Asian Journal of Chemistry; Vol. 27, No. 4 (2015), 1540-1542

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18795

Effect of Microwave Radiation on Wet Digestion of Rock-Sediment Samples and Comparison with Conventional Method

H.B. GUMGUM

Department of Physics, Faculty of Science, University of Dicle, 21280 Diyarbakir, Turkey

Corresponding author: Fax: +90 412 2488301; Tel: +90 412 2488274; E-mail: hbudakg@gmail.com

Received: 6 October 2014; *Accepted*: 11 November 2014; *Published online*: 4 February 2015; AJC-16832

The search for a rapid dissolution technique has lead several workers to investigate the use of a microwave oven as a heat source in a low temperature digestion system. In this study, three different copper ore samples from the Tigris river basin (Turkey) and the river sediment were digested by microwave radiation and recoveries of four elements (Co, Cu, Ni, Zn) were compared to those by the hot plate conventional method. The samples were digested with mixtures of hydrochloric acid, nitric acid and hydrofluoric acid. The concentrations of metal ions were determined by Perkin Elmer Optima 2100 DV inductively coupled plasma-optical emission spectrometry (ICP-OES). Analytic recoveries were equivalent to the standard hot plate method after a microwave digestion of only for few minutes.

Keywords: Copper ores, Determination, Digestion, Microwave, Heavy metal, Sediment.

INTRODUCTION

To obtain a suitable solution for instrumental element analysis of geological samples, conventional wet acid digestion procedures entail tedious and time and more chemicals consuming manipulations. The efficiency of the wet digestion procedures can be enhanced by using a microwave-heating system. Since its first introduction[1] microwave sample preparation has grown in sophistication and is now widely accepted. Proven advantages over traditional open beaker hot plate (conventional) techniques include reduced digestion time, elimination of environmental contamination, lower analytical blanks and improved recovery of volatile elements[2-7]. Conventional wet acid digestion procedures can require several hours or even several days to complete sample decomposition, while the same results were obtain in a few minutes by microwave wet acid digestion procedures.

In recent years, concern has increased over trace elements especially Co, Cu, Ni and Zn pollution and their geochemical problems. A number of review articles have been published detailing the use of microwave techniques for the heavy metal analysis[8-11]. In these reviews, details of the open and closed microwave digestion methods used to digest these samples, including the advantages and disadvantages of each technique were discussed and summarized the different microwave digestion procedures employed for biological, geological and water samples.

In this work, copper ores from Tigris river basin (Turkey) and Tigris river sediment samples were investigated (Fig. 1). There are four copper ore areas in the Tigris river basin *i.e.*, Maden, Hazro, Kulp and Sirvan ores. Maden ore is the most important of these because it is the oldest mine (Ergani Copper Plant). The environmental effects of the Maden copper ore was previously investigated[12-14]. The importance of pollution potential of copper mines are known[15]. A systematic exploration on the other ores has not yet been carried out and hence the reserve is not known and therefore the mines is being run on a primitive basis. Hazro and Kulp copper ores affect Batman stream and Sirvan copper ore can pollute Botan stream. The construction of Silvan dam over the Batman stream has not yet been completed and there is a project for a dam (Ilisu) construction on the lower side of the Tigris river. The heavy metal (Co, Cu, Ni and Zn) contents of these mines were determined to purpose a new project for the investigation of environmental effect of these copper mines on water and sediments of the Tigris river and its tributaries and biological samples.

Classic (conventional) and microwave dissolution techniques were applied to three different copper ores and Tigris river sediment samples and four heavy metals (Co, Cu, Ni, Zn) were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). For validation of the used methods a certified reference materials also used. The same procedures were applied to environmental matrix material (ERM-CC020) that is contaminated river sediment.

EXPERIMENTAL

Three different copper ore samples are taken *i.e.*, Hazro, Kulp and Sirvan copper ores and ground average particle size minus 100 mesh, were dried in air at 110 °C for 2 h. A 0.3-0.4 g portion of each sample was weighed into 100 mL Teflon beaker. All experiments were performed on three sets of sub-samples. Three different sediment samples were collected from the eastern side of Tigris river near Batman, Turkey. The samples were dried at room temperature and blended-homogenized as a new sample. The same procedure was applied to the sediment sample and a certified reference material, ERM-CC020 (contaminated river sediment). The different aliquots of concentrated HCl, HNO_3 and HF were added to each sample[13]. All the chemicals used were of analytical reagent grade.

Conventional decompositions are accomplished on a sandbox, using Teflon beakers, while microwave digestions were performed in a CEM MDS-2000 microwave oven, using pressure-resistant teflon vessels.

Concentrations of heavy metals Co, Cu, Ni, Zn were determined by a Perkin Elmer Optima 2100 DV inductively coupled plasma-optical emission spectrometry at the wavelengths (nm) of Co 228.616; Cu 234.754; Ni 221.647; Zn 213.856 (Table-1).

TABLE-1
OPERATING CONDITIONS OF ICP-OES

RF power (W)	1450
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	0.2
Nebulizer gas flow rate (L min^{-1})	0.8
Sample flow rate (L min^{-1})	1.5
View mode	Axial
Read	Peak area
Source equilibration time (s)	15
Replicates	3
Detector	CCD
Purge gas	Nitrogen
Shear gas	Air
Gas	Argon
Wavelengths (nm)	
Co 228.616; Cu 234.754; Ni 221.647; Zn 213.856	

Conventional sample preparation procedure: The samples weighed into 100 mL Teflon beakers are treated with various mixtures of acids (HCl-HNO_3-HF). After many attempts on different mixtures of these acids, 15 mL of aqua regia and 5 mL of concentrated HF were used for conventional sample decomposition. Teflon beakers which contain the samples and acids were heated near to dryness on a sandbox. The same heating process was repeated with 5 mL of aqua regia, to complete dissolution and removing residual HF. After addition of 5 mL of hot HCl (1 %), the filtered leachates were transferred into 50 mL of calibrated flasks and after cooling, diluted to volume with distilled water. The average of the analysis results is shown in Table-2.

Microwave sample preparation procedure: Various mixtures of acids added samples weighed into Teflon vessels and the vessels were placed inside the microwave oven (CEM MDS 2000), then different microwave heating programmes were applied. Our observations showed that using 5 mL of aqua regia and 2 mL of HF was given suitable results for microwave digestion of copper ores. After many experiments involved changing; power, pressure and time, a satisfactory programme were established[13,14]. Microwave digestion parameters for the investigated samples; power (%) 30-40, pressure (%) 40-50 and time (min) > 5 were applied.

A mixture of 5 mL of aqua regia and 2 mL of HF were added to the samples and left for 5-10 min to remove excess gases and after setting microwave oven parameters (Power (%): 30, pressure (%): 40 and time (min): 5), microwave digestion were performed. After cooling, the Teflon vessels were heated to dryness on a sandbox for removing HF. 5 mL of hot HCl (1 %) were added and the filtered leachates were transferred into 50 mL calibrated flask and diluted to volume with distilled water.

RESULTS AND DISCUSSION

Hazro copper ore: Average copper contents were found 3.32 % for conventional decomposition and 3.26 % for microwave digestion, with a recovery of 98.19 %. Cobalt contents were found 5.20 and 4.92 ppm, respectively. The concentrations of Ni and Zn were found 620 and 433 ppm in the conventional heating and 605 and 425 ppm in the microwave digestion with the recoveries of 97.58 and 98.15 %, respectively.

Kulp copper ore: It can be seen from the Table-2 that, according to the results of conventional heating, this ore contains 42.90 % copper. This value was found 41.68 % Cu with a recovery of 97.16 % as an average of applications of seven different microwave heating conditions. The cobalt content that found 1251 ppm by conventional heating can be accepted average 1170 ppm for seven microwave digestions. The conventional 1462 ppm Ni values were found average 1376 ppm by microwave techniques and zinc values were found 2451 and 2377 ppm for conventional and microwave applications, respectively.

Sirvan copper ore: Table-2 shows that this ore has the lowest copper and nickel contents while zinc has the highest one. The concentration of cobalt takes place between Hazro and Kulp ores.

Although the samples were different, the results were in accordance with those found in literature[16,17] as can be seen from Table-2. A good agreement between conventional values and microwave results were obtained for copper ores investigated and all of the results shows that, a few minutes of microwave heating are suitable for copper ore decomposition while 5-6 h required for conventional procedures.

Tigris river sediment: It can be seen from Table-2 that there are a good agreement between recoveries of heavy metals in the Tigris river sediment and certified reference material sample. The recovery differences between Cu, Co, Ni and Zn are 0.76; 2.17; 0.37 and 1.35, respectively.

Conclusion

Concentrations of heavy metals Co, Cu, Ni and Zn in different samples were determined using microwave radiation and conventional digestion procedures with ICP-OES analysis and recoveries were calculated by equation (Microwave concentrations/Conventional concentrations) × 100. Acceptable and

TABLE-2
ANALYTICAL RESULTS OBTAINED FROM COPPER ORES AND TIGRIS RIVER SEDIMENT[†]

Samples	Digestion methods		Recovery (%)[*]
	Conventional	Microwave	
Hazro copper ore			
Cu (%)	3.32 ± 0.11	3.26 ± 0.12	98.19
Co (mg kg^{-1})	5.20 ± 0.15	4.92 ± 0.20	94.62
Ni (mg kg^{-1})	620 ± 33	605 ± 24	97.58
Zn (mg kg^{-1})	433 ± 27	425 ± 30	98.15
Kulp copper ore			
Cu (%)	42.90 ± 1.26	41.68 ± 1.31	97.16
Co (mg kg^{-1})	1251 ± 110	1170 ± 106	93.53
Ni (mg kg^{-1})	1462 ± 82	1376 ± 71	94.12
Zn (mg kg^{-1})	2451 ± 196	2377 ± 214	96.98
Sirvan copper ore			
Cu (%)	1.13 ± 0.03	1.11 ± 0.04	98.23
Co (mg kg^{-1})	223 ± 17	215 ± 19	96.41
Ni (mg kg^{-1})	356 ± 23	341 ± 26	95.79
Zn (mg kg^{-1})	3580 ± 205	3571 ± 231	99.75
Tigris river sediment			
Cu (mg kg^{-1})	735.86 ± 13.25	726.18 ± 15.24	98.68
Co (mg kg^{-1})	35.12 ± 1.18	33.88 ± 1.53	96.45
Ni (mg kg^{-1})	68.55 ± 4.21	66.02 ± 3.18	96.31
Zn (mg kg^{-1})	390.23 ± 15.36	381.27 ± 12.11	97.70
ERM-CC020 (found)			
Cu (mg kg^{-1})	557.24 ± 14.12	554.13 ± 13.34	99.44
Co (mg kg^{-1})	31.92 ± 1.22	31.48 ± 2.42	98.62
Ni (mg kg^{-1})	153.15 ± 3.31	148.06 ± 2.15	96.68
Zn (mg kg^{-1})	2012.26 ± 12.37	1993.13 ± 13.21	99.05
ERM-CC020 (certified, mg kg^{-1}): Cu 560 ± 11; Co 32.8 ± 1.5; Ni 158 ± 6; Zn 2030 ± 40			

[†]Heavy metal (concentration ± standard deviation)
[*]Recoveries were calculated (Microwave/conventional concentrations) × 100

good recovery results were found in both sample decomposition systems.

REFERENCES

1. A. Abu-Samra, J.S. Morris and S.R. Koirtyohann, *Anal. Chem*., **47**, 1475 (1975).
2. R.A. Nadkarni, *Anal. Chem*., **56**, 2233 (1984).
3. L.B. Fischer, *Anal. Chem*., **58**, 261 (1986).
4. P.J. Lamothe, T.L. Fries and J.J. Consul, *Anal. Chem*., **58**, 1881 (1986).
5. M. Bettinelli, U. Baroni and N. Pastorelli, *Anal. Chim. Acta*, **225**, 159 (1989).
6. M. Achilli, R. Barban, B. Zucchi and W. Martinotti, *Water Air Soil Pollut*., **57-58**, 495 (1991).
7. M.K. Wong, W. Gu and T.L. Ng, *Anal. Sci*., **13(Suppl.)**, 97 (1997).
8. A. Zlotorzynski, *Crit. Rev. Anal. Chem*., **25**, 43 (1995).
9. F.E. Smith and E.A. Arsenault, *Talanta*, **43**, 1207 (1996).
10. K.J. Lamble and S.J. Hill, *Analyst*, **123**, 103 (1998).
11. Q.H. Jin, F. Liang, H.Q. Zhang, L.W. Zhao, Y.F. Huan and D.Q. Song, *Trends Analyt. Chem*., **18**, 479 (1999).
12. E. Ünlü and B. Gümgüm, *Chemosphere*, **26**, 2055 (1993).
13. B. Gümgüm, E. Ünlü, Z. Tez and Z. Gülsün, *Chemosphere*, **29**, 111 (1994).
14. B. Gümgüm and G. Öztürk, *Chem. Spec. Bioavail*., **13**, 25 (2001).
15. M. Arias, A. Nunez, M.T. Barral and F. Diaz-Fierros, *Sci. Total Environ*., **221**, 111 (1998).
16. D. McGrath, *Talanta*, **46**, 439 (1998).
17. M. Al-Harahsheh, S. Kingman, C. Somerfield and F. Ababneh, *Anal. Chim. Acta*, **638**, 101 (2009).