

Determination of the platinum – group elements (PGE) and gold (Au) in manganese nodule reference samples by nickel sulfide fire-assay and Te coprecipitation with ICP-MS

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Platinum group elements (PGE) and Au data in polymetallic oceanic ferromanganese nodule reference samples and crust samples obtained by inductively coupled plasma mass spectrometry (ICP-MS), after separation and pre-concentration by nickel sulfide fire-assay and Te coprecipitation, are presented. By optimizing several critical parameters such as flux composition, matrix matching calibration, etc., best experimental conditions were established to develop a method suitable for routine analysis of manganese nodule samples for PGE and Au. Calibrations were performed using international PGE reference materials, WMG-1 and WMS-1. This improved procedure offers extremely low detection limits in the range of 0.004 to 0.016 ng/g. The results obtained in this study for the reference materials compare well with previously published data wherever available. New PGE data are also provided on some international manganese nodule reference materials. The analytical methodology described here can be used for the routine analysis of manganese nodule and crust samples in marine geochemical studies.

[Key words : Platinum group elements (PGE), gold, manganese nodule reference samples, manganese crust, NiS fire-assay, ICP-MS]

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Introduction

Platinum group elements (PGE- Ru, Rh, Pd, Os, Ir and Pt) along with gold (Au) are gaining importance in understanding processes such as paleo-climate, weathering, diagenesis and enrichment, particularly in marine geochemical studies. Compared to the chemistry of the remaining PGE, platinum (Pt) changes its valency under changing redox conditions and this property has been extensively used for understanding the enrichment processes during sedimentation¹. The distribution of platinum, in the ferromanganese crusts in particular, has gained considerable attention after high Pt concentrations (up to 1.5 µg/g), were reported for Central Pacific seamount ferromanganese crusts². Hence, for a comprehensive understanding of the genesis and economic potential of ferromanganese crust deposits

and associated sediments, high precision PGE and Au data are required in addition to major, minor and trace-element compositions.

Despite striking advancements in analytical methods, PGE remain the most poorly studied group of elements, mainly due to analytical difficulties in generating accurate data for these elements, especially in complex matrices such as iron/manganese oxyhydroxides/oxides, and the low concentrations in other oceanic sediments. Determination of precious metals in geological samples is generally a two-step process. The first step involves preparation of a representative sample and then separation / pre-concentration of PGE and Au from the rock/ore matrix. For example, the low abundance of PGE in marine sediments requires use of a separation and pre-concentration method such as Pb/NiS fire-assay. The second step involves measurement of their

concentration in suitably prepared analyte solutions by highly sensitive instrumentation. Isotope dilution methods do not involve separation and pre-concentration steps³. The introduction of inductively coupled plasma mass spectrometry (ICP-MS) has led to the determination of PGE in natural systems at ng/g levels³⁻⁸. The nickel sulfide fire-assay (NiS-FA) method coupled with tellurium (Te) coprecipitation has been widely applied for the determination of PGE and Au in a variety of geological samples^{9,10}. However, a literature survey revealed that no systematic study has been carried out so far on the application of NiS-FA with Te co-precipitation and ICP-MS for the determination of PGE and Au in manganese nodule samples. Hence, the present study was undertaken to describe a method for the precise determination of PGE and Au in marine manganese deposits and to demonstrate a new extraction and measurement strategy utilizing NiS-FA, Te co-precipitation and ICP-MS combination.

Materials and Methods

Inductively coupled plasma mass spectrometer [ICP-MS], Perkin-Elmer Sciex, (Model ELAN DRC II ICP-MS, Toronto, Canada) was used throughout the study. The sample introduction system consisted of a standard Meinhard nebulizer with a cyclonic spray chamber attached to an autosampler (CETAC ASX-500) capable of handling 240 analyte solutions at a time. The standard and analyte solutions were aspirated for 85 seconds in each case for system equilibration before signal-integration and data acquisition. All quantitative measurements were performed using instrument software. Several well known isobaric interferences were programmed and applied corrections automatically through instrument software by monitoring another isotope of the interfering element¹¹. A muffle furnace (M/s Krishna Enterprises, Secunderabad, India) constructed with silicon carbide tiles and Kanthal heating elements held in ceramic tubes with digital temperature controller (maximum temperature upto 1150° C) was used for fusion. A Millipore vacuum filtration system consisting of a diaphragm operated vacuum pump and all glass filtration assembly was used for filtering solutions through 0.45 µm cellulose nitrate membrane filters (47 mm dia). Ni powder (-100 mesh) of 99.999% purity (Aldrich Chemical Company Inc. USA) and fire-clay crucibles (Southern Graphite Crucible Works, Salem, Tamil Nadu, India), were

used. The details of international manganese nodule and other reference samples are provided in Table 1.

NiS fire-assay procedure

A schematic presentation of the experimental protocol is presented in Fig. 1. Three types of fluxes were formulated for different rock types (Table 2) of which the intermediate flux was found to give satisfactory buttons for the manganese nodule and crust samples used in this investigation. A finely powdered and dried sample aliquot (2-10 g) along with intermediate flux in the correct proportion (see Table 2) was weighed directly into a disposable polythene bag (9" × 7") and mixed thoroughly. The polythene bag along with the contents was transferred to a fire clay crucible and fused in a muffle furnace at 1100°C for an hour. The molten sample was swirled to ensure proper mixing and heated for one more hour. The melt was then quickly poured into an iron mould and allowed to cool for an hour. If fusion was not satisfactory i.e., when a nice coherent bead was not obtained, the slag and the button were fused again¹². NiS buttons were weighed to check the recovery of NiS collected from the melt. If the bead weighed less than the weight of Ni and S powder combined, the button was discarded and fusion was repeated with a fresh sample aliquot. When a flux mixture consisting of sodium carbonate, sodium tetraborate, silica, nickel powder, and elemental sulfur with sufficient amount of sample are heated to ~1100° C, the heavier nickel sulfide phase is produced. The principle of nickel sulfide fire assay (NiS-FA) is based on the fact that PGE and gold are soluble in the molten nickel sulphide phase. Separation of the button from the slag containing the unwanted elements is based on the large difference in the specific gravity of the two phases.

The NiS button was cleaned (by removing any slag material adhering to it), powdered in an agate mortar and transferred to a 500 ml glass beaker and covered with a watch glass, 100 ml of conc. HCl was added and the beaker heated on a hotplate at 150°C. After reducing the volume of the solution to about 50 ml, an equal amount of distilled water was added and the solution was heated to boiling on a Bunsen burner. To the boiling solution, a combination of 2 ml of 1000 µg/ml Te and 5 ml of 20% SnCl₂ (freshly prepared) were slowly added with constant stirring until a black turbid precipitate was obtained. The solution was digested on a hotplate for at least 2 hours or until complete coagulation of the Te-precipitate took place,

Table 1 — Details of the international manganese nodule and PGE reference samples.

Sample No	Description of reference materials and location	Source
1.	No.2388 Manganese nodule: (Central Indian Ocean)	Analytical Chemistry & Standard Samples Division, National Metallurgical Laboratory Jamshedpur – 831 007, India
2.	NOD-A-1 Manganese nodule: (Blake Plateau in Atlantic Ocean)	Branch of Geochemistry, U.S. Geological Survey 923 National Center, Reston, Virginia 20192, USA
	NOD-P-1 Manganese nodule: (Central Pacific Ocean)	
3.	OOPE 601 OOPE 602 OOPE 603 Manganese nodule: (Pacific Ocean) “	Research Institute of Applied Physics of Irkutsk University 20, Gagarin Blvd. Irkutsk 664003, Russia
4.	GSPN-2 Manganese nodule: (Eastern Pacific Ocean)	Institute of Rock and Mineral Analysis Chinese Academy of Geological Sciences 26, Baiwanzhuangs St. Beijing 100037, China
	GSPN-3 Manganese nodule: (Central Pacific Ocean)	
5.	JMn-1 Manganese nodule: (Flat Floor of Southern Central Pacific Basin)	Geological Survey of Japan 1-1-3 Higashi, Tsukuba, Ibaraki 305, Japan
5.	JMn-1 Manganese nodule: (Flat Floor of Southern Central Pacific Basin)	Geological Survey of Japan 1-1-3 Higashi, Tsukuba, Ibaraki 305, Japan
6.	WGB-1 (Gabbro Rock)	CANMET Natural Resources Canada 555, Booth Street Ottawa, Ontario, Canada
	WMG-1 (Mineralized Gabbro)	
	WMS-1 (Massive Sulphide)	
	WPR-1 (Altered Peridotite)	
7.	SARM-7 (Precious Metal Ore)	MINTEK, P/Bag × 3015 Randburg 2125 Republic of South Africa

Table 2 — Summary of the flux components used in NiS fire-assay fusion for different rock samples (for 10 g sample).

Flux component	Normal flux (for acidic rocks)	Intermediate flux (for intermediate rocks)	Chromite flux (for ultramafic rocks)
Borax	40 g	80 g	120 g
Sodium carbonate	20 g	40 g	60 g
Sulphur powder	1.2 g	1.2 g	1.2 g
Nickel powder	2 g	2 g	2 g
Silica	3 g	6 g	10 g
Calcium fluoride	1 g	1.5 g	2 g

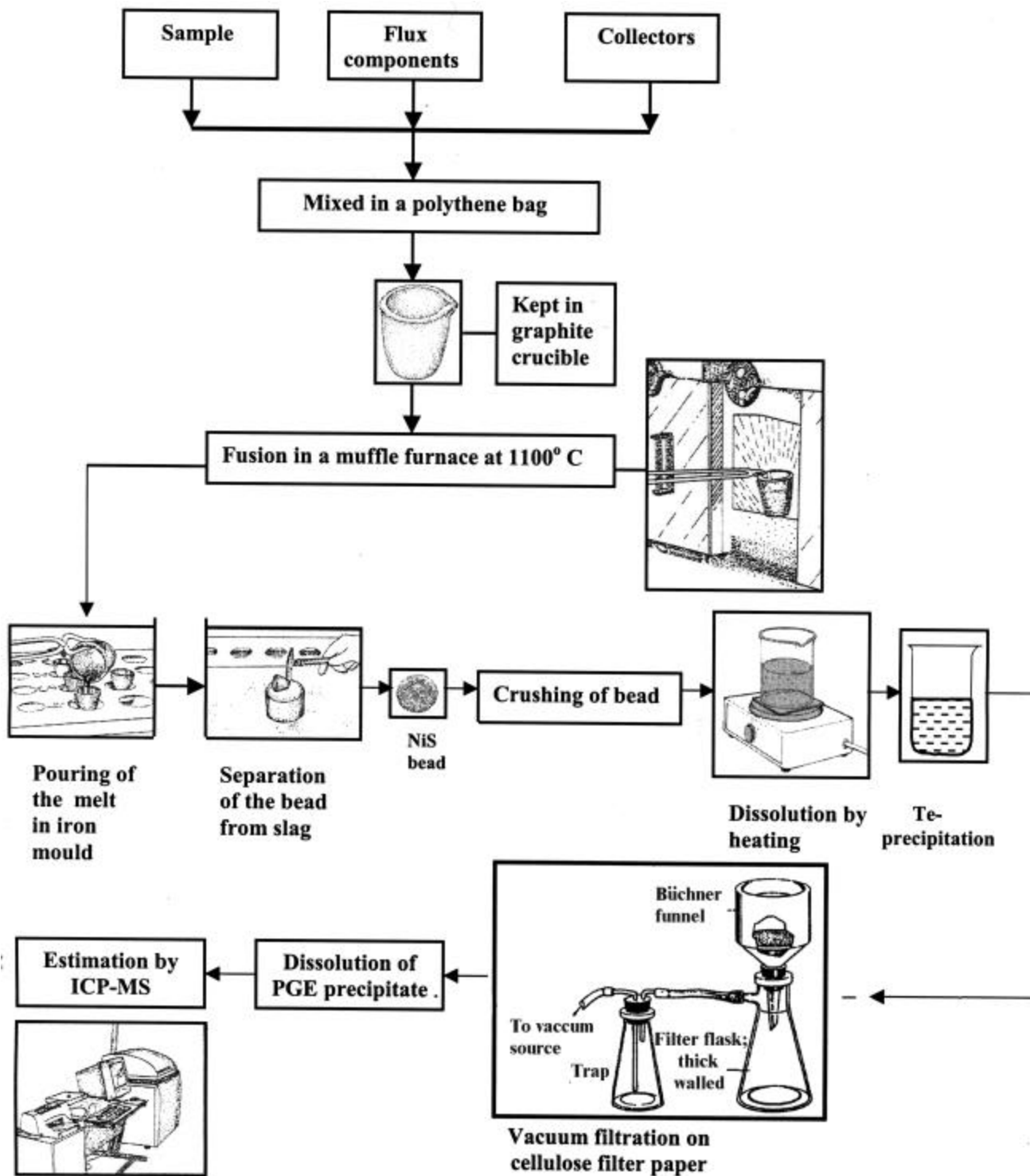


Fig. 1—Schematic representation of various steps involving separation, preconcentration and ICP-MS determination of PGE and Au in international manganese nodule reference samples.

giving a clear solution. The solution was cooled and vacuum filtered. The filter paper along with the Te-precipitate (gold telluride, TePtCl₂, TePdCl₂, etc) was quantitatively transferred to a 100 ml beaker and dissolved in 4 ml of freshly prepared aqua regia by heating at 150°C for 5 minutes. The filter paper was then discarded and heating of the sample solution continued till a clear solution was obtained. If undissolved particles were present, a further 4 ml of aqua regia was added and heating continued till a clear solution was obtained. The solution was cooled and quantitatively transferred to a 50 ml volumetric flask, 5 ml of 0.2 µg/ml Cd and Tl solution was added for internal standardization and the volume was made up to 50 ml. The diluted solution was filtered through a Whatman 40 filter paper if any suspended particles were noticed. Since osmium (Os) is partially lost as tetraoxide during fusion and follow-up procedure, the values obtained may not be quantitative. Hence, Os data are not reported here.

Mass spectrometric measurements and internal standardization

Operating conditions of the ICP-MS were optimized using a procedure described earlier¹¹, such that a uniform sensitivity was obtained for all the masses across the entire mass range. The precision for six-replicate measurements of the raw counts was < 5% RSD for PGE and Au. The monitored isotopes

and the potential isobaric interferences are indicated in Table 3. Cadmium (Cd) and thallium (Tl) were selected as internal standards because of the close proximity of these masses to light (Ru, Rh and Pd) and heavy (Ir, Pt and Au) PGEs respectively. All data acquisitions were made in peak hopping mode covering the mass ranges 101 – 114 amu and 191-205 amu, which cover all the analyte masses as well as internal standards. To check the internal consistency of the calculated concentrations, Ru, Pd, Ir and Pt concentrations were some times calculated using two isotopes for these studies. ¹⁰²Ru, ¹⁰⁶Pd, ¹⁹¹Ir, and ¹⁹⁴Pt, were used in addition to those mentioned in Table 3. Rh and Au are mono-isotopic. In most of the cases, the calculated concentrations agreed within 2% of each other. In view of this, finally one isotope for each element was chosen (Table 3). Online interference corrected and blank subtracted raw counts were used for calculating the concentrations of different elements.

Results and Discussion

Calibration strategy

Since ferromanganese crust or nodule samples with certified concentrations are not available, external calibration was performed using solutions of identically prepared PGE-international reference materials, WMG-1 and WMS-1, to minimize matrix

Table 3 — Isotopes selected for analysis, potential oxide, doubly charged and other polyatomic ion interferences¹³

Isotope	Abundance (%)	Oxide, hydroxide and other polyatomic ion interfering species	Remarks
¹⁰¹ Ru	17.10	⁸⁴ SrOH, Ar, ⁶¹ Ni, ⁶⁴ NiCl	The most abundant isotope, ¹⁰² Ru (31.6), has isobaric overlap of a minor isotope of ¹⁰² Pd (0.96)
¹⁰³ Rh	100.00	⁸⁷ RbO, ⁸⁶ SrOH, ⁸⁷ SrO, ⁶³ CuAr, ²⁰⁶ Pb ²⁺	Monoisotopic
¹⁰⁵ Pd	22.2	⁸⁸ SrOH, ⁸⁹ YO, ⁶⁵ CuAr	The most abundant isotope, ¹⁰⁶ Pd (27.3) has isobaric overlap from a minor isotope of ¹⁰⁶ Cd (1.20)
¹⁹³ Ir	62.60	¹⁷⁷ HfO	Most abundant isotope
¹⁹⁵ Pt	33.8	¹⁷⁹ HfO	Most abundant isotope
¹⁹⁷ Au	100.00	¹⁸¹ TaO	Monoisotopic

Table 4 — Concentrations (ng/g) of PGE and Au in WMG-1 and WMS-1 which were used for instrument calibration

	Ru	Rh	Pd	Ir	Pt	Au
WMG-1	35±5	24±2	382±13	46±4	731±35	110±17
WMS-1	99±16	225±16	1185±44	235±25	1741±142	279±33

Source: W.S. Bowman, Catalogue of Certified Reference Materials, CCRMP 94-1E, 67-70

and other interference effects. WMG-1 and WMS-1 have certified values for all the precious elements (Table 4). Multiple internal standards (Cd and Tl) were used to monitor and correct for fluctuations in matrix, instrumental drift, solution flow-rate, nebulizer and sampler orifice blockages, aerosol transport effects and the effects resulting from the presence of a large quantity of Te in the analyte solution. Very close agreement (< 2%) of values obtained by using different isotopes for Ru, Pd, Ir and Pt demonstrates that the interference effects by matrix elements are not significant. Linear calibration curves were obtained for all elements from the two calibration standards. A minimum quantity of 5 g of calibration standard have to be used for obtaining good calibrations.

NiS collection, purity requirements of nickel powder and detection limits

Because of the heterogeneous distribution of PGE and Au in various types of geological materials¹⁴, preconcentration of these elements by NiS fire-assay technique is best suited as it can handle larger amounts of samples (5-50 g). The Te-coprecipitation step enhances the recovery of PGE and Au, while ICP-MS is the most sensitive analytical technique. At low concentrations, the reagent blank becomes the limiting factor for the accurate determination of these elements. It was observed that laboratory grade nickel powder when used for NiS fire-assay, yielded very high blank values (Table 5) affecting the accuracy of the whole procedure and detection limits. High purity nickel powder (99.999%, -100 mesh) yielded extremely low blank values. (Table 5). These values are much lower than the concentrations reported for procedural blanks¹⁵. Hence, all the investigations were carried out using the high purity nickel powder. For manganese nodule samples relatively bigger buttons were obtained compared to those obtained for normal rock samples. This may be due to the presence of relatively large proportions of other sulfide forming elements such as As, Cu, Fe, Sb, Zn, in the sample, which also get collected into the NiS button. The detection limits obtained were in the range of 0.004 to 0.016 ng/g (Table 5).

Manganese nodule reference materials

USGS Nod-A-1 and Nod-P-1 - reference samples are the first reference materials available with certified data for major, minor and rare earth elements (REE)¹⁶⁻¹⁹. However, reasonably accurate PGE and Au data are not available for these reference samples.

Table 5 — Concentration (ng/ml) of PGE and gold obtained in procedural blanks with different grades of nickel powder and detection limits obtained in this study

Element	Concentrations*		Detection Limits (ng/ml) [@]
	High pure nickel powder-	Laboratory grade nickel powder ⁺	
Ru	0.001	29.86	0.016
Rh	0.002	16.87	0.010
Pd	0.001	1.95	0.010
Ir	0.001	9.70	0.005
Pt	0.003	37.58	0.004
Au	0.001	8.74	0.010

* Average of three determinations; - 99.999% pure Nickel Powder – 100 mesh (Aldrich Chemical Company, Inc., USA) ;
⁺ SD Fine Chemicals, India.

[@] Detection limits were calculated using WMS-1 (5 g) sample solution prepared by the present procedure.

Balaram⁶ and Axelsson *et al.*¹⁹ provided preliminary PGE and Au data on direct acid digested solutions by quadrupole ICP-MS and inductively coupled plasma double focusing sector field mass spectrometry (ICP-SFMS) respectively. However, reliability of data obtained in both these studies is poor, because separation and pre-concentration procedures-necessary for eliminating matrix and other interference effects were not adopted. This study, for the first time, provides accurate data on all PGE and Au for these reference materials (Table 6). These data are also broadly in agreement with those obtained by Baker & Krogh-Jensen⁸ by isotope dilution-MC-ICP-MS.

Indian polymetallic nodule sample No.2388 - An ocean-bed polymetallic nodule reference sample (No.2388) was collected from the Central Indian Ocean jointly by two Indian laboratories namely: National Metallurgical Laboratory (NML), Jamshedpur, and the National Institute of Oceanography (NIO), Goa, in 1981. Consequently, a collaborative investigation of the sample was carried out for a few major and minor elements by 10 Indian research laboratories including NGRI. More recently the same reference sample was extensively characterized for several trace elements including rare earth elements and some PGE^{6,18}. But the method used for solution preparation for the analysis of PGE and Au was by direct acid digestion of 2 g sample, without using separation or preconcentration procedures, before ICP-MS analysis. Hence, some of the elements like Pd were overestimated due to

Table 6 — Concentrations (ng/g) of PGE and Au obtained in manganese nodule reference samples by NiS-FA with Te-coprecipitation and ICP-MS in comparison with data obtained from other laboratories

Element	NOD-A-1				NOD-P-1			
	This Study*	Choudhary & Paul ²⁰	Axelsson <i>et al</i> ¹⁹	Baker & Krogh-Jensen ⁸	This study*	Choudhary & Paul ²⁰	Axelsson <i>et al</i> ¹⁹	Baker & Krogh-Jensen ⁸
Ru	30±3	-	22	18	23±3	-	12	6.8
Rh	27±3	-	<70	-	7±1	-	<110	-
Pd	9±2	-	<470	3.0	8±2	-	<480	5.0
Ir	5±2	-	16	16.0	2±1	-	6	1.5
Pt	450±25	453	520	520	118±10	123	120	112
Au	9±3	-	<9	-	4±2	-	<9	-

RSD < 10% in most cases, * Average of six determinations.

Table 7 — Concentration (ng/g) of PGE and Au obtained in international polymetallic nodule reference samples by NiS-FA with Te-coprecipitation and ICP-MS in comparison with data from other laboratories wherever available

Sample	Ru		Rh		Pd		Ir		Pt		Au	
	This Study*	Literature (21-25)	This Study*	Literature (21-26)	This Study*	Literature (21-26)	This Study*	Literature (21-26)	This Study*	Literature (21-26)	This Study*	Literature (21-26)
No.2388	26±4	-	11±2	-	8±2	-	3±1	-	95±5	-	3±1	-
OOPE 601	31±4	-	13±3	-	6±1	6	5±2	-	188±11	190	8±3	8
OOPE 602	22±3	-	7±1	-	7±1	6	2±1	-	100±6	100	5±2	5
OOPE 603	28±3	-	19±3	-	5±1	3	5±2	-	180±9	210	5±2	-
GSPN-2	29±4	-	10±2	-	4±1	-	<1	-	132±5	-	9±3	-
GSPN-3	20±3	-	9±2	-	4±1	-	<1	-	71±6	-	4±2	-
JMn-1	26±3	50	10±2	1.9	3±1	1.6	2	0.58	159±14	41	9±3	1.1

* Average of six determinations

Precision <10% RSD in most cases

Not available

Table 8 — Concentration (ng/g) of PGE and Au obtained in international polymetallic nodule reference samples by NiS-FA with Te-coprecipitation and ICP-MS in comparison with data from other laboratories wherever available

Sample	Ru		Rh		Pd		Ir		Pt		Au	
	This Study*	Certified value [@]	This Study*	Certified value [@]	This Study*	Certified value [@]	This Study*	Certified value [@]	This Study*	Certified value [@]	This Study*	Certified value [@]
WPR-1	30±3	22±4	15±2	13.4±0.9	245±20	235±9	20±2	13.5±1.8	276±17	285±12	45±3	42±3
WGB-1	2±1	0.3	2±1	0.32	15±2	13.9±2.1	2±1	0.33	8±2	6.1±1.6	4±1	2.9±1.1
SARM-7	415±9	430±57	235±10	240±13	1551±81	1530±32	77±4	74±12	3811±150	3740±45	327±20	310±15+

* Average of six determinations; precision <10 RSD%

@ W.S. Bowman, Catalogue of Certified Reference Materials, CCRMP 94-1E, 67-70.

• Govindaraju²¹ (for SARM-7).

- not available

Table 9 — Comparative data (in ng/g) of PGE and gold in a few manganese crust samples from central Indian Ocean by NiS-FA and ICP-MS from two different laboratories

Sample	Ru		Rh		Pd		Ir		Pt		Au	
	USGS	NGRI	USGS	NGRI	USGS	NGRI	USGS	NGRI	USGS	NGRI	USGS	NGRI
ANS-1	17±1	11±2	40±4	35±3	13±1	13±1	11±1	7±2	636±30	580±20	18±2	21±2
ANS-2	1±1	6±1	13±1	6±1	5±1	13±1	6±1	2±1	149±8	65±5	7±1	16±3
ANS-3	1±1	8±2	13±2	17±2	6±2	13±2	6±1	2±1	166±10	88±6	11±1	277±18
ANS-4	30±3	25±2	33±3	30±3	10±1	13±2	10±1	7±2	610±25	523±19	10±1	9±1
ANS-5	20±3	18±3	38±4	35±3	8±2	11±1	9±1	7±2	568±22	512±20	13±1	9±1
ANS-6	12±2	8±1	31±3	28±3	11±1	13±2	8±1	5±1	673±30	623±25	14±2	26±2
ANS-7	12±1	10±2	7±2	6±2	4±2	15±2	4±1	2±1	101±10	80±8	19±2	13±1
ANS-8	15±3	12±2	9±2	8±2	11±1	11±1	5±1	3±1	110±9	89±7	29±3	16±2
ANS-9	12±2	8±1	6±1	6±2	6±1	12±2	3±2	2±1	102±8	79±6	15±2	7±1
ANS-10	31±4	20±2	23±3	21±3	20±2	11±1	10±1	6±2	286±21	229±20	18±2	10±1
ANS-11	15±1	5±1	10±1	5±1	8±1	9±1	5±1	1±1	111±10	36±3	13±1	3±1
ANS-12	12±2	10±2	13±2	13±2	7±1	11±2	5±2	4±1	148±11	150±11	11±1	8±1
ANS-13	17±1	14±2	25±2	21±2	13±2	11±1	10±1	6±2	292±20	223±20	22±2	22±2

NGRI : NiS fire-assay (1100°C) – Te coprecipitation – ICP-MS estimation

USGS : NiS fire-assay (1200°C) – ICP-MS estimation

polyatomic interference effects. In order to provide more accurate data for PGE and Au this sample was analyzed using the present procedure (Table 7).

Other reference samples: For OOPE 601, OOPE 602, OOPE 603, GSPN-2 and GSPN-3 certified values for major, minor and several trace elements including REE were published by Russian and Chinese laboratories^{23,24}. PGE and Au values obtained in the present study are furnished in Table 7. For JMn-1, not even indicative values were available for comparison with the results obtained in this study²⁵. However, Pleassen & Erzinger²² determined PGE and Au in JMn-1 using NiS fire assay and ICP-MS. But the data does not match with the concentrations reported for PGE and Au in manganese nodules in general (Table 7), probably due to calibration problems.

Accuracy and precision

Assessment of the accuracy of an analytical method is difficult, especially when dealing with elements such as the PGE and Au. Meaningful inter-laboratory comparison is severely hampered if sufficient data are not available for a reasonable comparison. Limited data available for Nod-A-1 and Nod-P-1 and almost negligible data for the rest of the reference samples makes the accuracy assessment exercise extremely difficult. However, the Pt values obtained in this study for Nod-A-1 and Nod-P-1 are comparable with those obtained by fire-assay

spectrographic method by Choudhury & Paul²⁰ and also broadly agree with those obtained by isotope dilution-MC-ICP-MS⁸. But for other manganese nodule reference samples, no such data are available for comparison. Therefore, to assess the accuracy of the procedure, CCRMP reference samples (WPR-1, WGB-1) and South African reference sample, (SARM-7) were analyzed by adopting exactly the same procedure that was followed in the present study. The overall agreement of results is reasonably good and shows no evidence of systematic error (Table 8). In general, the precisions of the measurements have been better than 10% RSD in most cases. Concentrations for Pd, Ir, and Au obtained in this study are similar to those reported for a few manganese nodules from widely varying locations and geological environments within the Atlantic, Indian and Pacific oceans²⁶. In addition, sample splits of a few ferromanganese crusts collected from parts of the Equatorial Indian Ocean floor were analyzed at NGRI, India and at the USGS laboratory, USA for Pt, Pd, Rh, Ru, Ir and Au. Data of some of the samples are presented in Table 9. The anomalous value obtained for gold in sample ANS-3, may be due to non-homogeneity of the sample, particularly with respect to gold. Close agreement of results from the two laboratories (Table 9) was obtained in spite of marginally varying analytical procedures demonstrating the accuracy of the present analytical methodology.

Conclusion

Nickel sulfide fire-assay, Te-coprecipitation, and ICP-MS combination was found to be useful for the determination of PGE and Au in manganese nodule and crust samples at ng/g levels. Flux composition, fusion, calibration using international PGE reference materials and other details described here, are useful in detecting extremely low concentrations of PGE and Au in these samples. PGE and Au data provided for manganese nodule reference samples in this study will be useful in interlaboratory comparisons. There is good agreement between the concentration values obtained for PGE and Au in this study with those from the literature. The methodology described here can be used, on a routine basis for obtaining accurate and precise data of PGE and Au in manganese nodule and crust samples for marine geochemical studies.

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