Microwave Digestion for the Determination of Platinum Group Elements, Silver and Gold in Chromite Ores by ICP-MS

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This paper describes an effective acid digestion procedure for chromite samples utilising a laboratory microwave oven for the determination of gold, silver and platinum group elements by inductively coupled plasma mass spectrometer. The procedure was evaluated by the analysis of some standard reference materials, PTM-1, CHR-Pt+ and CHR-Bkg together with a few chromite ore samples from the Sukinda Valley. The data obtained on Au, Ag, Ru, Rh, Pd, Os, Ir and Pt in the standard reference materials showed good agreement with the rreference values. Cesium was used as an internal standard. The detection limits obtained for these elements were in the range of 0.01 to 0.07 ng/g. The proposed microwave digestion, in combination with ICP-MS method of estimation was found to be particularly useful for rapid quantitative estimation of precious elements in chromite ore samples. This method can in general also be utilised for prospecting studies of precious metals in all mafic and ultramafic rocks.

INTRODUCTION

Ultramafic rocks and their hosted chromite deposits are the important sources of economically viable deposits of the platinum-group elements. The precious metals are found together in the periodic table and are also found together in nature, with Pt and Pd predominating in all known deposits[1]. To understand the genetic relationship between the ultramafic hosts and platinum-group element deposits and to document the abundance levels of these metals, their distributiuon and fractionation trends, a systematic and comprehensive noble metals database in highly desirable. Several studies revealed that all the six platinum group elements and gold can be associated with chromites, in concentration levels that range from ug/g to tens of ug/g[2-4]. Determination of these elements in geological materials containing ng/g and ug/g amounts requires very sensitive, reliable and rapid instrumental techniques such as Graphite Furnace Atomic Absorption Spectrometer (GF-AAS), Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Despite the significant progress recently observed in the analytical instrumentation[5], sample preparation of geological samples continues to be a major problem because of the refractory nature of some of them. Sample

preparation and development of methods have also become a growing field along with instrumental improvements[6, 7].

Dissolution of chromite ores by classical open vessel dissolution is very often incomplete due to the refractive nature of these materials[8, 9]. Though the use of phosphoric acid facilitates dissolution of chromite ores and chromite[10], phosphate ions severelly interfere with ICP-MS analysis. It has been noticed by us that presence of even 2% phosphoric acid reduces the respective signals of all precious elements to an extent of more than 80% making the analysis by ICP-MS very difficult. Dissolution by fusion methods and by use of oxidizing agents is not very effective. These procedures also increase the total dissolved solids in the sample solution[11] causing matrix and other interferences in the subsequent chemical analysis by instrumental methods. The use of sodium peroxide fusion for an effective decompositin of refractory materials, matrix problems due to high concentration of sodium, the interference effect of zirconium on Ag when ziroconium crucibles are used for fusion have been thoroughly reviewed by Van Loon and Barefoot[12] and Perry *et al.*[13] For these reasons, the most common method for the determination of platinum-group of metals is the fire assay, the advantages being the use of a large sample and the collection of the PGEs in a NiS button, or for Au a lead button. Unfortunately, this procedure is very tedious and labour-intensive and also depends on the experience of the analyst. In addition, Au is collected less efficiently than lead fire-assay. Few studies[14] indicated that significant proportion of Au and lesser quantities of PGE are dissolved during HCl digestion of NiS button, resulting in reduced recoveries. In this paper, an effective procedure has been described for the digestion of a noble metal bearing copper-nickel matte, a couple of chromite reference samples, and some chromite ore samples from the Sukinda ultramafic field, Orissa, India and their subsequent estimation of precious metals by ICP-MS.

EXPERIEMNTAL

The ICP-MS instrument used was a Plasma Quad PQ1 (VG Elemental Analysis, UK) controlled by an IBM PC-XT micro computer and associated software (issue 3.1). The details of the instrument are given elsewhere[15]. The isotopes used in this study and potential interferences from doubly-charged ions, metal oxides and other polyatomic species are indicated in Table-1. Single isotopes were used for the quantification of all the elements. These isotopes were selected taking into consideration their natural abundance levels and the freedom from the interference effects by other elements present in chromite ores. Some isotopes such as ^{197}Au are monoisotopic and thus no choice is available. ^{133}Cs was used as an internal standard. 0.5% solution of SARM-7 was used for calibration for the instrument of different elements. This will minimise the matrix and other interference effects[16].

TABLE-1

ISOTOPES SELECTED FOR ANALYSIS, POTENTIAL OXIDE, DOUBLY-CHARGED
AND OTHER POLYATOMIC ION INTERFERENCES, DETECTION LIMITS, AND
AVERAGE CRUSTAL ABUNDANCES OF ALL THE PRECIOUS ELEMENTS

Element	Detection limits* (ng/g)	Average crustal abundance[23] (ng/g)	Isotope	% Abundance	Oxide, hydroxide, polyatomic ion interfering species	Remarks
Ru	0.07	0.4	^{101}Ru	17.00	^{84}SrOH$^+$, Ar^{61}Ni$^+$, ^{64}NiCl$^+$	The most abundant isotope ^{102}Rh(31.6) has isobaric ore laps ^{102}Pd(0.96)
Rh	0.01	0.4	^{103}Rh	100.00	^{86}SrOH$^+$, ^{87}SrO$^+$, ^{65}CuAr$^+$	Monoisotopic
Pd	0.05	4.0	^{105}Pd	22.20	^{88}SrOH$^+$, ^{89}YO$^+$, ^{65}CuAu$^+$	The most abundant isotope ^{106}Pd(27.3) has an isobaric overlap of ^{106}Cd(1–20)
Ag	0.02	70.0	^{107}Ag	51.84	^{67}ArZn$^+$, ^{91}ZrO$^+$, ^{90}ZrOH$^+$	Most abundant isotope
Cs	0.01	3000.0	^{133}Cs	100.00	—	Used as an internal standard
Os	0.03	0.4	^{192}Os	41.00	^{192}Pt(0.78), ^{176}YbO, ^{176}HfO, ^{176}LuO	Most abundant
Ir	0.01	0.4	^{193}Ir	62.60	^{177}LuO	Most abundant isotope
Pt	0.02	2.0	^{195}Pt	33.80	^{179}HfO	Most abundant isotope
Au	0.02	4.0	^{197}Au	100.00	^{181}TaO	Monoisotopic

*Calculated from 0.5% solution of SARM-7.

All the dissolutions were done using a Computer Controlled Model Qwave
3000 Microwave Oven (Question Corporation, Mercerville, New Jersey, USA)
with fume exhaust, rotating carousel, PTFE lining and 10 multi-ply 120 mL high
pressure digestion vessels capable of operation at up to 625 psi and 230°C. This
unit has a pressure monitor system with feedback to enable computer control of
the pressure and temperature within the vessels. The operating conditions of the
microwave oven are given in Table-2.

The details of the precious metal reference samples and field samples are given
in Table-3.

Reagents

Spectroscopic single element standard solutions used were obtained from Alfa
Products, USA, and E. Merck, Germany. All the acids and other reagents used

were of Electronic/Analytical grade. All solutions were prepared using double distilled water.

TABLE-2
CONDITIONS FOR THE MICROWAVE DIGESTION OF CHROMITE

Microwave power output	900 W
Microwave power duration time	25 min
Maximum pressure	381 psi
Maximum temperatue	205°C

TABLE-3
DETAILS OF STANDARD REFERENCE MATERIALS AND FIELD SAMPLES

Sample name	Material	Source
SARM-7	Platinum ore	MINTEK South Africa
PTM-1	Noble metals bearing nickel-copper matte	CCRMP, Canada
CHR-Pt+	Chromite	WIG, France
CHR-Bkg	Chromite	WIG, France
Su-1	Chromite	Sukinda Valley Orissa, India
Ti-1	Chromite	Sukinda Valley Orissa, India
Ka-1	Chromite	Sukinda Valley Orissa, India
KL-1	Chromite	Sukinda Valley Orissa, India
KT-1	Chromite	Sukinda Valley Orissa, India

Microwave Digestion Procedure

Initially a series of experiments were carried out on 0.5 g samples of PTM-1, CHR-Pt and CHR-Bkg by adding varying amounts of aquaregia, HF and $HClO_4$ and changing of microwave conditions. Finally, the following digestion procedure was found to give maximum recoveries for all the elements of interest in chromite ores and other related samples and the results were also reproducible on replicate samples.

0.5 g subsample was weighed into a PFA-microwave digestion vessel; 5 mL of aquaregia, 3 mL of HF and 2 mL $HClO_4$ were added. Latter 1 mL of 10 μg/mL cesium was added to act as an internal standard. The samples were digested in the microwave oven using the operating conditions furnished in Table-2. After cooling the vessels to room temperature under tap water, the samples were transferred to PTFE teflon beakers (100 mL) and the contents were evaporated to incipient dryness on hot plate (220°C) in a laboratory fume

cupboard. Same quantities of aquaregia, HF and $HClO_4$ were added once again and evaporated to incipient dryness. Then the residue was dissolved by the addition of 20 mL of 1:1 HNO_3 and heating. The contents were cooled and the volume made to 100 mL with double distilled water. PTM-1, SARM-7, CHR-Bkg gave very clear solutions. CHR-Pt+ had minute quantity of black material which was filtered off before ICP-MS measurements. This black material was present even after repetition of microwave digestion cycle once more. All the other samples gave clear solutions. Three replicates of each sample were dissolved by this method and each sample was analyzed twice in the case of standards and once in the case of field samples.

TABLE-4

CONCENTRATIONS (ug/g) OF PRECIOUS METALS OBTAINED BY ICP-MS IN
PRECIOUS METAL ORE REFERENCE SAMPLES IN COMPARISON WITH
CERTIFIED VALUES

Element	PTM-1		CHR-Pt+		CHR-Bkg	
	ICP-MS value*	Certified value[24]	ICP-MS value*	Certified value[24]	ICP-MS value*	Certified value[24]
Ru	0.34 ± 0.03	0.35	0.80 ± 0.01	9.2	0.07 ± 0.01	0.067
Rh	0.94 ± 0.01	0.90	1.00 ± 0.05	4.7	0.03 ± 0.01	0.009
Pd	7.89 ± 0.47	8.10	83.13 ± 4.15	90.9	0.11 ± 0.01	0.070
Ag	65.80 ± 4.6	66.00	23.24 ± 1.39	—	20.06 ± 0.65	—
Os	0.11 ± 0.01	0.14	0.89 ± 0.09	1.9	0.03 ± 0.01	0.027
Ir	0.40 ± 0.03	0.30	1.25 ± 0.11	6.2	0.71 ± 0.06	1.028
Pt	5.75 ± 0.41	5.80	58.01 ± 2.32	58.0	0.10 ± 0.01	0.050
Au	1.70 ± 0.15	1.80	4.51 ± 0.27	4.3	0.04 ± 0.01	0.028

*Average of six determinations.

TABLE-5

CONCENTRATIONS (ug/g) OF PRECIOUS ELEMENTS IN SOME CHROMITE ORE
SAMPLES FROM THE SUKINDA VALLEY, ORISSA

Element	Su-1	Ti-1	Ka-1	Kl-1	Kt-1
Ru	0.12 ± 0.01	0.10 ± 0.01	0.08 ± 0.01	0.05 ± 0.01	0.03 ± 0.01
Rh	0.06 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.03 ± 0.01
Pd	0.24 ± 0.02	0.19 ± 0.02	0.17 ± 0.01	0.21 ± 0.01	0.21 ± 0.02
Ag	570.83 ± 17.11	35.65 ± 1.75	19.78 ± 1.20	64.37 ± 1.95	1452.68 ± 43.56
Os	0.03 ± 0.01	0.04 ± 0.01	0.08 ± 0.01	0.05 ± 0.01	0.07 ± 0.01
Ir	0.08 ± 0.01	0.11 ± 0.01	0.12 ± 0.01	0.11 ± 0.01	0.03 ± 0.01
Pt	0.12 ± 0.01	0.08 ± 0.01	0.07 ± 0.01	0.09 ± 0.01	0.14 ± 0.01
Au	0.07 ± 0.01	0.08 ± 0.01	0.05 ± 0.01	0.09 ± 0.01	0.13 ± 0.01

*Average of three determinations.

RESULTS AND DISCUSSION

Interferences, Internal Standards and Detection Limits

The isotopes chosen for analytical measurements and the potential, isobaric, doubly-charged and molecular ion species which may influence the accuracy of the analysis are presented in Table-1. Under the operating conditions used in this study, the degree of oxide formation levels of Sr, Y, Yb, Hf, Lu and Ta were found to range between 0.01 to 0.1% with corresponding hydroxide levels being considerably lower. Thus the effect of these interfering species on the accuracy of determination of these elements was minimal. From the initial semiquanititative survey[17] it was found that Cs concentrations in these samples were very low (less than 40 ng/g). Cs was also found to behave similar to the precious elements under typical plasma conditions and does not suffer from significant spectroscopic interferences. This was noted by monitoring the ICP-MS signal under different conditions, *i.e.*, varying amounts of different elements in the concentration range normally expected in the samples under investigation. Use of [209]Bi was also tried, but it was found to behave differently from precious elements. Hence [133]Cs was used as an internal standard and its concentration maintained at 100 ng/mL in all the samples, calibration and blank solutions. The detection limits (3σ values) for these elements ranged between 0.01 to 0.07 ng/g (Table-1). These were calculated from the concentrates obtained for these elements from 0.5% SARM-7. Procedural blanks were used for background correction.

Sample Dissolution, Precision and Accuracy of Determination

Chromite ores are difficult to dissolve using normal dissolution procedures adopted for silicate rock and other geological materials. The most innovative source of energy for wet digestion procedures is the use of microwaves[18]. Because the digestion is performed under synergistic effects of temperature and pressure, microwave digestion is more efficient than conventional means of heating[19–22]. The pressure/temperature *vs.* time profiles (Fig. 1) obtained for the microwave dissolution reveal that a pressure of around 350 psi and a temperature of about 205°C were maintained in the decomposition vessel for a minimum period of 25 min. The ICP-MS in combination with microwave was examined here for its potential use as a rapid turnaround method for the analysis of chromite ores for gold, silver and platinum group metals. One of the striking advantages of the use of microwave digestion is the use of very low quantities of reagents. This will not only reduce the cost of dissolution but also reduce the concentrations of impurities. As a result, low blanks were obtained resulting in very low level detection limits for all the elements of interest in these investigations (Table-1). The very low detection limits obtained in comparison with average crystal abundances (Table-1) demonstrate that these elements can be directly estimated very accurately at natural abundance levels in most rock formations by ICP-MS. The data obtained for PTM-1 CHR-Pt+. CHR-Bkg are given in Table-4. These results show that the measured values are generally well within the range of reference values for certain elements such as Ag, Au, Pt, Pd in all the samples. For other elements like Os, Ir the agreement is very good only in the case of
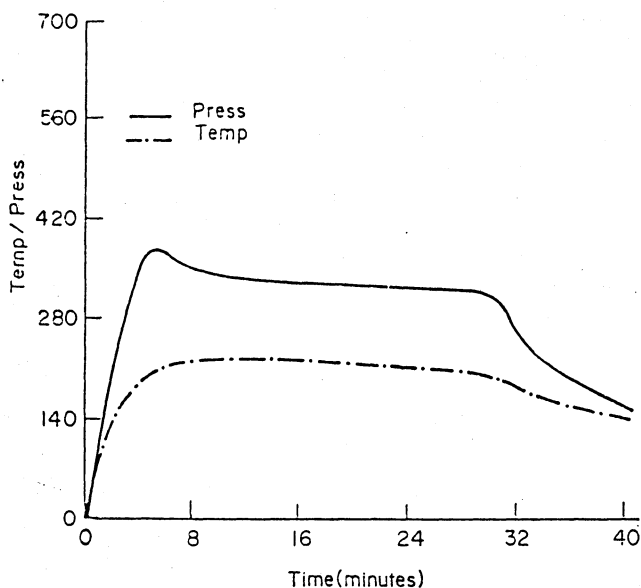
Fig. 1   Pressure *vs.* time and temperature *vs.* time profiles of typical microwave-digestion program adopted in the present investigations. It can be seen that a maximum pressure 381 psi was attained within 6 min. of the start.

PTM-1 and CHK-Bkg in whcih the concentrations of these elements are low, In the case of CHR-Pt+ very low recoveries were obtained for Ru, Rh and Ir suggesting that even microwave dissolution is not fully effective in this particular case. For Os low recoveries are expected due to the formation of volatile OsO_4 compound as these samples were subjected to open dissolution procedure after microwave-digestion. Overall precisions better than $\pm 10\%$ RSD were obtained for majority of the elements with comparable accuracy. It can also be very clearly seen that the recoveries of Pt, Pd, Ag and Au are very good and are within acceptable range. The results obtained for Pt, Pd, Ag and Au in CHR-Pt+ indicate that complete decomposition of sample is not required for obtaining quantitative recovery for these elements using the proposed microwave dissolution method. The silver values obtained in the study for CHR-Pt+ and CHR-Bkg can be valuable at the time of assigning certified values for silver for these standards.

Conclusions

This study demonstrates the effectiveness and utility of microwave digestion of "difficult to dissolve" samples such as chromites for subsequent estimation by a very high sensitive analytical technique such as ICP-MS. In addition, microwave dissolution unlike fusion dissolution gives sample solution with very low total dissolved solids suitable for ICP-MS analysis. The other advantages of microwave dissolution include yielding very low blank levels, use of relatively small amounts of acids and other reagents apart from allowing very fast sample dissolutions. This investigation of microwave dissolution followed by ICP-MS estimation

reveals that there is a good potential for the determination of high concentrations of Pd, Pt, Au and Ag with reasonable accuracy. The procedure can also be used for rapid dissolution of several other related rock types as well as for either exploration or for a comprehensive understanding of precious metal geochemistry of chromite ores or other ultramafic rocks. On the other hand the principal disadvantage of microwave digestion technique is that only small amounts of sample can be used which may not be representative of the sample very often.

ACKNOWLEDGEMENTS

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