

Research Article

Rapid Microwave Digestion Procedures for the Elemental Analysis of Alloy and Slag Samples of Smelted Ocean Bed Polymetallic Nodules

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The use of microwave digester for digestion of alloy and slag samples of smelted ocean bed polymetallic nodules has permitted the complete digestion of samples, thereby replacing the tedious classical methods of digestion of samples. The digestion procedure includes two acid-closed digestions of samples in a microwave oven. Owing to the hazardous nature of perchloric acid, it was not used in developed digestion procedure. Digested sample solutions were analyzed for concentrations of various radicals and the effectiveness of the developed digestion methodology was tested using certified reference materials. It was found that the developed method is giving results comparable with that obtained from conventionally digested samples. In this digestion procedure, time required for digestion of samples was reduced to about 1 hour only from 8-9 hours of conventional digestion.

1. Introduction

Ocean bed polymetallic nodules or manganese nodules found on the deep seafloor have been recognized as an alternate source for certain metals, when land deposits get exhausted. India is one of the eight pioneer investors in the world with exclusive rights over an area of 75,000 sq. Km in the Central Indian Ocean for the exploration and future exploitation of these mineral deposits [1]. These nodules contain metals like copper, nickel, cobalt, manganese, iron, lead, zinc, aluminum, and so forth [2]. Generally, these nodules contain a little over 2% of copper, nickel, and cobalt together, ~10% iron, 20% manganese and around 18% silica. Metal entities such as Cu, Ni, Co, Mo, and Zn are accommodated in the complex cage of iron and manganese hydroxides. Nickel and copper oxides are distributed and associated with the manganese oxide phase. Cobalt, present as cobaltic oxide, is associated with iron oxide phase [3]. Though manganese is the major element in ocean nodules, little attempt has been made on its extraction owing to

its extensive terrestrial deposits [4]. A significant amount of R&D efforts are in progress around the world towards developing schemes for extraction of valuable metals from these nodules [5, 6]. Initially, the extraction of only three metals, namely, nickel, copper and cobalt from manganese nodules was considered. After 1978, manganese extraction was added to improve the process economics and to reduce the amount of waste [3]. The technologies so far developed for extraction of valuable metals from manganese nodules are of two types: hydrometallurgical in which metals are leached from the nodules by acid or alkaline reagents, and pyrometallurgical, in which the hydroxides of metals are reduced and the melted metals are separated [2, 7, 8]. At National Metallurgical Laboratory (NML), Jamshedpur, India a pyro-hydrometallurgical route for recovery of valuables from manganese nodules is under development. In this process direct reduction smelting—matte formation—pressure leaching of manganese nodules samples were adopted. The process under development at NML, Jamshedpur for processing of manganese nodules consists of reduction roasting of nodules

followed by direct smelting of roasted nodules in an electric-arc furnace. In this process a manganese-rich slag and an iron-nickel-cobalt alloy are produced. From the alloy, the individual metals are recovered through matte formation and subsequent pressure dissolution of matte. It was reported in the literature that similar type of alloy can be used for recovery of individual metals and similar type of slag can be used for production of silicomanganese [9]. The alloy and slag obtained after electrothermal smelting of roasted manganese nodules are intermediate products in recovery process of valuable metals from manganese nodules. It is required to analyze the alloy and slag samples to ascertain the overall effectiveness of the roasting and smelting processes. With this, it is essential to know the radical concentrations in slag and alloy for further improvement and/or modification in extraction methodology. The alloy and slag samples are analyzed for radicals such as Si, Fe, Mn, Cu, Ni, Co, CaO, MgO, and Al₂O₃ using their appropriate methods of analysis. The wet chemical analysis by orthodox conventional method or by advanced instrumental methods needs sample in solution phase for analysis. Conventional wet sample preparation methods for the decomposition of solid samples are performed either with a reflux system or in a beaker on a laboratory hot plate. Common to both methods is the temperature limitations as a consequence of the boiling point of the solution used for digestion. The conventional digestion of alloy and slag samples of smelted manganese nodules is carried out using hydrochloric acid (HCl), nitric acid (HNO₃), and perchloric acid (HClO₄). Among these the fuming of perchloric acid itself takes 6-7 hours. So the digestion cannot be completed in a single working day. This poses serious problems for laboratories having high sample load. With this, the conventional digestion procedure is prone to many drawbacks such as long time requirement, high manpower input, high reagents consumption, and loss of volatile components during heating.

Recent development in the area of digestion technique resulted into a microwave digester. Microwave digestion technique is a closed vessel digestion technique, which utilizes the added advantage of elevated pressure for quick digestion of samples. As microwave heating is internal as well as external, the heat conduction stage is avoided because energy is instantly transferred to the sample by absorptive polarization rather than molecular collisions [10]. Use of microwave digester for sample preparation is gaining substantial important day by day. Many researchers used this method for sample preparation and validated the same [11–14]. Therefore, microwave-assisted closed vessel digestion was tried for alloy and slag samples of smelted manganese nodules. Our present study is focused on microwave digestion and subsequent analysis of digested samples. In our paper, we discussed the microwave digestion procedure for alloy and slag samples obtained during a new extraction process for smelted manganese nodules (under development at NML, India). The microwave digestion method developed during our study was validated using CRM. Developed microwave digestion procedure reduces the time of digestion from 8-9 h to about 1 h only and it substantially reduced the volume of acid required for digestion. In the developed

method, the use of perchloric acid for digestion was completely eliminated.

2. Experimental

2.1. Equipment and Materials. Ethos-1 (Milestone SRL, Italy) microwave digester was used for the digestion of smelted manganese nodules slag and alloy samples. The digester has TFM (tetrafluoromethoxil) vessels of 75 mL capacity. Maximum magnetron of digester is 1500 W and can be programmed according to desired temperature of digestion. Samples were digested in triplicate using three TFM vessels, out of which one is the control vessel having temperature and pressure measurement probes to control the digestion procedure. In forth vessel reagent blank was taken. The manganese nodule samples were received from National Centre for Antarctic and Ocean Research (NCAOR), Goa, India. The nodule samples were crushed and finally grounded to $-150\ \mu$ size. The grounded samples were mixed with desired amount of Low Diesel (LD) oil (reductant) and further milled/mixed for 40 minutes. This mixture was pelletized using disc pelletizer. The nodule pellets were air dried followed by oven drying at 100°C for 6 h. The oven dried pellets were roasted in a pot furnace at 750°C in argon atmosphere. The roasted nodules are then smelted in a 50 KVA electric arc furnace with coke and quartz. After smelting process a manganese-rich slag and an iron-nickel-cobalt alloy are produced. These are used for digestion studies.

2.2. Reagents. The chemicals and reagents used were of analytical reagent grade. HCl (35% m/v), HNO₃ (69% m/v) and HClO₄ (71–73% m/v) (all from Merck India) were used during digestion. Deionized water (Millipore System, USA) was used where required.

2.3. Certified Reference Materials. Certified reference materials were used in this paper: Ocean bed polymetallic nodules No. NML 2388, Manganese ore No. NML 66.2 and Ferrosilicon No. NML 31.2. (NML: National Metallurgical Laboratory, Jamshedpur, India).

2.4. Digestion Procedures. (i) *Choice of Acid.* In this developed protocol, we use nitric and hydrochloric acid. Nitric acid is a strong oxidizing agent widely used for liberating metals from various types of matrices as highly soluble nitrate salts. Hydrochloric acid is used for dissolution of samples as it preserves the metals in solution. The classical hot-plate dissolution of samples having a matrix similar to our samples requires perchloric acid dissolution with nitric and hydrochloric acid. However the perchloric acid handling requires great care. Combustible materials and most organic compounds contaminated with perchloric acid are highly flammable [11]. Perchloric acid particularly catches fire with easily oxidisable materials. Hence the use of perchloric acid was eliminated in this dissolution protocol.

(ii) *Conventional Digestion of Samples.* The smelted manganese nodules alloy and slag samples were grounded separately to $-75\ \mu$ size using agate-coated planetary ball mill.

TABLE 1: Conditions for Microwave digestion of samples.

Experiment Number	Sample weight (gram)	HCl (mL)	HNO ₃ (mL)	Power (Watt)	Temperature (°C)	Digestion time (minutes)	Ventilation time (minutes)
M ₁	0.1	16	2.00	500	150	90	30
M ₂	0.1	10	3.50	500	150	90	30
M ₃	0.1	16	2.00	500	150	40	10
M ₄	0.1	10	3.50	500	150	40	10

Note: M stands for Microwave digestion.

TABLE 2: Concentrations of radicals present in microwave and conventionally digested alloy samples.

S. No.	Detail of Experiment	Si (%)	Fe (%)	Mn (%)	Cu (%)	Ni (%)	Co (%)
1	M ₁	NF	62.60	4.63	12.30	15.82	1.18
2	M ₂	NF	62.67	4.60	12.40	15.69	1.18
3	M ₃	NF	62.63	4.68	12.40	15.65	1.22
4	M ₄	NF	62.50	4.49	12.48	15.66	1.26
5	C	NF	62.53	4.42	12.46	15.67	1.22

Note: NF : Not found.

TABLE 3: Concentrations of radicals present in microwave and conventionally digested slag samples.

S. No.	Detail of Experiment	SiO ₂ (%)	FeO (%)	MnO (%)	Al ₂ O ₃ (%)	MgO (%)	CaO (%)	Cu (%)	Ni (%)	Co (%)
1	M ₁	21.95	8.82	44.36	4.12	16.90	1.84	0.57	0.58	0.029
2	M ₂	21.86	8.89	44.30	4.02	16.99	2.07	0.56	0.63	0.025
3	M ₃	21.80	8.87	44.22	4.06	16.90	2.10	0.54	0.58	0.029
4	M ₄	21.92	8.83	44.20	4.20	17.03	1.98	0.56	0.65	0.030
5	C	21.95	8.90	44.25	4.08	17.02	2.06	0.58	0.62	0.028

Note: In both the Tables shown above, C stands for Conventional digestion. All concentrations are in %, w/w. All results are mean value of triplicate measurement.

TABLE 4: Mass balance of analysis of digested alloy and slag samples.

S. No.	Alloy sample		Slag sample	
	Exp. Detail	Mass balance (%)	Exp. Detail	Mass balance (%)
1	M ₁	96.53	M ₁	99.17
2	M ₂	96.54	M ₂	99.35
3	M ₃	96.58	M ₃	99.10
4	M ₄	96.39	M ₄	99.40
5	C	96.30	C	99.49

TABLE 5: Comparison of concentrations of radicals obtained in CRM digested by microwave digester and conventional method.

S. No.	Radicals	Certified Value	Microwave digested sample	Conventionally digested sample
1	SiO ₂ (%)	16.07	16.11	16.18
2	Fe (%)	14.94	15.00	15.07
3	Mn (%)	21.28	21.31	21.37
4	Al ₂ O ₃ (%)	1.65	1.64	1.63
5	Ca (%)	1.80	1.79	1.81
6	Cu (%)	0.49	0.49	0.49
7	Ni (%)	0.71	0.71	0.70
8	Co (%)	0.14	0.14	0.14

Note: All results are mean of triplicate measurement. All concentrations are % w/w.

TABLE 6: The Standard Deviations and Relative Standard Deviation of measurement for radical concentrations of microwave and conventionally digested CRMs.

S. No.	Radical	Microwave Digestion			Conventional Digestion		
		Mean Value (%) ($n = 3$)	SD	RSD (%)	Mean Value (%) ($n = 3$)	SD	RSD (%)
1	SiO ₂	16.11	0.01	0.06	16.18	0.01	0.06
2	Fe	15.00	0.02	0.13	15.07	0.02	0.13
3	Mn	21.31	0.03	0.14	21.37	0.01	0.05
4	Al ₂ O ₃	1.64	0.01	0.61	1.63	0.01	0.61
5	Ca	1.79	0.002	0.11	1.81	0.02	1.10
6	Cu	0.49	0.0002	0.04	0.49	0.002	0.4
7	Ni	0.71	0.0006	0.08	0.70	0.003	0.4
8	Co	0.14	0.0	—	0.14	0.0	—

About 100 g. of each sample was separated from main bulk by coning and quartering and used for digestion. For conventional digestion of samples, 0.5 g. sample, 40 mL 1 : 1 HCl, 10 mL HNO₃, and 10 mL HClO₄ was used. First of all 0.5 g. sample was mixed with 40 mL 1 : 1 HCl in a beaker and covered beaker was kept for digestion on a hot plate for about 1 h. at about 100°C. Then 10 mL concentrated HNO₃ was added and the whole content was boiled till evolution of nitrous fumes ceased (for about 30 minutes). Finally, 10 mL HClO₄ was mixed and the whole content of beaker was refluxed for 6-7 h. The content of beaker was extracted with 20 mL 1:1 HCl and filtered with 40 no. Whatman filter paper. The residue was used for estimation of silica gravimetrically. After silica estimation, this residue was fused with KHSO₄ and with the help of 20 mL 1 : 1 HCl, the fused mass was added to the filtrate obtained previously. The filtrate volume was made 250 mL by adding de ionized water. This filtrate was used for estimation of other radicals. All digestion experiments were carried out in triplicate with a reagent blank.

(iii) *Microwave Digestion of Samples.* For microwave digestion, samples were prepared in similar manner described earlier. Quantity of sample, reagent volumes, and digestion parameters used during microwave digestion are tabulated in Table 1. All microwave digestions were carried out in triplicate with a reagent blank. After digestion of samples, preparation of samples for analysis was done in similar manner as described in conventional digestion of samples.

(iv) *Analysis of Digested Samples.* Digested sample were analyzed for Si, Fe, Mn, Cu, Ni, and Co. For analyzing Cu, Ni, Fe, and Co, flame atomic absorption spectrometer (GBC Avanta, Australia) with air-acetylene flame was used [15]. Hollow cathode lamp (HCL) is used as source of light. Analysis of Cu, Ni, Co, and Fe is done at 327.4 nm, 341.5 nm, 240.7 nm, and 248.3 nm wavelength, respectively. Si is analyzed by gravimetric method [16–19]. Al₂O₃, CaO, and MgO are analysed by complexometric titration using EDTA [16–20]. Aluminum is complexed with EDTA by boiling with excess of reagent. The excess of reagent is back titrated with standard zinc acetate solution at pH 5 to 5.5 using xyenol orange indicator. A blank is also determined simultaneously and from the EDTA used up, Al₂O₃ is computed (IBM manual, 1979). CaO+MgO is determined by EDTA

complexometry using ammoniacal buffer in the presence of Eriochrome black-T indicator [17]. CaO alone was estimated using EDTA titration in presence of triethanolamine and potassium hydroxide using Patton and Reeder's indicator [17].

3. Results and Discussion

Total four sets of microwave digestion experiments were carried out for both alloy and slag samples with reagent blanks. These four sets of microwave digestion experiments were denoted by notation M₁, M₂, M₃, and M₄ for experiment 1, 2, 3, and 4, respectively (Table 1). The digested samples were analyzed for concentrations of desired radicals in triplicate. The alloy and slag samples were also digested by conventional route and analyzed for radical concentrations. These results of analysis for digested alloy samples are shown in Table 2. Similarly the results of analysis of digested slag samples are shown in Table 3.

Applying law of conservation of mass, the mass balance of analysis for all microwave and conventionally digested samples were prepared and shown in Table 4.

Addition of concentrations of all radicals for digested alloy sample is coming about 96%. Rest 4% are carbon and sulphur which we did not shown in this study. Addition of concentrations of all radicals for digested slag sample is coming about 99%. From mass balance calculation, it is clear that we succeeded to analyze the digested alloy and slag samples almost completely. From Table 4, it is also clear that the radical concentrations are almost same in all cases, regardless of the method of digestion used. However the most appropriate set of digestion conditions for microwave digester must possess lowest time and reagent volume requirement. On this criterion, the digestion conditions described at M₄ of Table 1 seem to be most promising. Taking in to account of low time of digestion and low reagent volume requirement, the digestion conditions described at M₄ of Table 1 was used to digest Certified Reference Materials (CRMs) in microwave digester. After digestion, the CRMs were analyzed for radical concentrations. The CRMs were also digested by conventional digestion procedure and analyzed separately. The results of analysis were depicted in Table 5.

TABLE 7: Detailed digestion conditions selected for digestion of samples in microwave digester.

Step	Power (W)	Time (minutes)	T ₁ (°C)	T ₂ (°C)	Pressure (bar)
1	500	5	100	80	10
2	500	10	110	90	10
3	500	25	150	100	10

Note: Ventilation time given = 10 minutes.

TABLE 8: Conventional digestion versus developed microwave digestion.

S. No.	Parameter	Conventional digestion	Microwave digestion
1	Sample weight	0.5 gram	0.1 gram
2	Acid requirement	40 ml 1 : 1 HCl, 10 mL HNO ₃ and 10 ml HClO ₄	10 mL HCl and 3.5 mL HNO ₃
3	HClO ₄ requirement	Yes	No
4	Digestion time	Total 8-9 h.	40 minutes digestion time and 10 minutes ventilation time required. Additional 20 minutes is required for loading & unloading of digestion vessels in digester. So, total time required is 1 h. 10 min.
5	Time required for analysis of radicals	Time requirement for analysis of radicals is same irrespective of method of digestion	

Statistical treatment was given to the results of analysis obtained for digested Certified Reference Materials. The standard deviations (SDs) and relative standard deviations (RSDs) of measurement are given in Table 6.

3.1. Dissolution Procedure Adopted. From Table 6, it appears that, the digestion conditions taken for microwave digestion of CRMs are giving satisfactory results. Here we use 0.1 g. sample, 10 mL HCl, and 3.5 mL HNO₃. Digestion temperature given was 150°C with 40 minutes digestion and 10 minutes ventilation time. The detailed digestion program used for M₄ is given in Table 7. For digesting the samples, three-staged increment of temperature was adopted. As per manufacturer's instruction, this is required for efficient and trouble-free working of microwave digester. In all steps, the magnetron power of microwave digester was fixed at 500 W, while time and temperature were increased progressively. In Table 7, T₁ is the main temperature of digestion vessel, while T₂ is the temperature of vessel surroundings. Pressure given for digestion represents the maximum permitted pressure for digestion, beyond which the digester will automatically stop the digestion procedure. However during digestion of samples, maximum pressure reached was only 3 bar.

Digestion conditions required for this developed protocol are compared with digestion conditions required for conventional digestion of samples. The same is tabulated in Table 8.

4. Conclusion

Sample digestion in pressurized TFM vessel using microwave heating proved to be a very rapid method for the complete digestion of alloy and slag samples of smelted manganese nodules as it drastically reduces the time and reagent requirements of digestion. Different combinations of HCl and HNO₃ were tried at different digestion temperature, however best

digestion was achieved with 10 mL HCl and 3.5 mL HNO₃. In microwave digestion experiments 0.1 gram of samples was used and the results of analysis of microwave digested samples are comparable with that of 0.5 gram samples digested via conventional route. The developed protocol was validated using CRM. The use of perchloric acid at high temperature and high pressure is hazardous due to its potentially explosive nature and hence the requirement of perchloric acid is completely eliminated in our digestion methodology.

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References

- [1] R. Sharma, "First nodule to first mine-site: development of deep-sea mineral resources from the Indian ocean," *Current Science*, vol. 99, no. 6, pp. 750–759, 2010.
- [2] Premchand and R. K. Jana, "Processing of polymetallic sea nodules: an overview," in *Proceedings of The 3rd Ocean Mining Symposium*, pp. 237–245, Goa, India, November 1999.
- [3] S. Agarwal, K. K. Sahu, R. K. Jana, and S. P. Mehrotra, "Recovery of Cu, Ni, Co and Mn from sea nodules by direct reduction smelting," in *Proceedings of The Eighth Ocean Mining Symposium*, pp. 131–136, Chennai, India, September 2009.
- [4] T. C. Alex, K. M. Godiwalla, S. Kumar, and R. K. Jana, "Extraction of silicomanganese from marine and low grade mineral resources," in *Proceedings of the Eleventh International Ferroalloy Congress (INFACON-XI '07)*, vol. 1, New Delhi, India, 2007.
- [5] D. Kmetova, M. Stofko, and S. Kmet, "Ammoniacal leaching for extraction of non-ferrous metals from deep-sea nodules,"

- International Journal of Mineral Processing*, vol. 15, no. 1-2, pp. 145–153, 1985.
- [6] Y. F. Shen, W. Y. Xue, W. Li, S. D. Li, and X. H. Liu, “Recovery of Mn^{2+} , Co^{2+} and Ni^{2+} from manganese nodules by redox leaching and solvent extraction,” *Transactions of Nonferrous Metals Society of China*, vol. 17, no. 5, pp. 1105–1111, 2007.
- [7] P. H. Cardwell, W. S. Kane, and J. A. Olander, “Separation of metals leached from ocean floor nodules,” in US Patent, 1976, 3, 894, 139.
- [8] R. K. Jana, “Leaching of sea nodules in acidic chloride- sulphide media,” *Transactions of The Institution of Mining and Metallurgy*, vol. 102, p. 191, 1993.
- [9] R. K. Jana, N. S. Randhawa, R. K. Minj, and K. M. Godiwalla, *National Seminar on Ploymetallic Nodules*, RRL, Bhubaneswar, India, 2005.
- [10] A. J. Kemp and C. J. Brown, “Microwave digestion of carbonate rock samples for chemical analysis,” *Analyst*, vol. 115, no. 9, pp. 1197–1199, 1990.
- [11] H. M. Kingston and L. B. Jassie, *Introduction to Microwave Sample Preparation. Theory and Practice*, ACS Professional Reference Book, American Chemical Society, Washington, DC, USA, 1988.
- [12] M. G. D. M. Tamba, R. Falciani, T. D. López, and A. G. Coedo, “One-step microwave digestion procedures for the determination of aluminium in steels and iron ores by inductively coupled plasma atomic emission spectrometry,” *The Analyst*, vol. 119, no. 9, pp. 2081–2085, 1994.
- [13] L. A. Fernando, W. D. Heavner, and C. C. Gabrielli, “Closed-vessel microwave dissolution and comprehensive analysis of steel by direct current plasma atomic emission spectrometry,” *Analytical Chemistry*, vol. 58, no. 2, pp. 511–512, 1986.
- [14] K. Smita, S. R. Ranjan, and K. Jayanta, *Electronic Waste*, 181, 2010.
- [15] S. Michael and B. W. Bernhard, *Atomic Absorption Spectrometry*, Wiley-VCH, Weinheim, Germany, 1999.
- [16] I. V. Arthur, *A Text Book of Quantitative Inorganic Analysis. The English Language Book Society and Longmans*, Green & Co., 3rd edition, 1961.
- [17] IBM Manual, *Manual of Procedures for Chemical and Instrumental Analysis of Ores, Minerals and Ore Dressing Products*, Controller, Indian Bureau of Mines (IBM), Nagpur, India, 1979.
- [18] L. B. Fisher, “Microwave dissolution of geologic material: application to isotope dilution analysis,” *Analytical Chemistry*, vol. 58, no. 1, pp. 261–263, 1986.
- [19] W. B. Scott, *Standard Methods of Chemical Analysis*, vol. 1, Technical Press, London, UK, 5th edition, 1939.
- [20] G. Schwarzenbach and H. Flaschka, *Complexometric Titrations*, Methuen, London, UK, 2nd edition, 1969, Translated by H. M. N. H. Irving.



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