b) *aqua regia* (c) *aqua regia*	n.a. n.a. Rh from Pt	n.a. n.a. hydrol. pptn.	XRF Rh, AAS, PES grav. or PES	71 11,20 44–46
Rh	57	see 57, Pt, Pd, Rh				
Rh, Pt, Pd	58	Pb, NiS, Cu_2S collection	removal of collector	dissolve collector. Na_2O_2 fusion of acid-insol.	PES	18–21
Rh	62	see 62, Pd, Pt Rh, Ru, Ir (Au, Ag)				
Rh	63	see 63 Pt, Pd, Rh				
Rh	64	see 64, Pd, Pt, Rh, Ru				
Rh, Pt, Pd	65	Pb, NiS, Cu_2S collection	removal of collector	fusion of acid-insol. with Na_2O_2, pptn. with Zn, chlorination	Rh, grav. Pt, Pd, PES	2,7,11,18–21
Pd, Pt	4, 5, 6	fire-assay	collect with Au		OES, PES	2,7,36,75,93,94

continued

Table 2—*continued*

Element(s) determined	Material code (see Table 1)	Decomposition with	Separation required from	Type of separation	Final determination	References
Pd	8	n.a.	n.a.	n.a.	SSMS	91,92
Pd	9, 10	n.a.	n.a.	n.a.	OES	75,93,94
Pd	11	n.a.	n.a.	n.a.	by difference OES	75,93,94
Pd	14	(a) convert into metal (b) dissolve in dil. HCl	n.a. n.a.	n.a. pptn. with DMG	grav. + OES grav.	2,7,75,93,94 2,7,11,50
Pd	18, 21 pure Pd > 100 mg	n.a.	n.a. n.a.	(a) pptn. with DMG (b) direct	grav. AAS, PES	2,7,11,50 11,20
Pd	18, 21 pure Pd > 100 mg		n.a.	pptn. with DMG	grav.	2,7,11,50
Pd	21 impure Pd < 100 mg	n.a.		(a) pptn. with DMG (b) direct	grav. AAS, PES	2,7,11,50 11,20
Pd	21 impure Pd > 100 mg			pptn. with DMG		2,7,11,50
Pd	26	see 26, Pt, Pd				
Pd	28	see 28, Pt, Pd				
Pd	29	see 29, Pt, Pd				
Pd	31	see 31, Pt, Pd, Rh				
Pd	34	ignition, *aqua regia*	filtration		<10%, PES, AAS >10%, DMG grav.	11,20 2,7,11,50
Pd	35	ignition, *aqua regia*	filtration	treatment of insol. by fire-assay	<3%, PES, AAS >3%, DMG grav.	11,20 2,7,11,50
Pd	41, 42	(a) H_2SO_4 decomposition (b) lead fire-assay	Ag pptn., filtration, fuse, scorify and cupel	remove Ag	AAS, PES AAS, PES	11,20 7,11,20
Pd	43, 44	see 43, 44, Pt, Pd, Rh (Au, Ag)				
Pd	45	see 45, Ru, Pd, Pt(Ag, Au)				
Pd, Pt(Ag, Au)	47	H_2SO_4 decomp. or Pb fire-assay	collection into silver	HNO_3 parting	AAS, PES	2,7,11,20,44
Pd, Pt	50	*aqua regia*	separation of Pt and Pd	DMG pptn. of Pd	Pd, Pt grav.	2,7,41
Pd, Pt, Ru(Ag)	52	HNO_3	Pd from Ag	Pd from Pt,	Pd(Ag) grav.	2,7,11,50

			of Pt and Pd	of Pd		
Pd, Pt, Ru(Ag)	52	HNO_3	Pd from Ag by AgCl pptn.	Pd from Pt, Ru with DMG	Pd(Ag) grav. Pt, Ru PES	2,7,11,50 20
Pd, Pt(Au, Ag)	53	*aqua regia*	pptn. of Ag as AgCl	pptn. of Au with oxalic acid oxalic acid	Pt or Pd > 5%, AAS, PES > 5%, grav.	11,20 2,7,11
Pd	57	see 57, Pt, Pd, Rh				
Pd	58	see 58, Rh, Pt, Pd				
Pd, Pt(Ag)	59	Ag-bead collection HNO_3 treatment	removal of Ag	pptn. as AgCl	AAS, PES	7,11,20
Pd, Pt(Ag, Au)	60	(a) as for 59 above (b) Pb-button collection	removal of lead	$HClO_4$ dissol. HCOOH pptn.	Pd(Ag) grav. Pt(Au) AAS, PES	7,11,35 11,20
Pd, Pt(Ag, Au)	61	(a) as for 60(b) above (b) Cu_2S coll.	removal of matrix coll.	$HClO_4$ dissol. HBr dissol.	AAS, PES AAS, PES	11,20,35 11,20,21
Pd, Pt, Rh, Ru, Ir(Ag, Au)	62	Pb-button or Cu_2S collection	removal of matrix coll.	$HClO_4$, HBr HBr	AAS, PES	11,20,21,35
Pd	63	see 63, Pt, Pd, Rh				
Pd, Pt, Ru, Rh	64	*aqua regia*, Na_2O_2 fusion of residue	separate Pd	DMG pptn. acidify, fusion	Pd grav. Pt, Ru, Rh, PES	2,7,11,50 11,20
Pd	65	see 65, Rh, Pt, Pd				
Pd, Pt, Ir	66	NiS, Cu_2S	remove Ru	dissolve in HCl or HBr, fume residue with $HNO_3 + HClO_4$	AAS, PES	18–21
Pd, Pt (Ag, Au)	67	(a) Ag bead coll. (b) Pb-button coll.	remove Ag remove Pb	dissolve in HNO_3 dissolve in $HClO_4$	AAS, PES AAS, PES	2,7,11,20 11,20,35
Ir	2	see 2, Ru, Os	Ru, Os	Use residue from distill.	PES	20
Ir	8	n.a.	n.a.	n.a.	SSMS	91,92
Ir	9, 10, 11	n.a.	n.a.	n.a.	OES	75,93,94
Ir	16	conversion into metal	n.a.	n.a.	grav. + OES	2,7,11,75,93,94
Ir	18, 22 pure < 10%	(a) conversion into metal (b) n.a.	n.a. n.a.	n.a. n.a.	grav. PES	2,7,11,50 20
Ir	18, 22 pure > 10%	convert into metal	n.a.	n.a.	grav. + OES	2,7,11,75,93,94
Ir	22, impure < 10%	n.a.	n.a.	n.a.	PES	20

continued

Table 2—*continued*

Element(s) determined	Material code (see Table 1)	Decomposition with	Separation required from	Type of separation	Final determination	References
Ir	22, impure > 10%	n.a.		bromate hydrol. + chlorination	grav. + OES	2,7,11,75,93,94
Ir, Pt	32	(a) HF or H_2SO_4 (b) NaOH or Na_2O_2	Ir, Pt soln. Ir, Pt, ppte.	plus oxidant plus reductant	PES PES	20,31 20,31
Ir, Pt	49	(a) n.a. (b) *aqua regia* (c) chlorination (d) Zn-fusion HCl dissoln.	n.a. Ir < 5% heat with pressure $IrCl_3$ insol. insol. *aqua regia* dissoln.	n.a. bromate hydrol. $PtCl_4$ volatile sep. Ir from Pt by bromate hydrol.	XRF Pt grav. Ir PES grav. Pt grav. Ir PES	71,73 44–46 20 7 44–46 20
Ir	56	chlorination	$IrCl_3$ insol.	$NiCl_2$ sol.	grav.	7
Ir	62	see Pd, Pt Rh, Ru Ir(Ag, Au)				
Ir, Pt, Pd	66	Cu_2S, NiS collection	HBr or HCl dissolution	acid-insol., expel RuO_4 with $HClO_4$	PES	18–21
Pt	4, 5, 6	see 4, 5, 6 Pd, Pt				
Pt	8	n.a.	n.a.	n.a.	SSMS	91,92
Pt	9, 10	n.a.	n.a.	n.a.	OES	75,93,94
Pt	11	n.a.	n.a.	n.a.	OES by diff.	
Pt	17	convert into metal	n.a.	n.a.	grav. + OES	2,7,75,93,94
Pt	18, 23, pure Pt < 100 mg	n.a.	n.a.	(a) n.a. (b) NH_4Cl or $N_2H_4.HCl$ pptn.	AAS, PES grav.	11,20 2,7,41
Pt	18, 23, pure Pt > 100 mg	n.a.	n.a.	pptn.	grav.	2,7,41
	18, 23, impure Pt < 100 mg	see 18, 23 pure				
Pt	18, 23, impure Pt > 100 mg	see 18, 23 pure				
Pt	24, 25	H_2SO_4–H_3PO_4	pptn. of Pt	use H_2S, HCOOH or $Na_2S_2O_3$	spectrophot. or AAS, PES	22,23 11,20
Pt Pd	26	see Pt. 24. 25	separation	DMG–$CHCl_3$	Pt spectrophot.	22,23

Pt, Rh	27	H_2SO_4–H_3PO_4	treatment of insol. by fire-assay Au collection	oxalic acid pptn. of Au Pt, Pd recovery in filtrate	Pt spectroph. Rh AAS, PES	22,3 11,20
Pt, Pd, Rh	28	see 27, above	see 27	see 27, also DMG–$CHCl_3$ extraction	Pt spectroph. Pd, Rh AAS, PES	22,23 11,20
Pt, Pd	29	see 26, above				
Pt, Rh	30	see 27, above				
Pt, Pd, Rh	31	see 28, above				
Pt	33	ignite, disssolve in *aqua regia*	recover residue Pt fire-assay	n.a.	(a) <50 mg phot. (b) >50 mg grav.	22,23 2,7,11,50
Pt	35	see 35, Pd			(a) <100 mg PES (b) >100 mg grav.	11 2,7,11,50
Pt	41, 42	see 41, 42, Pd	see 41, 42, Pd	see 41, 42, Pd	AAS, PES	11,20
Pt, Pd, Rh (Ag, Au)	43	Pb, NiS or Cu_2S collect.	collector removal	HCl, HBr or $HClO_4$ treat.	AAS, PES	11,18–21
Pt	45	see 45, Ru, Pd Pt(Ag, Au)				
Pt	47	see 47, Pd, Pt Ag, Au				
Pt	48	see 48, Rh, Pt				
Pt, Pd, Rh, Ir Ru(Au, Ag)	51	*aqua regia* (a) (b)	sep.& Pt from others n.a.	bromate hydrol. n.a.	Pt grav. others, PES others, PES	2,7,11,44–46 20 20
Pt	52	see 52, Pd, Pt Ru(Ag)				
Pt	53	see 53, Pd, Pt (Ag, Au)				
Pt	54	*aqua regia*	pptn. of Pt	use HCOOH	grav.	2,7,11,50
Pt	55	see preceding entry				
Pt, Pd, Rh	57	(a) Cu_2S, NiS (b) *aqua regia*	insol. insol.	fuse insol. fuse insol.	Pt, Pd, grav. Rh, PES, AAS	2,7,11,50 11,20
Pt	58	see 58, Rh, Pt, Pd				
Pt	59	see 59, Pd, Pt(Ag)				

continued

Table 2—*continued*

Element(s) determined	Material code (see Table 1)	Decomposition with	Separation required from	Type of separation	Final determination	References
Pt	60	see 60, Pd, Pt(Ag, Au)				
Pt	61	see 61, Pd, Pt (Ag, Au)				
Pt	62	see 62, Pd, Pt, Ir Rh, Ru,(Ag, Au)				
Pt, Pd, Rh	63	(a) Cu_2S, NiS (b) Pb-button	dissolve acid-insol.		Pt grav. Pd, Rh PES, AAS	2,7,11 18–21
Pt	64	see 64, Pd, Pt Ru, Rh				
Pt	65	see 65, Rh, Pt, Pd				
Pt	66	see 66, Pd, Pt, Ir				
Pt	67	see 67, Pd, Pt(Ag, Au)				
Pt	1	see 1, Rh, Ir, Pd(Au) use *aqua regia* solution			grav.	2,7,11,50

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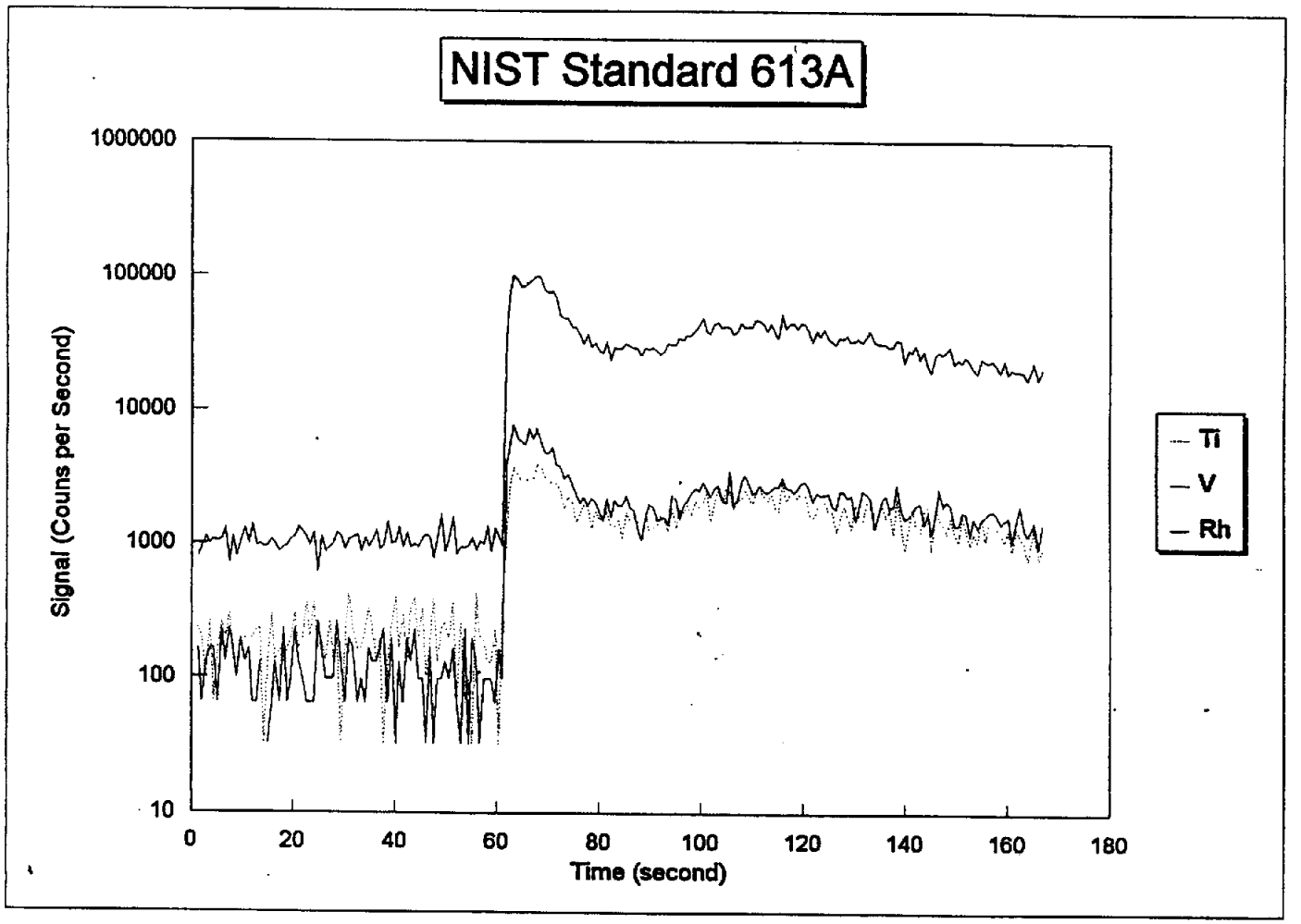
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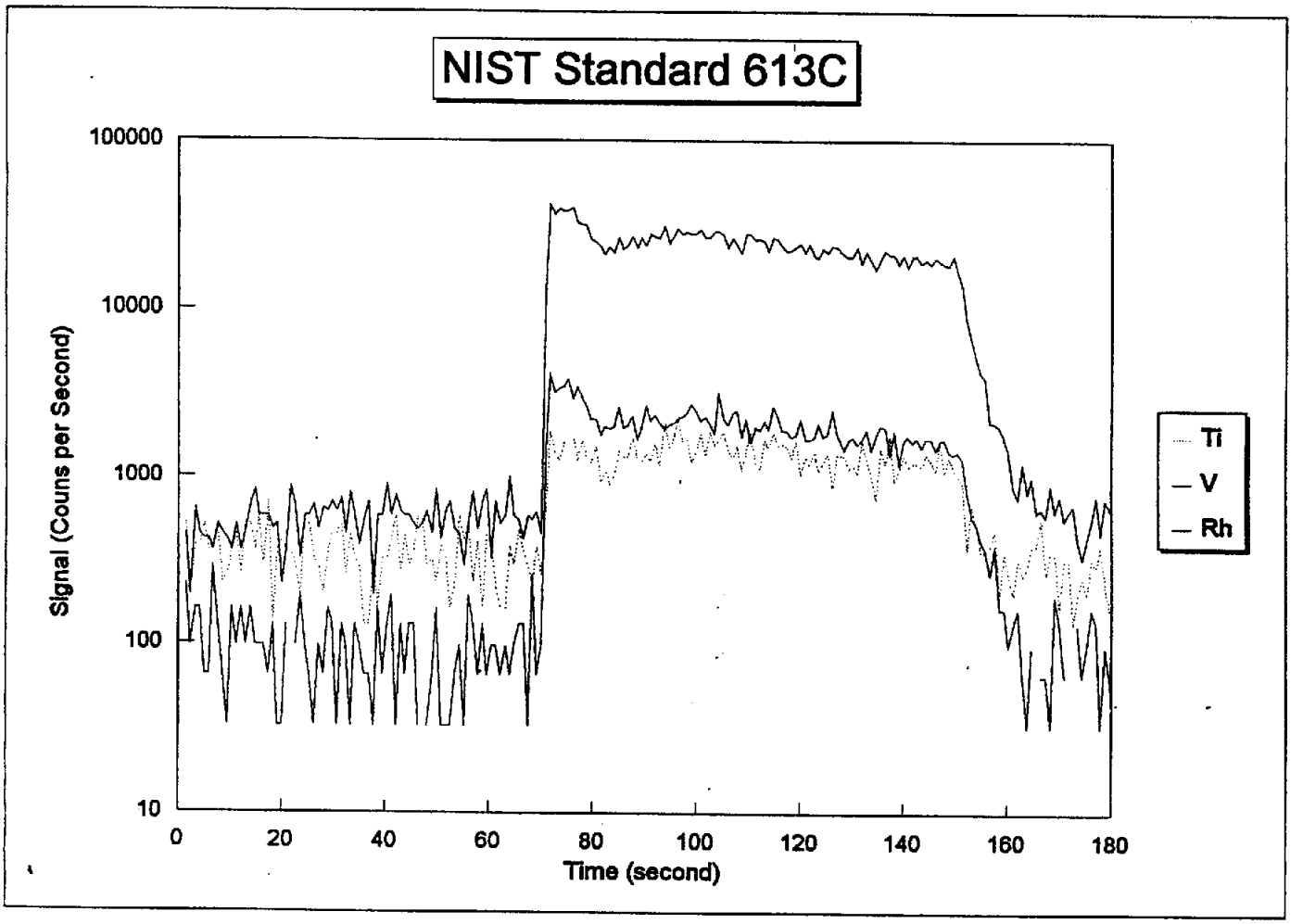
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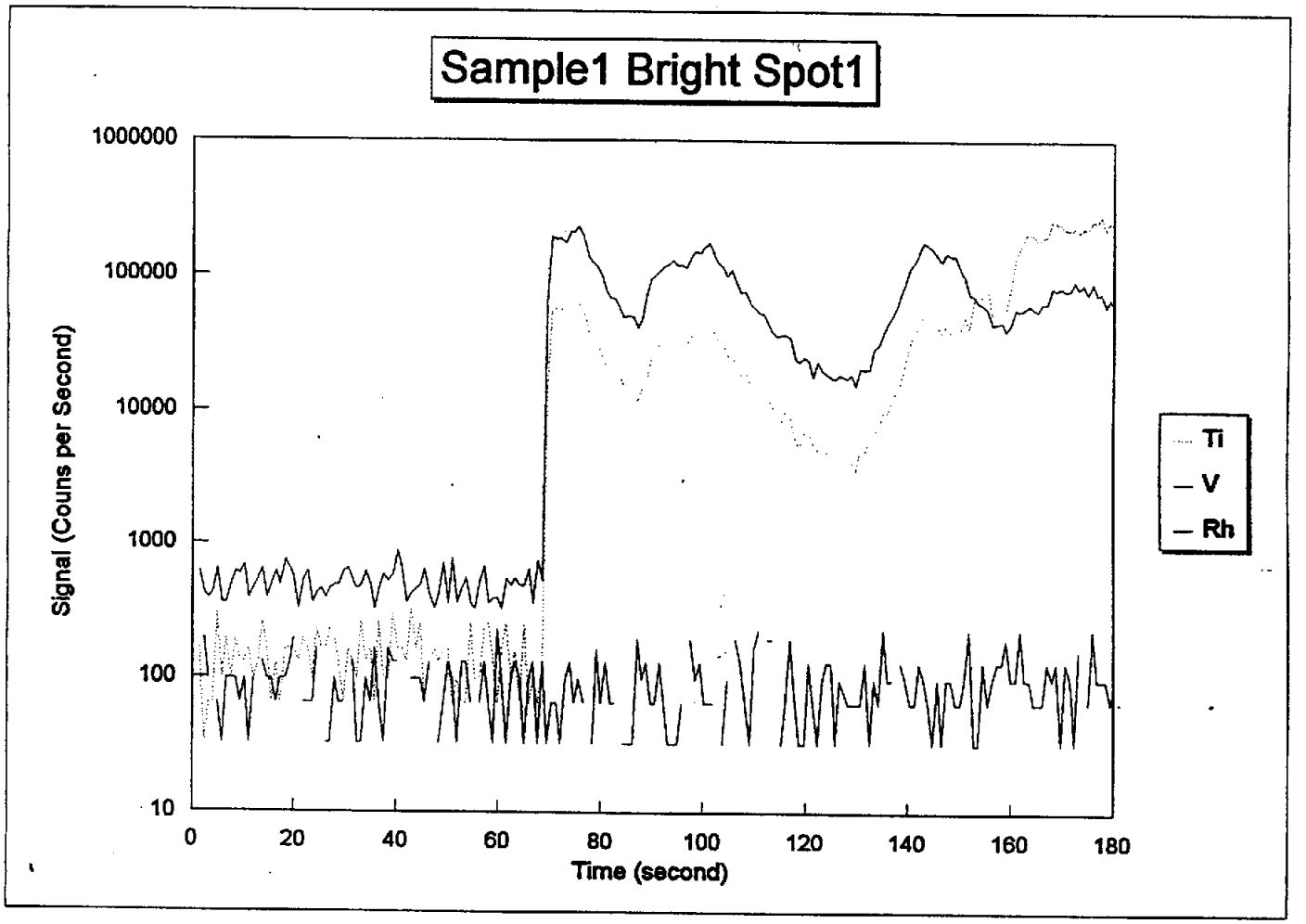
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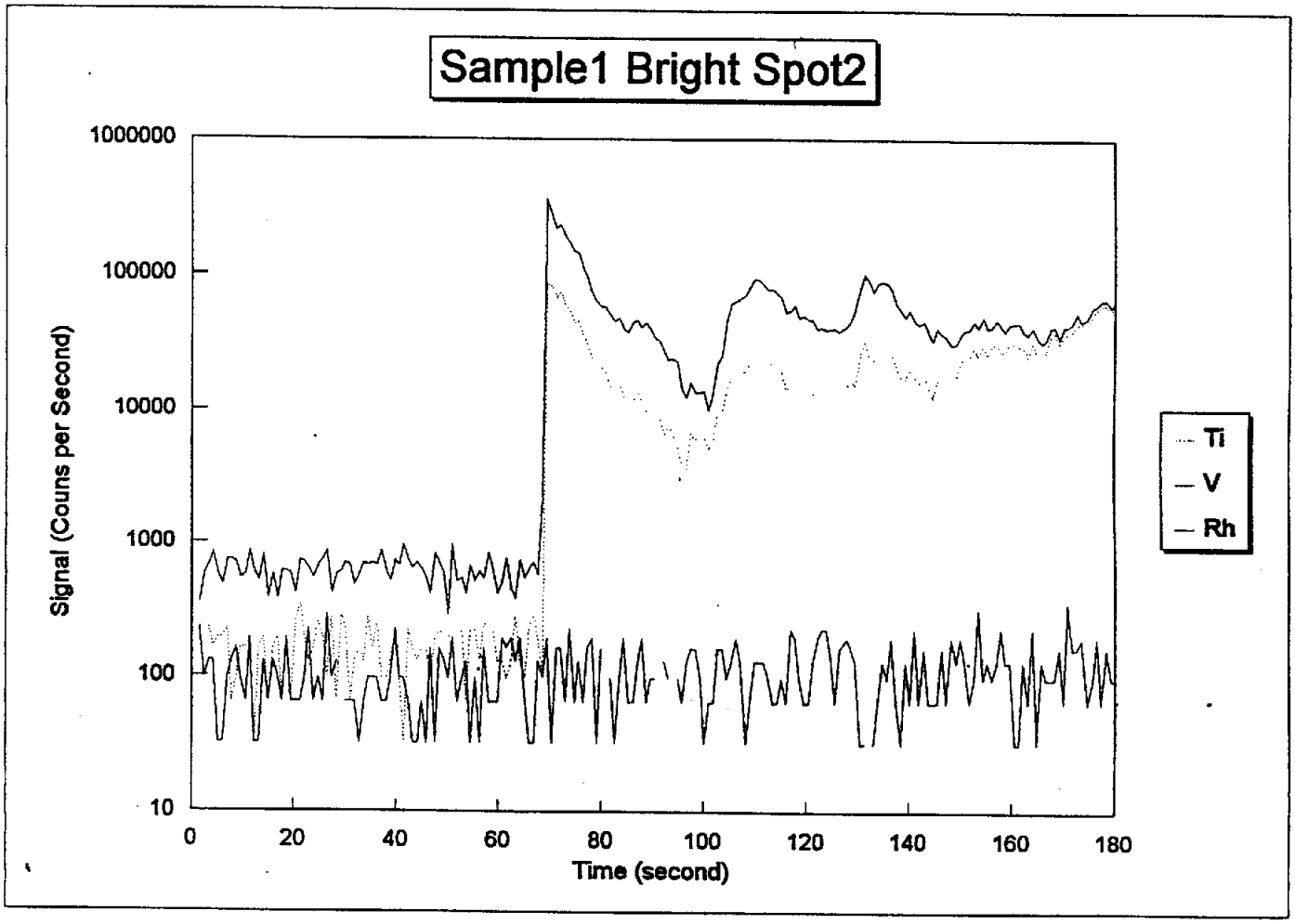
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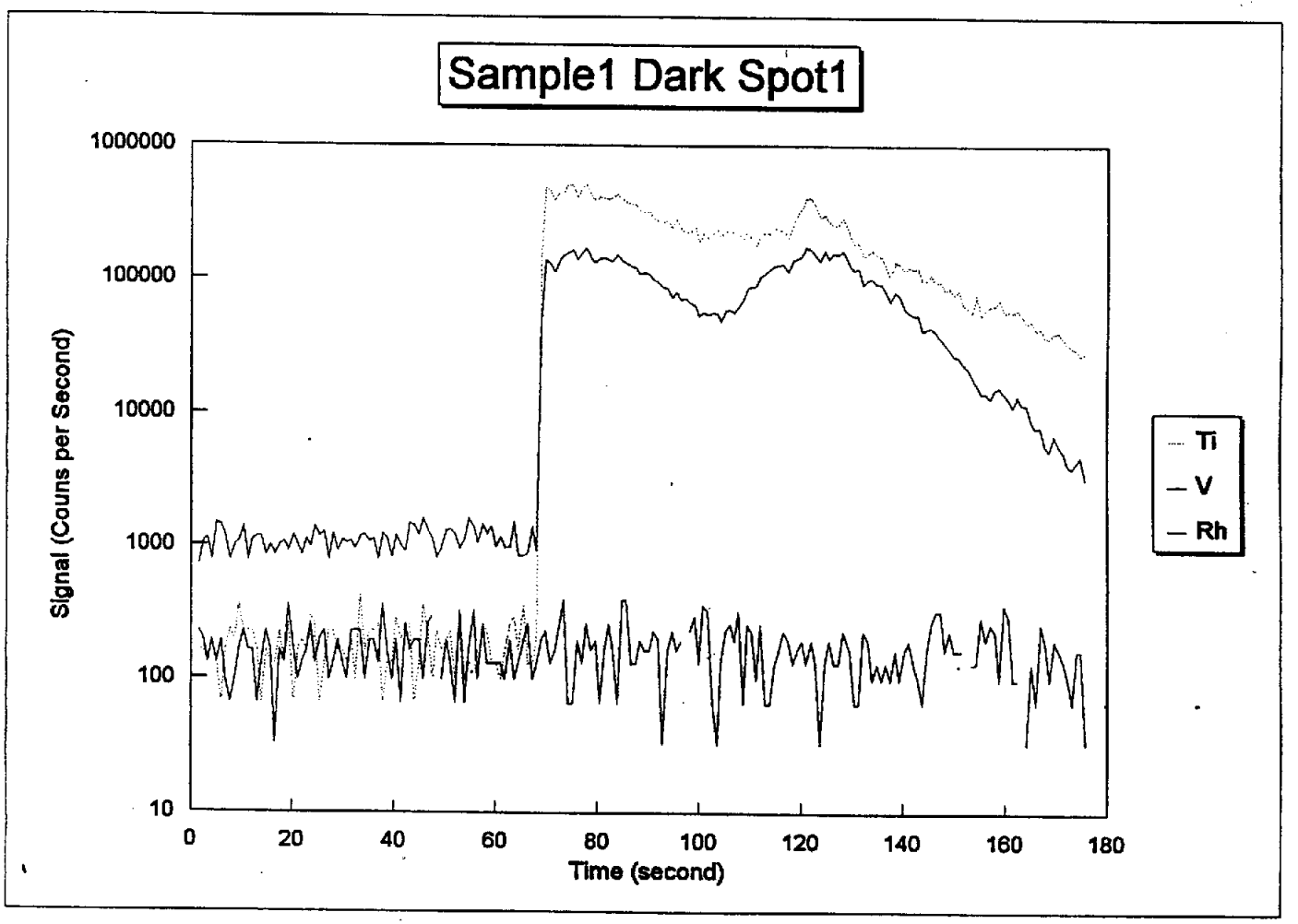
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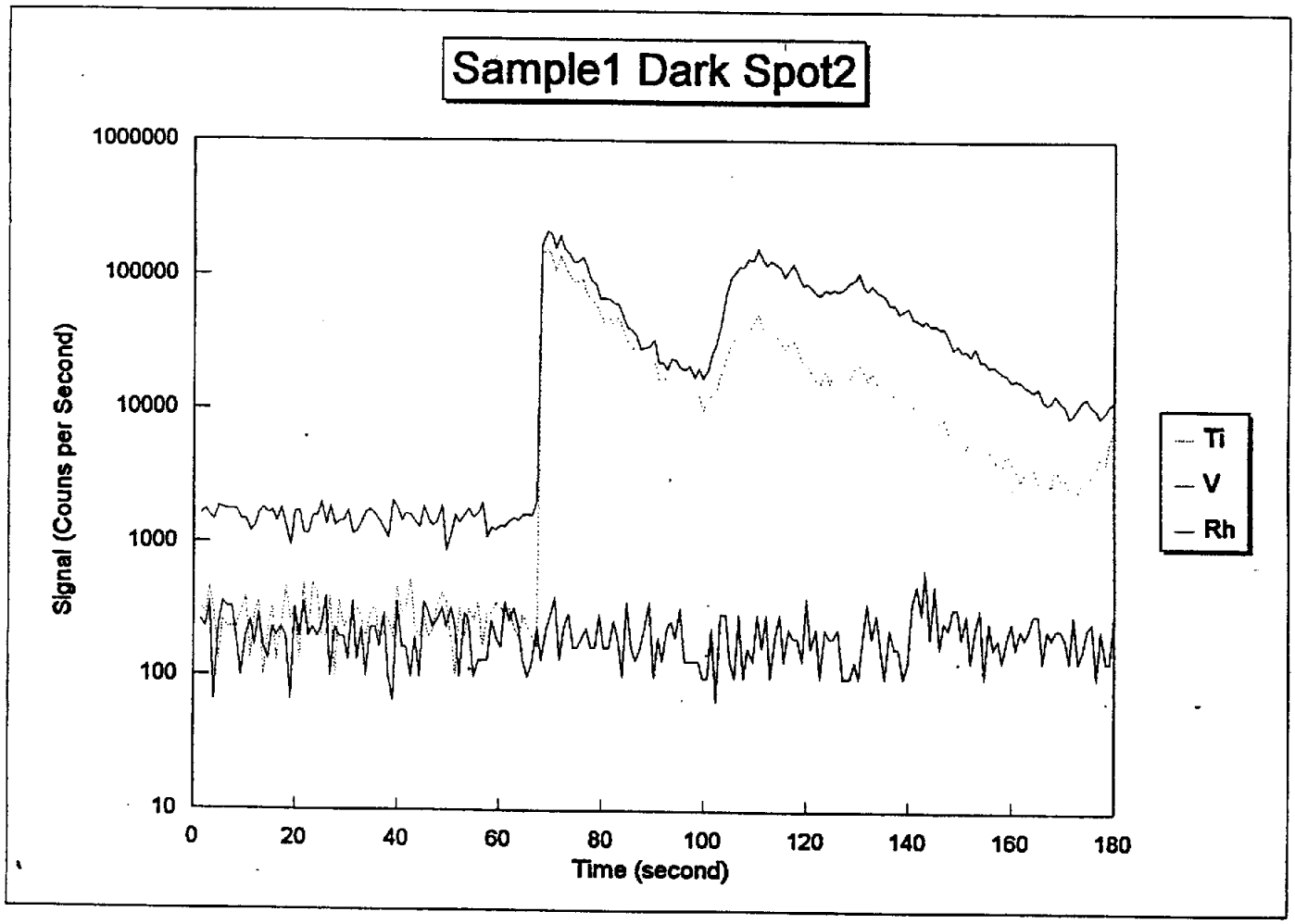
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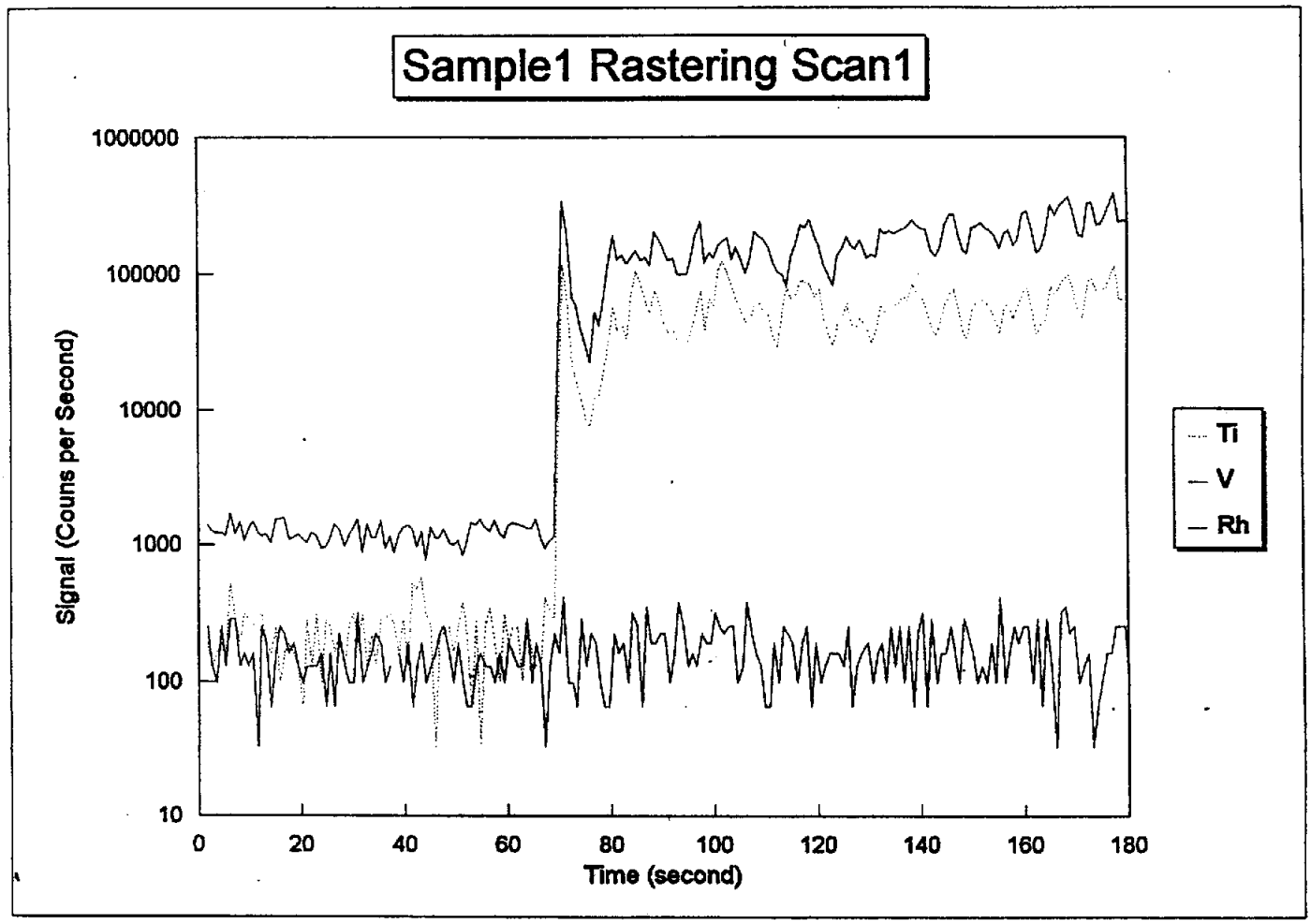
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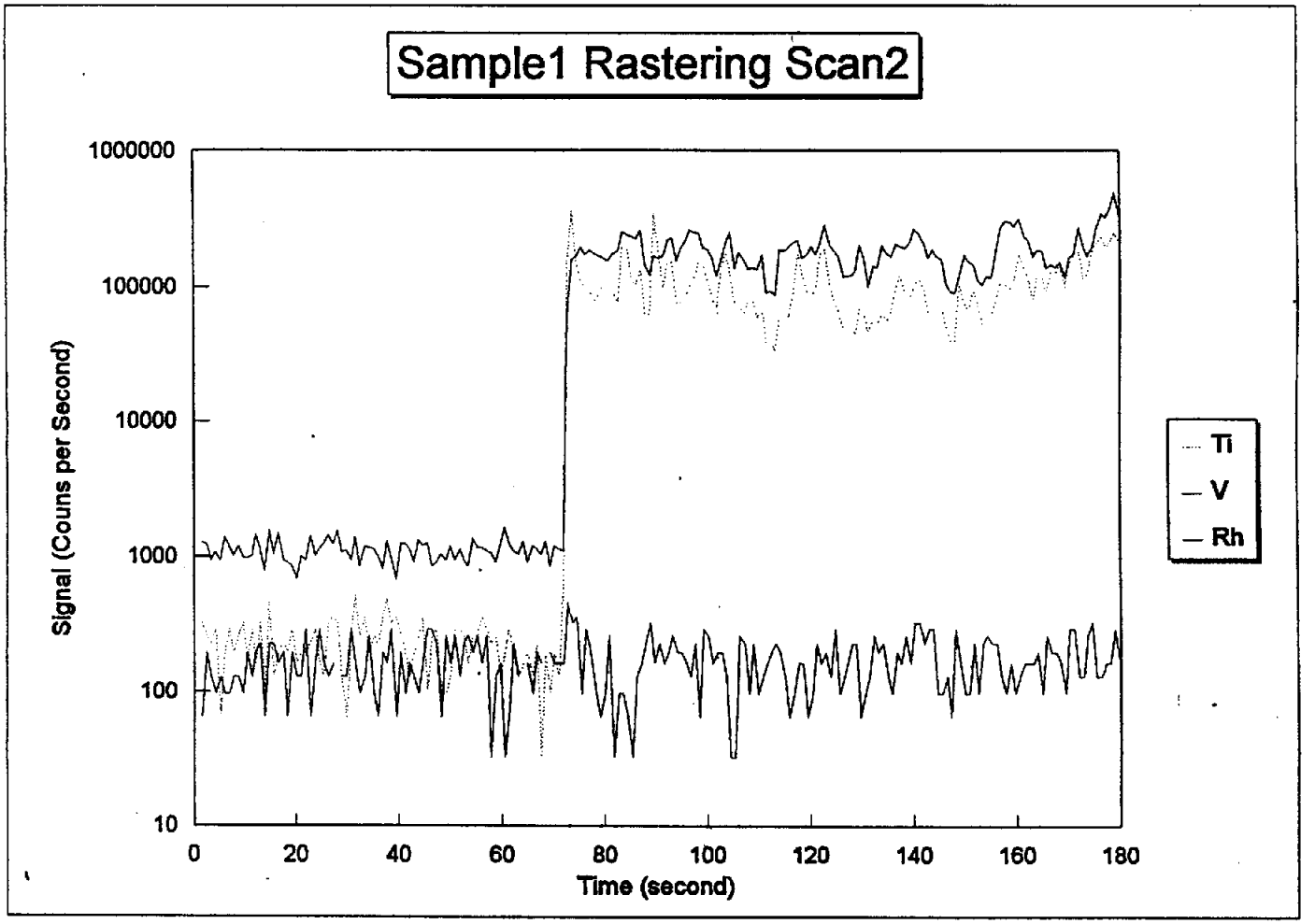
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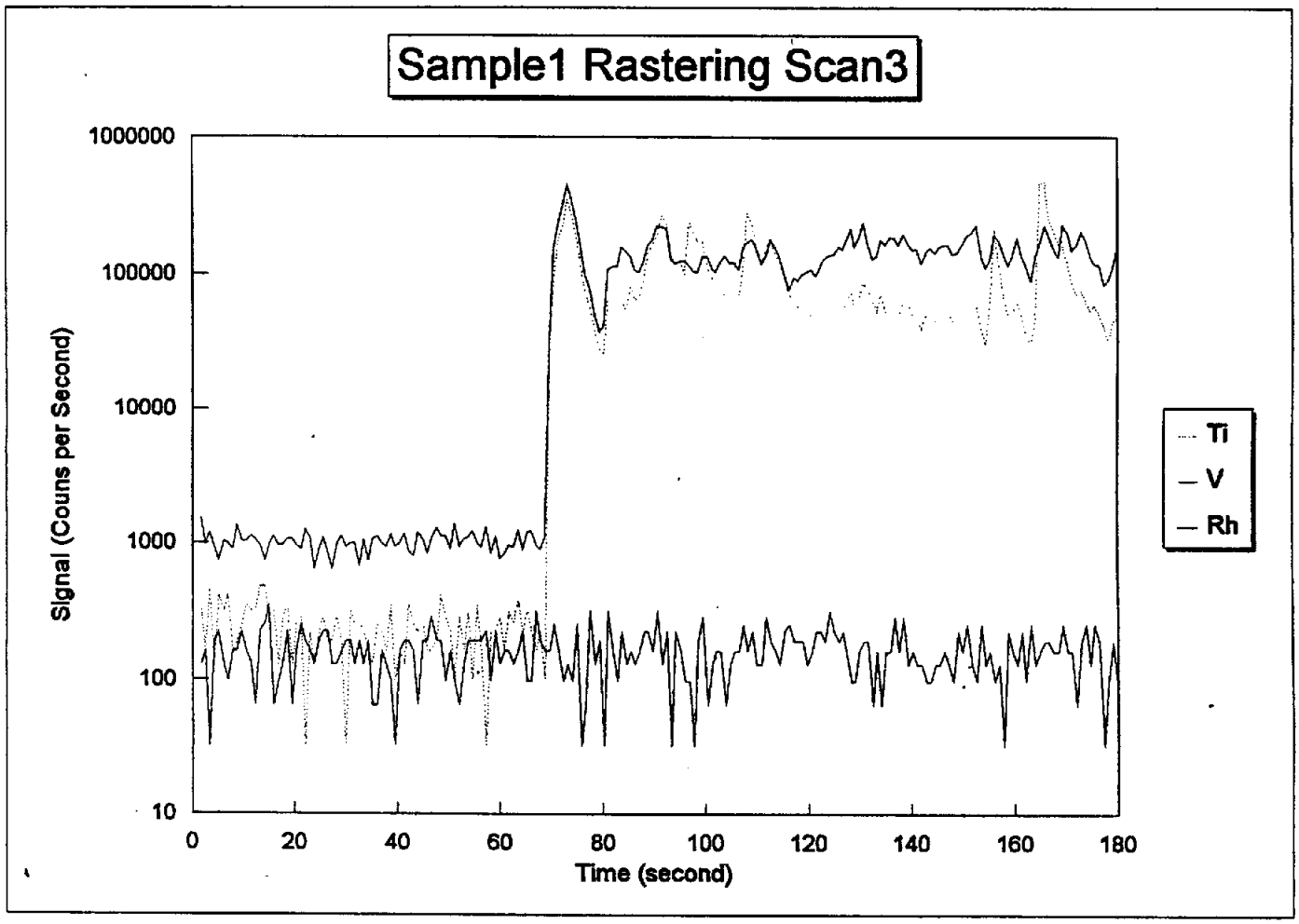
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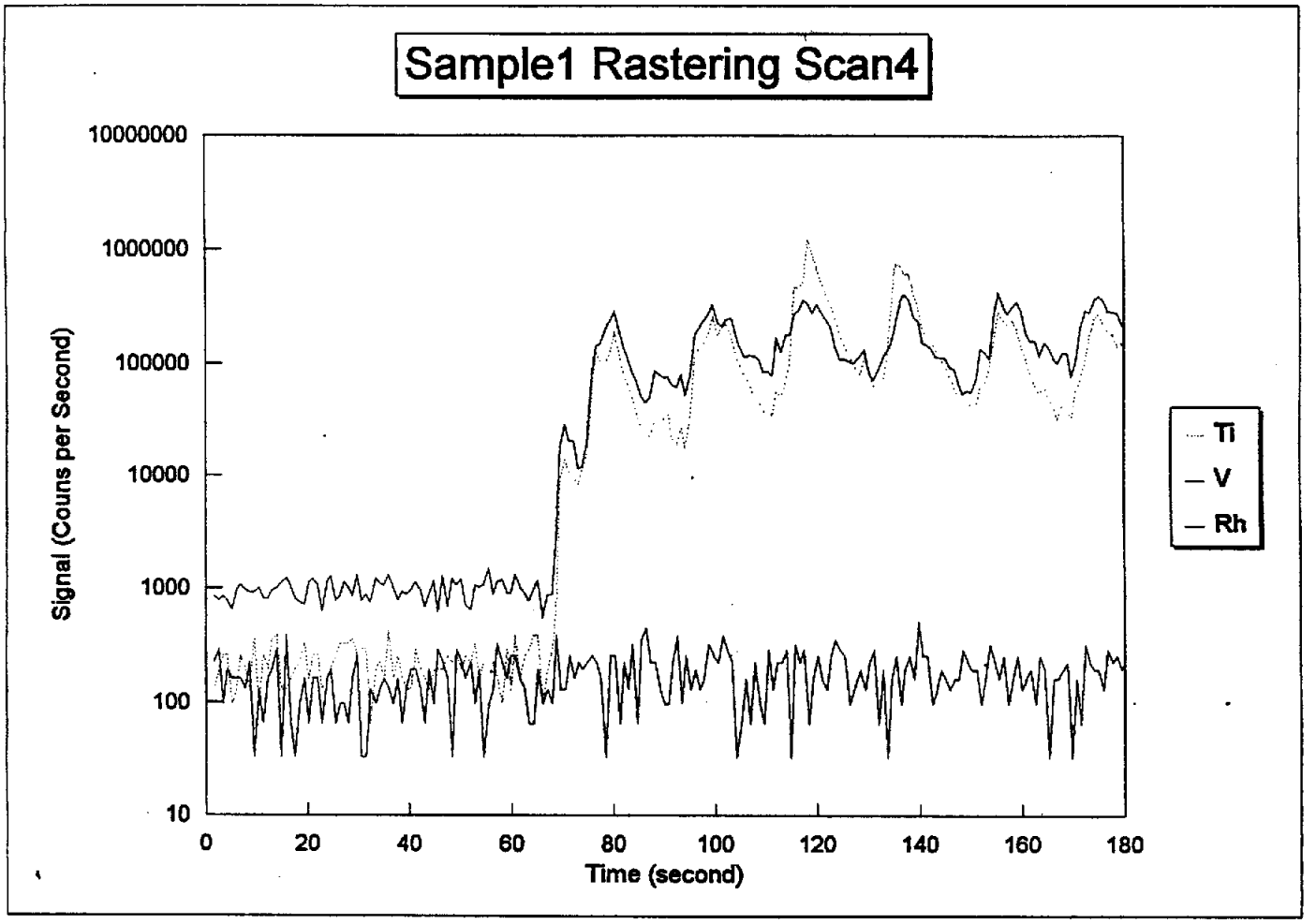
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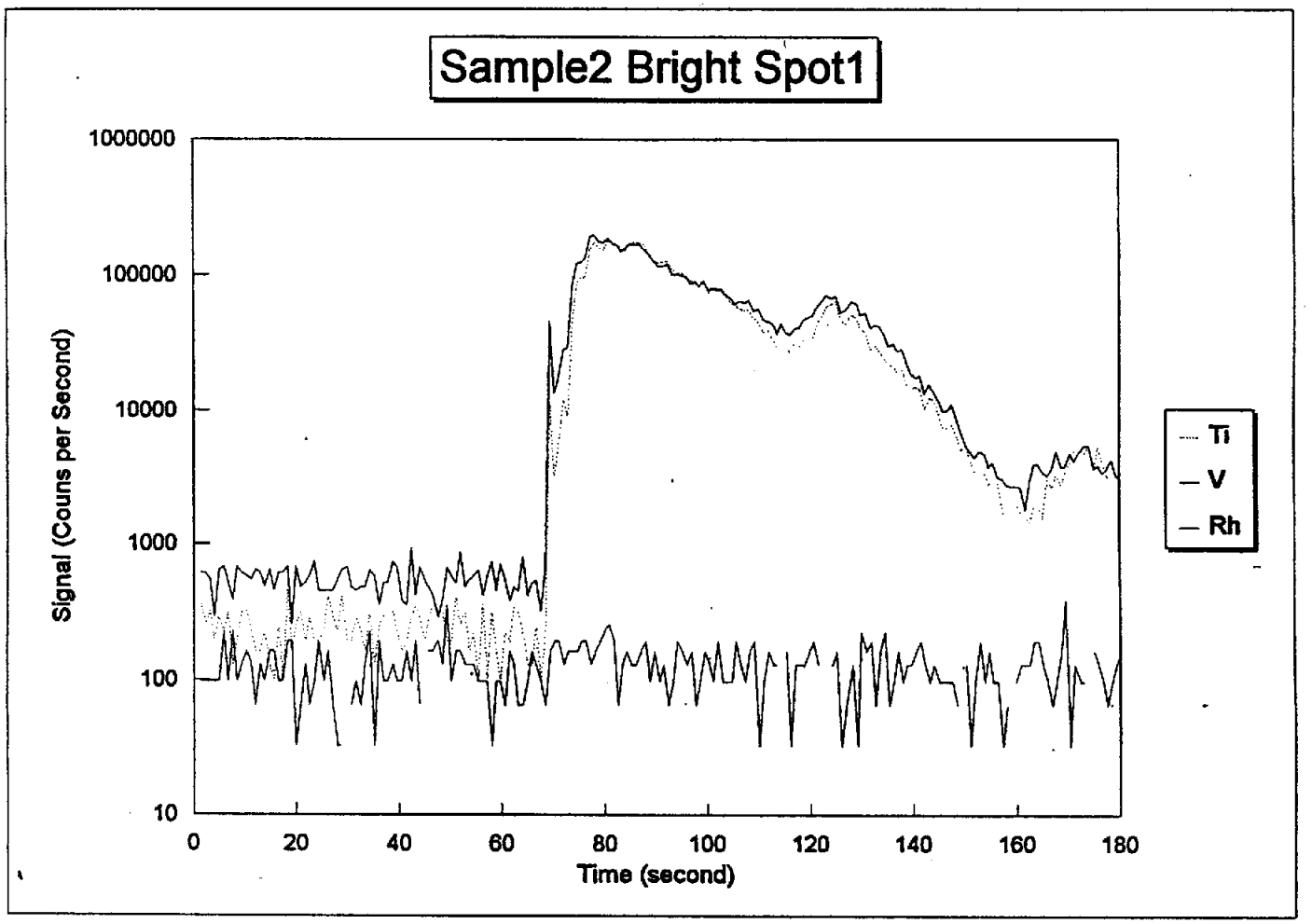
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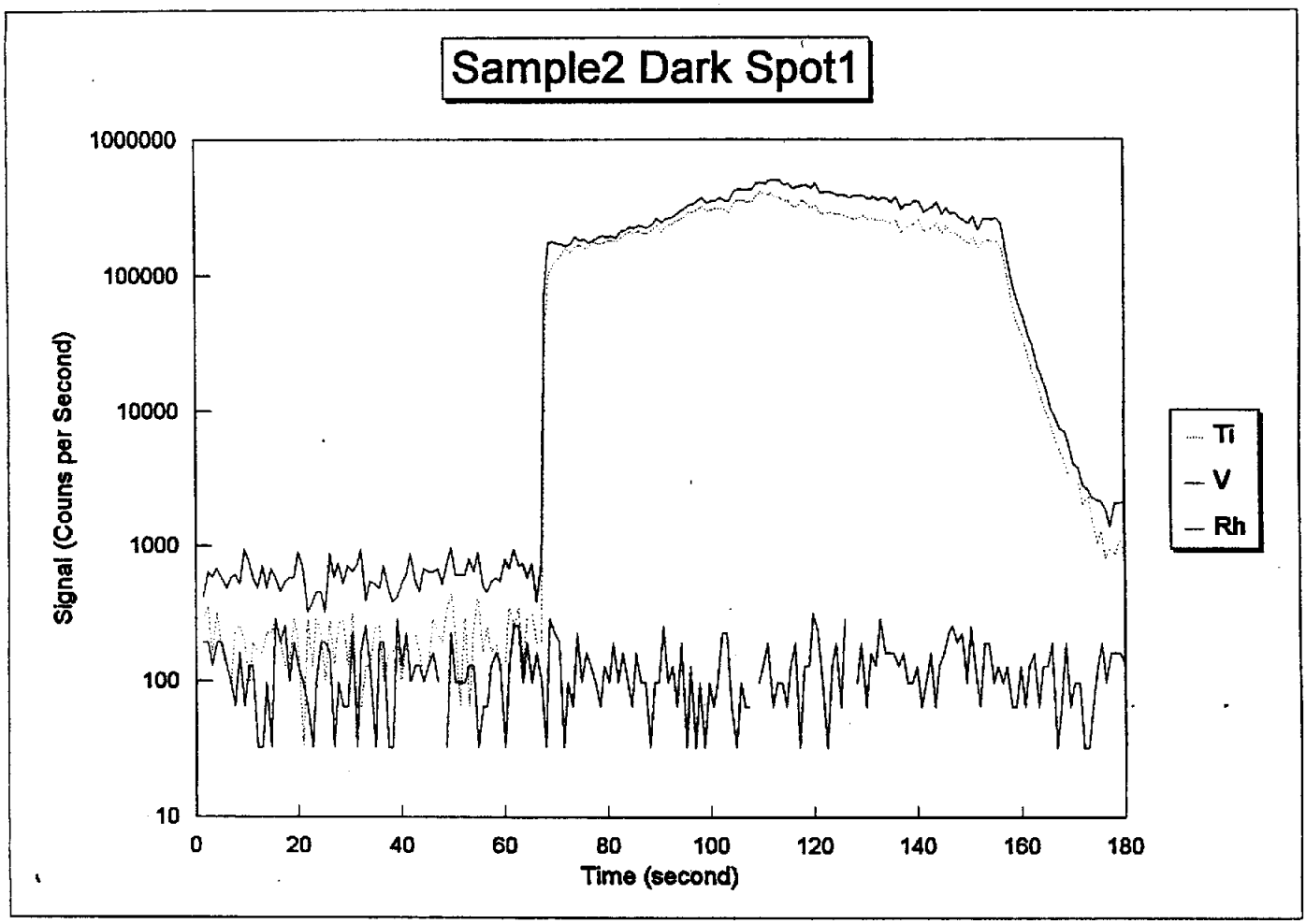
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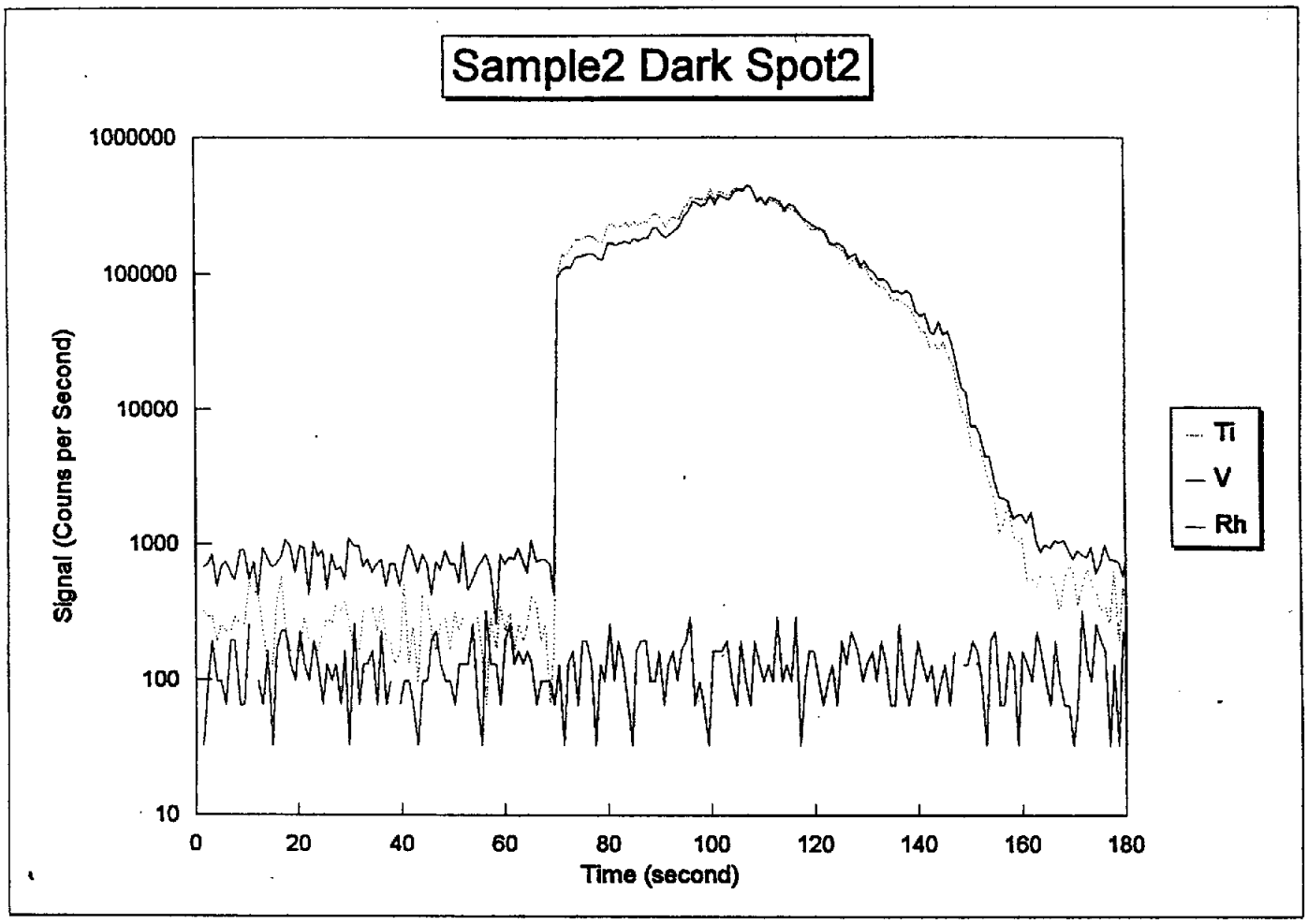
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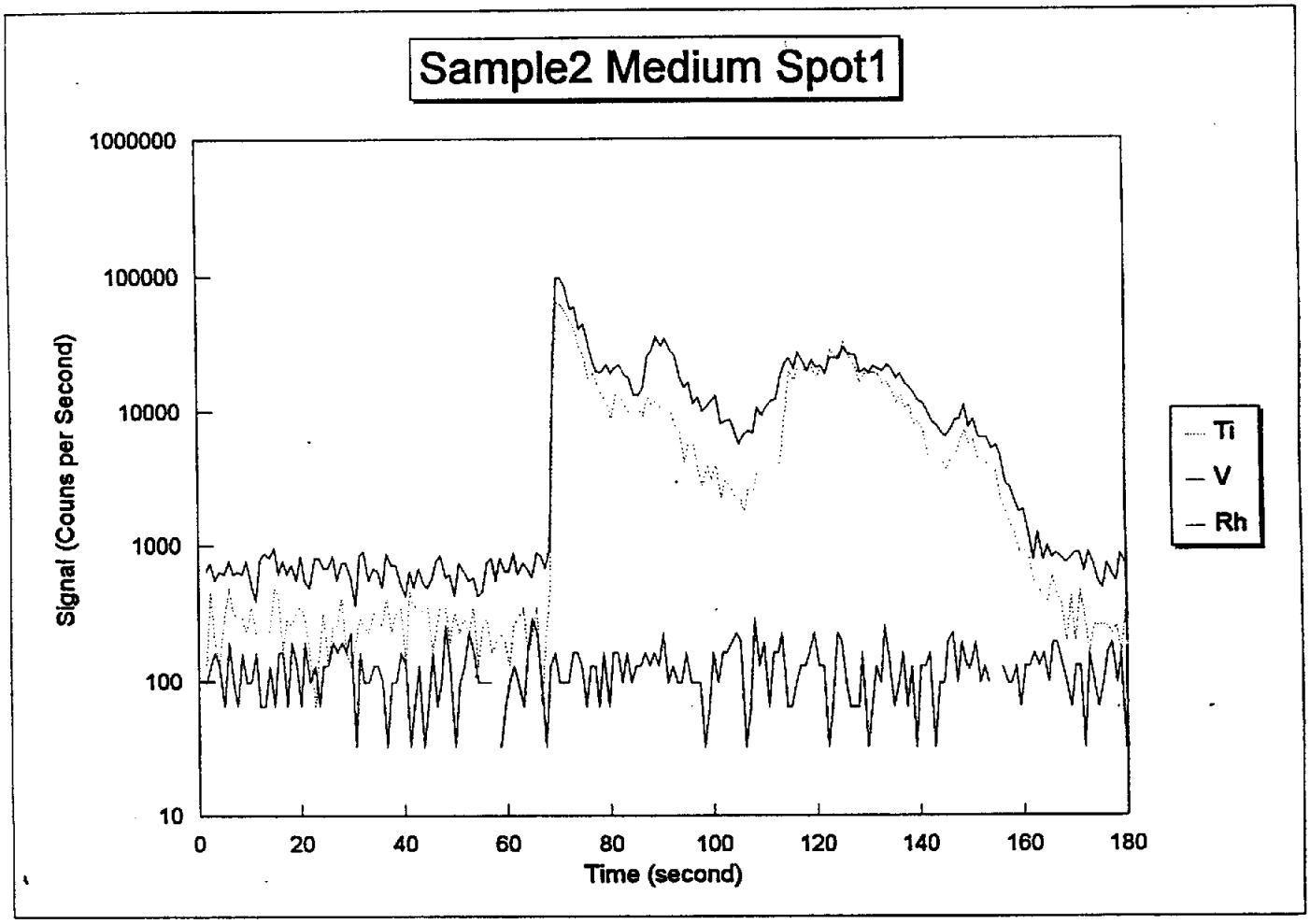
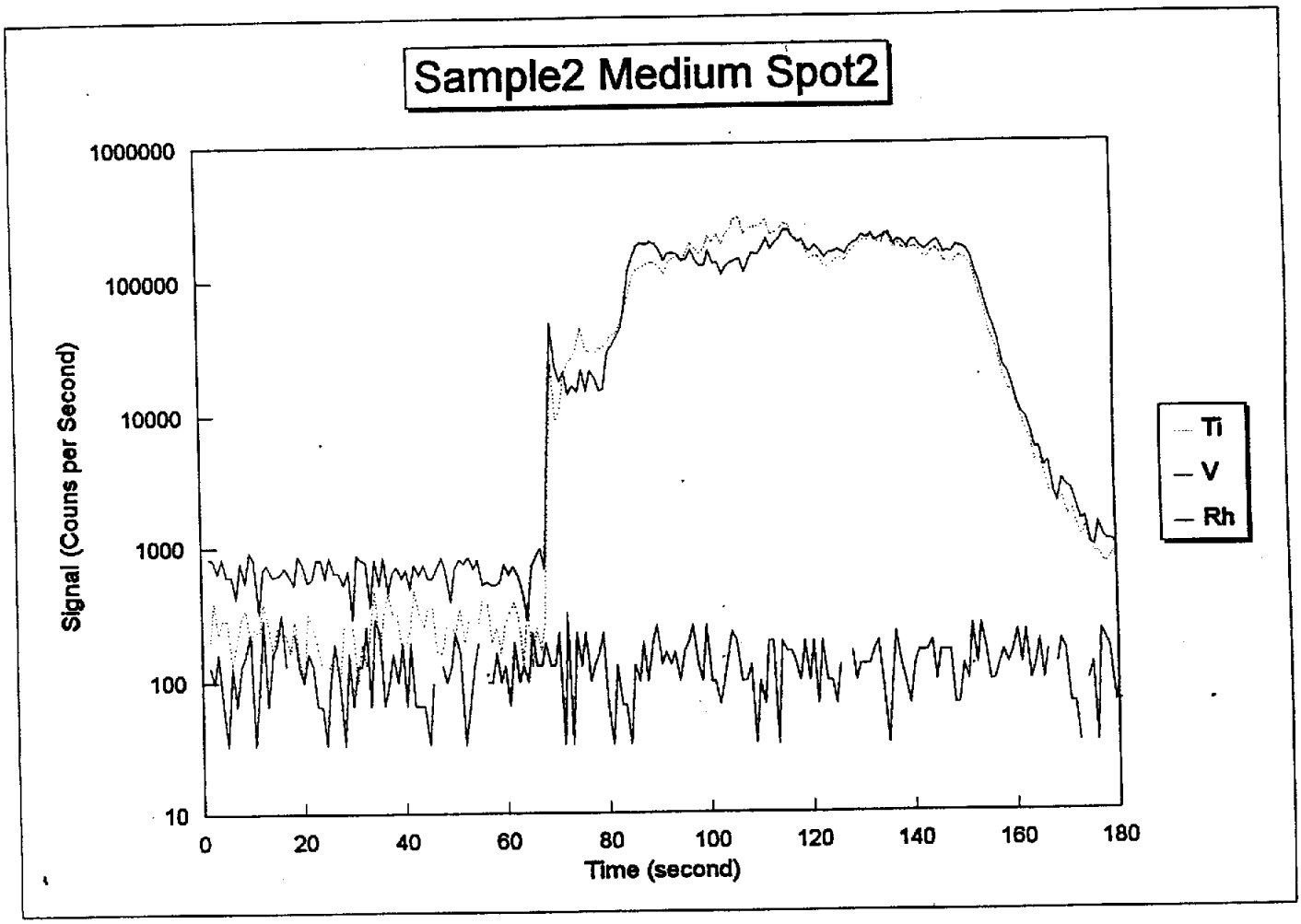
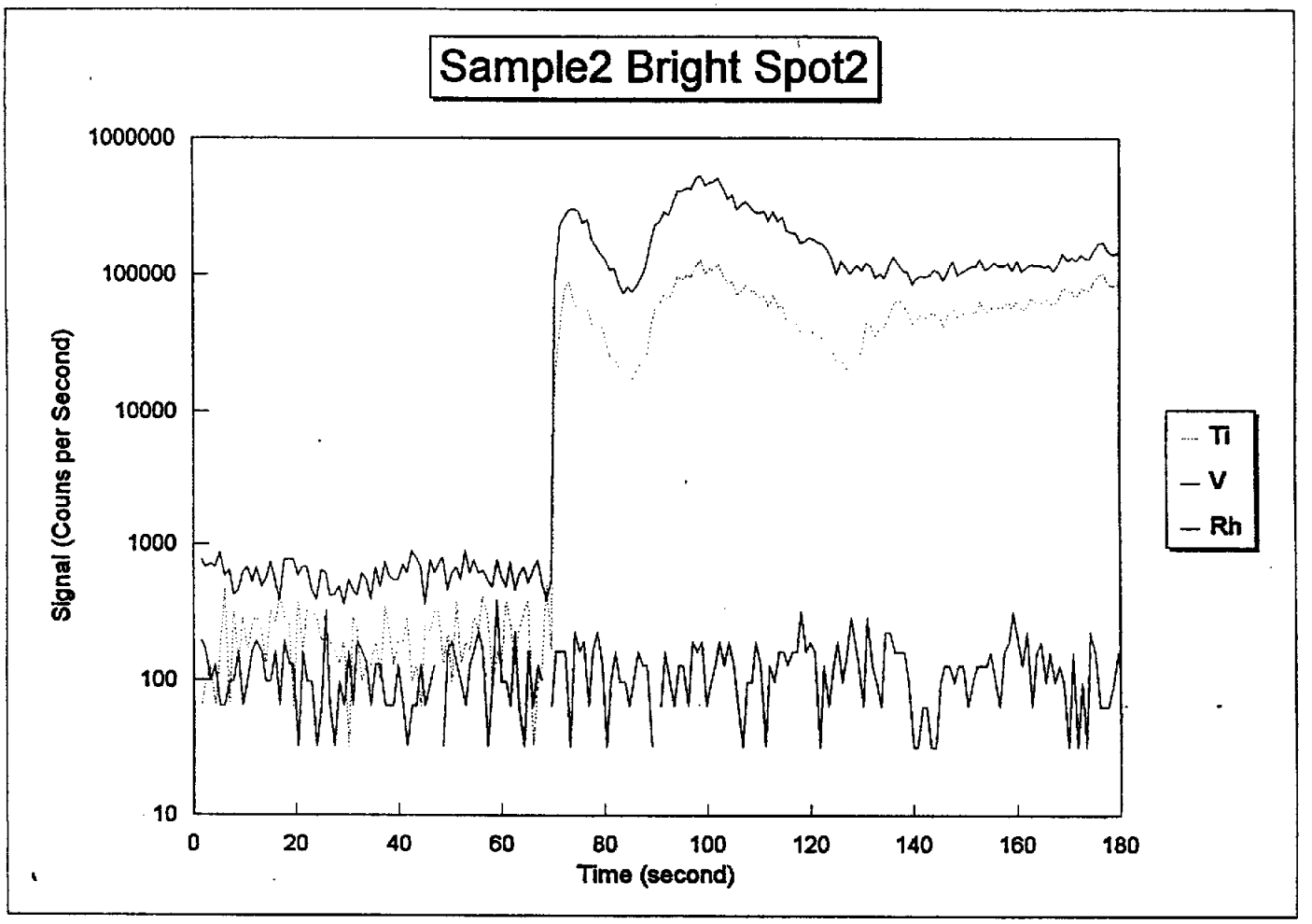
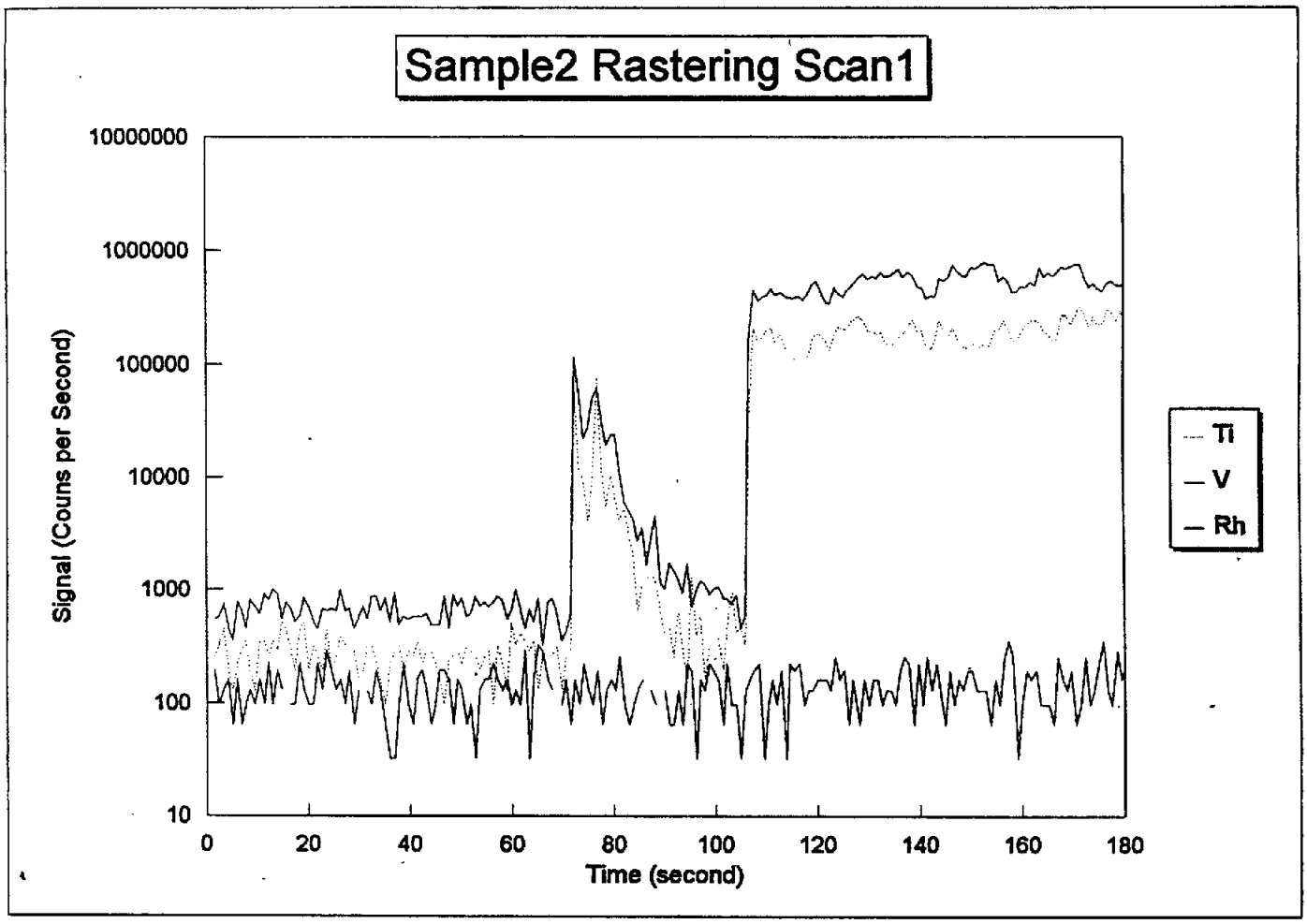
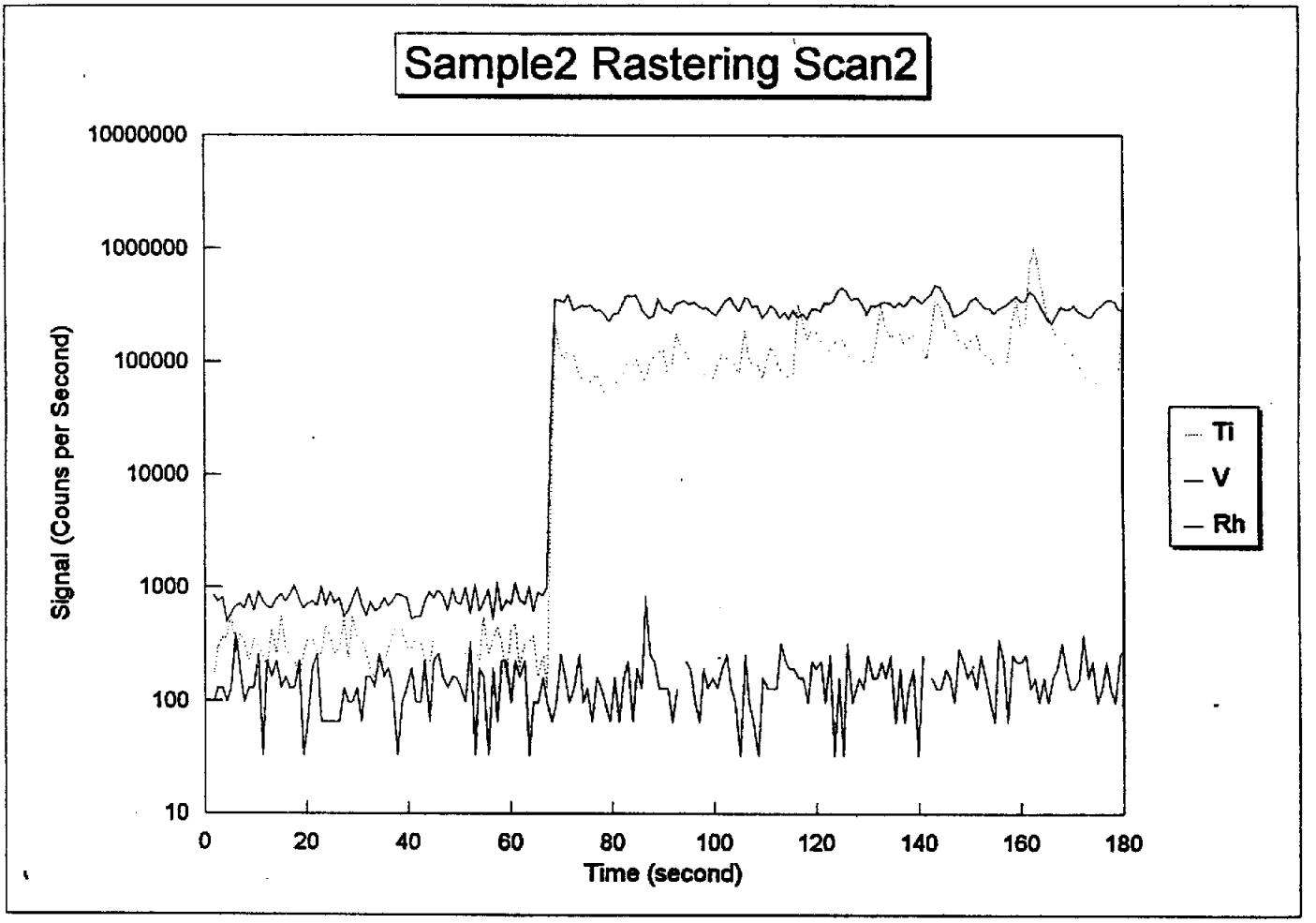
Signal (Couns per Second)
0
20
40
60
80
100
120
140
160
180
Time (second)
Ti
V
Rh

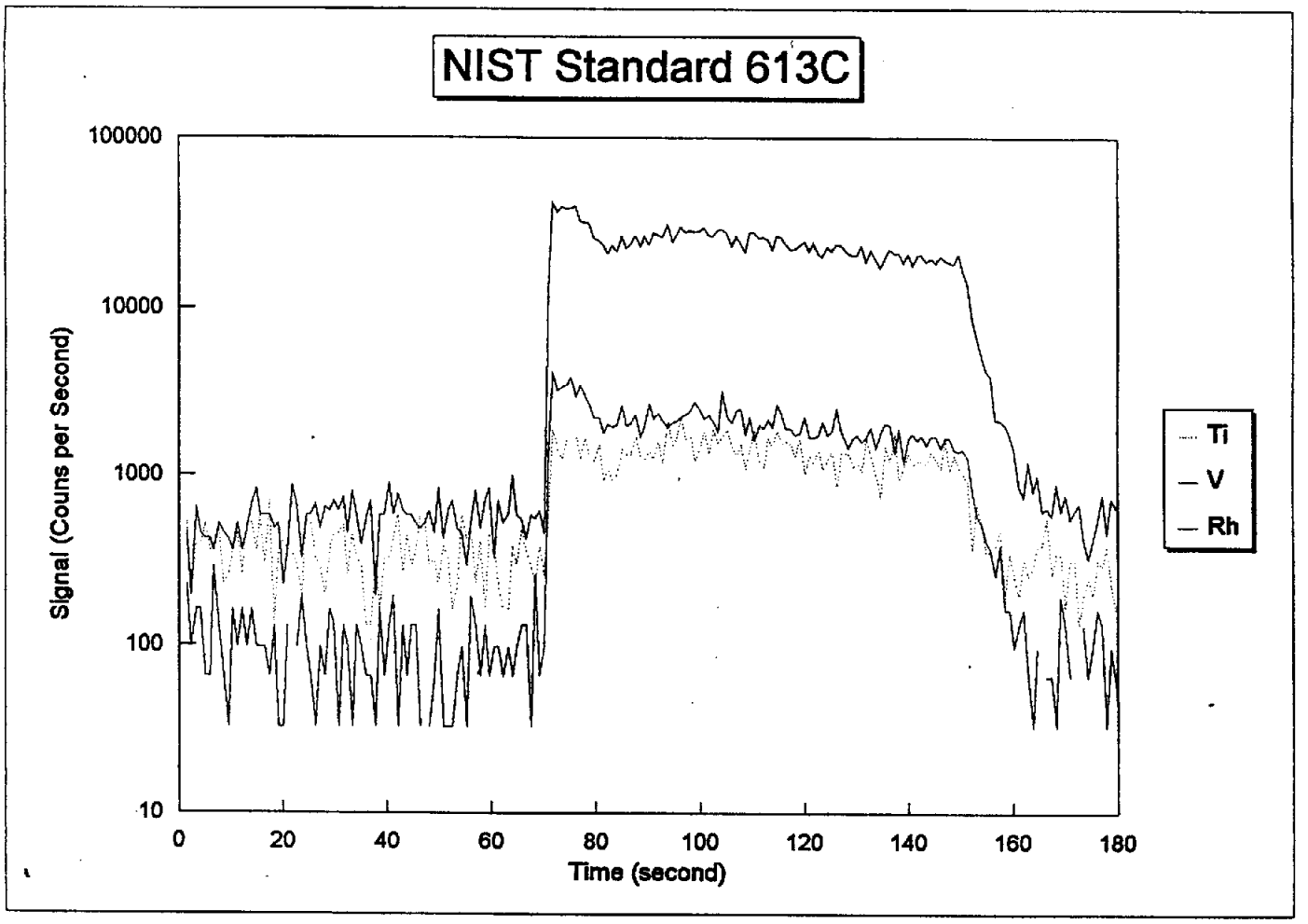

Sample2 Medium Spot1
1000000
100000
10000
1000
100
10
Signal (Couns per Second)
0
20
40
60
80
100
120
140
160
180
Time (second)
Ti
V
Rh

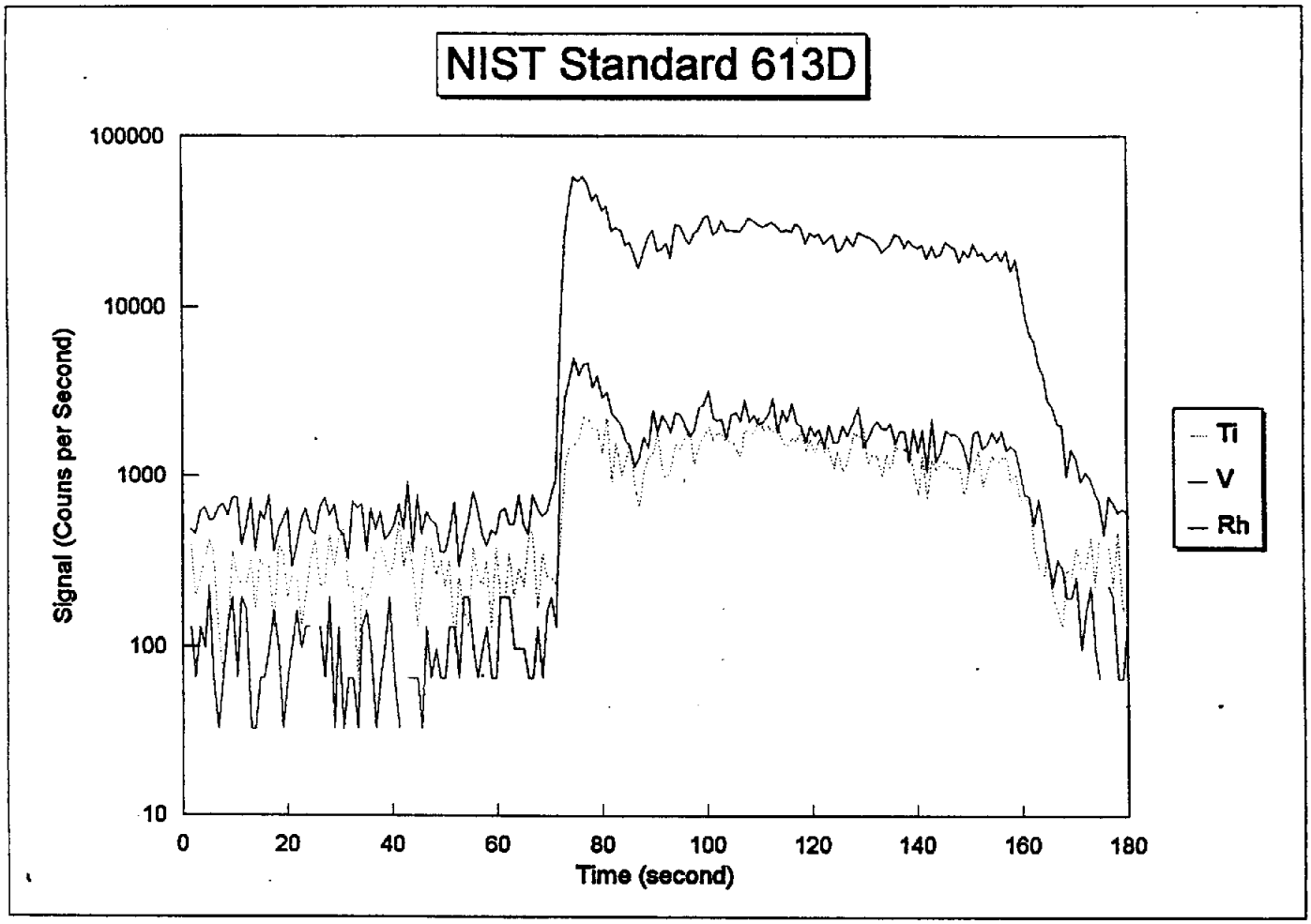

Sample2 Medium Spot2
1000000
100000
10000
1000
100
10
Signal (Couns per Second)
0
20
40
60
80
100
120
140
160
180
Time (second)
Ti
V
Rh


Sample2 Bright Spot2
1000000
100000
10000
1000
100
10
Signal (Couns per Second)
0
20
40
60
80
100
120
140
160
180
Time (second)
Ti
V
Rh


Sample2 Rastering Scan1
10000000
1000000
100000
10000
1000
100
10
Signal (Couns per Second)
0
20
40
60
80
100
120
140
160
180
Time (second)
Ti
V
Rh


Sample2 Rastering Scan2
10000000
1000000
100000
10000
1000
100
10
Signal (Couns per Second)
0
20
40
60
80
100
120
140
160
180
Time (second)
Ti
V
Rh


NIST Standard 613C
100000
10000
1000
100
10
Signal (Couns per Second)
0
20
40
60
80
100
120
140
160
180
Time (second)
Ti
V
Rh


NIST Standard 613D
100000
10000
1000
100
10
Signal (Couns per Second)
0
20
40
60
80
100
120
140
160
180
Time (second)
Ti
V
Rh

ACTLABS

ACTIVATION LABORATORIES LTD

Invoice No.: 16193
Work Order: 16428
Invoice Date: 21-OCT-98
Date Submitted: 07-OCT-98
Your Reference: LETTER
Account Number: I012

I. M. SHERWIN LTD.
1863 HOLLYWOOD CRESCENT
VICTORIA, BRITISH COLUMBIA
V8S 1J2
ATTN: IAN M. SHERWIN

CERTIFICATE OF ANALYSIS

1 ROCK(S)(PREP.REV1) were submitted for analysis.

The following analytical packages were requested. Please see our current fee schedule for elements and detection limits.

REPORT 16193 CODE 1B-RH-NICKEL SULPHIDE INAA(INAA.REV1)

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CERTIFIED BY:

DR E.HOFFMAN/GENERAL MANAGER

1336 SANDHILL DRIVE, ANCASTER, ONTARIO, CANADA L9G 4V5 • TEL: 905-648-9611 • FAX: 905-648-9613
E-MAIL: ACTLABA@IBM.NET or 102040.700 @ COMPUSERVE.COM

Activation Laboratories Ltd. Work Order: 16428 Report: 16193

Sample ID	Rh ppb
1	<0.1

PRICE LIST

Prices given below are meant to provide a guideline, and are subject to change without notice. Some discounts are available for large number of analyses.

1. Solution ICP-MS analysis

Category	HF/HNO_3 acid dissolution	Sodium peroxide sinter	Water
UVic SEOS research	$70.00	$60.00	$40.00
Collaborators	$85.00	$70.00	$50.00
Non-Collaborators	$100.00	$80.00	$60.00
Commercial	$110.00	$90.00	$70.00

For HF/HNO_3 acid dissolution and sodium peroxide sinter analysis, users are required to submit powder samples, otherwise an extra fee of $8.00 per sample will be charged for sample preparation. If users require major element analysis (SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, Fe_2O_3, MnO, Cr_2O_3, P_2O_5, TiO_2 and loss of ignition), $32.00 per sample will be added to the cost.

2. LAM analysis*

Category	Analysis (per hour)(1)	Data reduction (per hour)(2)	Half Day (20 analyses)(3)	Whole day (40 analyses)(4)
UVic SEOS research	$75.00	$30.00	$350.00	$560.00
Collaborators	$100.00	$40.00	$470.00	$750.00
Non-Collaborators	$150.00	$60.00	$700.00	$1120.00
Commercial users	$200.00	$80.00	$940.00	$1500.00

(1) The user is also charged for 1.5 hours per day instrument optimisation.
(2) 3 hours per 20-analysis run (including data downloading and reduction).
(3) 1.5 hour instrument optimisation + one 20-analysis run (2 hour) + 3 hours data downloading and reduction.
(4) 1.5 hour instrument optimisation + two 20-analysis run (4 hour) + 6 hours data downloading and reduction.

* Analyses are later reduced, producing concentrations with in-house written software. Time for data reduction by lab staff is charged. The concentration of at least one analytically suitable major element (e.g. Ca, Mg, and Si) is required before LAM analysis.