Analysis of Geochemical Samples by Microwave Plasma-AES

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ABSTRACT

Accurate and reliable analytical techniques and methodologies possessing high sensitivity and selectivity, coupled with convenience and economy and applicable to real-world situations, are required for geochemical studies. Quantitative analysis of major, minor, and some trace elements were performed in several geochemical reference samples using a new microwave plasma-atomic emission spectrometry (MP-AES) technique. A range of rock, soil, sediment, and water reference materials were chosen to evaluate the performance of this technique. A set of sample decomposition/digestion methods, which included a closed digestion technique utilizing a multi-acid mixture in a closed vessel and a fusion digestion technique utilizing lithium meta-borate in a glassy carbon crucible, were used for the determination of all major and minor elements in addition to Si, and more than 15 trace elements in sample

solutions at the ng/g and sub-ng/g levels. Matrix interference effects encountered from concomitant elements, acid type and concentration, calibration strategies adopted, detection limits, accuracy and precision obtained were discussed. The analytical wavelengths selected were based on sensitivity and interference effects from other concomitant elements present in different sample solutions.

The detection limits for several elements were found to be in the 0.05 to 5 ng/g range, which approached those of an ICP-AES technique but were much superior to flame AAS. Precisions of $\leq 3\%$ RSD were obtained for major and minor elements and $\leq 6\%$ RSD for trace elements with comparable accuracies for most determinations. The results obtained in this study clearly indicate that MP-AES is a suitable atomic emission spectrometry technique for the accurate determination of major, minor, and selected trace elements required in geochemical studies.

tal analytical techniques. The past seven decades have seen a succession of advanced instrumental analytical techniques for chemical analysis particularly in the fields of geology, industry, agriculture, and the environment. Some of these are (a) flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS), (b) X-ray fluorescence spectrometry (XRF), (c) instrumental neutron activation analysis (INAA), (d) inductively coupled plasma atomic emission spectrometry (ICP-AES), (e) inductively coupled plasma mass spectrometry (ICP-MS), (f) inductively coupled plasma time of flight mass spectrometry (ICP-TOF-MS), and (g) sector field or high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS), most of which have the capability to carry out rapid multi-element/isotopic analysis at and below ng/g levels (1-8).

The recently introduced microwave plasma atomic emission spectrometry (MP-AES) represents yet another very important addition to this array of analytical techniques (9). Microwave-induced plasma (MIP) has received considerable attention during the past three decades as an alternative powerful excitation source (10-16). Different gases such as hydrogen, argon, helium, neon, nitrogen, and even combinations of some of these gases were successfully utilized for producing microwave plasmas. In this direction, Hammer (9) developed a novel magnetically excited MIP emission source. Unlike previous MIP sources, which coupled energy from the microwave electric

INTRODUCTION

Scientific and technological revolutions are always very closely associated with either a new material or a new investigating analytical tool. Among these two, perhaps the analytical instrument plays a dominant role since an analytical tool is ultimately the key to characterizing the materials. In addition, the rapid and constant developments of human activities have

increased the need for chemical characterization of different materials for their major, minor, trace and ultra-trace constituents. It enables important decisions to be made daily in varied fields, such as science, technology, industry, trade, environment, health, economy, and legal affairs. In earth science studies including mineral exploration, several earth materials, such as rocks, ores, soils, sediments and water, have to be analyzed for their major, minor, and trace constituents using different instrumen-

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field, this source coupled energy from the magnetic field. The resultant plasma shape allowed easy entrainment of wet sample aerosol into the core of the plasma, such as was produced by a conventional ICP nebulizer and spray chamber. In our earlier studies (17), this technique was utilized for the generation of precise data of precious metals, gold, silver, platinum, and palladium in some rock and ore materials for mineral exploration studies. In this study, an attempt is made to summarize the performance characteristics of MP-AES and its potential as an analytical tool in geochemical studies with some practical examples from this area.

EXPERIMENTAL

Instrumentation

The Agilent® 4100 MP-AES instrument was used in these studies (Agilent Technologies, USA). This is a fast sequential multi-element analytical instrument using a microwave excitation assembly to create a concentrated axial magnetic field around a conventional torch. This focuses and contains the microwave energy where it is needed to produce toroidal plasma with a cooler central channel which is suitable for stable introduction of liquid samples with a conventional sample introduction system. More details of the MP atomic source, optical system and detector of the instrument, are provided elsewhere (9). The emission intensities for different elements studied depends on gas flow, sample flow rate, and microwave power. The plasma gas flow, nebulizer gas flow, observation height, and other operating parameters were optimized for obtaining higher stability of the plasma and maximum emission intensity. The optimum operating parameters and other instrumental details such as the optical resolution of the instrument are presented in Table I.

Principle

The basic aim of any analytical atomic spectroscopy technique is to identify elements and quantify their concentrations in different kinds of materials. The principle of this technique is similar to any other emission technique such as

flame emission or the well-known ICP-AES. The intensity of each emitted line will be directly proportional to the concentration of a particular element. Few steps are involved in this procedure such as sample introduction into the high temperature source, atom formation, excitation and emission,

TABLE I
Operating Parameters of MP-AES

Instrumentation	Agilent 4100 Microwave Plasma AES with 4107 Nitrogen Generator
Plasma Conditions	
Plasma Gas	N ₂ by using both Air Compressor and N ₂ Generator (air compressor feeds the air to the N ₂ generator) Alternately, N ₂ gas cylinder or liquid N ₂ Dewar can also be used
Power of Magnetron Output	1 kW
Gas Flows	
Plasma Gas Flow-Nitrogen	20 L/min
Intermediate Flow-Nitrogen	1.1 L/min
Pre-optics Protection (POP) Gas -Air	25 L/min
Nebulizer Pressure	140–240 kPa (Optimize each group of elements)
Nebulizer	OneNeb™ inert concentric for HF and high TDS solutions
Spray Chamber	Double-pass glass cyclonic
Solution Uptake	1.4 mL/min (pumped)
Pump Tubing	1.02 mm i.d. PVC
Plasma Torch	Quartz torch
Plasma Viewing	Axial
Data Acquisition Parameters	
Sample Uptake Delay	8 s
Stabilization Time	15 s
Read Time	5 s
No. of Replicates	3
Background Correction	Auto or FLIC (Fast Linear Interference Correction)
Optical System	Czerny-Turner monochromator with 600 mm focal length and fixed entrance slit
Optical Resolution	< 0.050 nm (measured as full width at half maximum).
Detector	Back thinned solid state CCD detector (532 x 128 pixels)
Analytes (Wavelengths)	Data as shown in Tables III to VI

measurement of the emitted light intensity of a particular element of interest at a specified wavelength, and computation of the concentration by comparing it with that of a known concentration. MP-AES also involves the measurement of electromagnetic radiation emitted from the atoms (Figure 1). Liquid and gas samples may be injected directly into the instrument, while solid samples require samples to be in solution form. The sample solution is converted to an aerosol and directed into the central channel of the plasma. A schematic diagram of the principle of MP-AES is shown in Figure 1. More details are provided by Hammer (9).

Geological and Environmental Reference Materials Used

A range of geological and environmental materials (Table II) were utilized to study and understand the potential of this technique for geochemical and environmental applications.

Sample Decomposition Methods

For Major, Minor, and Trace Elements in Rocks, Soils, and Sediments

A 0.5 g sample was digested in a closed Savillex vessel (Savillex Corporation, USA) with 20 mL HF:HNO₃:HClO₄:HCl (7:3:1:1) and kept on a hot plate at 1300 °C for 30 hours (to ensure 100% dissolu-

tion). Finally, the vessels were opened, the acid content was evaporated to near dryness, the residue dissolved in 10 mL of 1:1 nitric acid, and the final volume made up to 100 mL (5% acid solution) with Millipore® Milli-Q™ water (18 MΩ), then stored in 60-mL bottles as described by Balaram et al. (18). All samples studied in this investigation yielded clear solutions.

Fusion Decomposition Method

A 0.1 g sample and 0.5 g lithium metaborate were weighed, mixed thoroughly, transferred into a glassy carbon crucible (10 mL), and fused at 1050 °C for 30 minutes in a muffle furnace. The crucible was cooled and the separated bead transferred into a beaker with 25 mL of 10% HNO₃ solution. The solution was continuously stirred with a magnetic stirrer for about 20 minutes for complete dissolution of the bead. The solutions were made up to 100 mL with Millipore water (18 MΩ) and filtered to remove any suspended carbon particles, then stored in 60-mL polyethene bottles. More details on the fusion sample preparation are provided by Roy et al. (19).

Analysis

During the analysis, the nebulizer system was washed with 1% HNO₃ and Millipore water for 40 seconds. The data on each sample were acquired after 60 seconds of nebulization to stabilize the plasma. Procedural blanks, calibration, sample and reference sample solutions were analyzed in that order.

RESULTS AND DISCUSSION

In recent years, MP-AES has slowly been emerging as one of the most powerful and popular analytical tools for the analysis of different materials. As already described, this technique is also based on the spontaneous emission of photons from atoms and ions that have been excited in magnetically excited microwave nitrogen

Fig. 1. Schematic diagram explains the principle of microwave plasma atomic emission spectrometry (MP-AES). Instrument used is also shown.

TABLE II
Details of Geological and Environmental Reference Materials Used in This Study

S. No.	Sample	Rock Type	Source
1	MRG-1	Gabbro	CCRMP-CANMET-MMSL (NRCan), Ottawa, ON, Canada
2	SY-2	Syenite	CCRMP-CANMET-MMSL (NRCan)
3	SO-1	Soil	CCRMP-CANMET-MMSL (NRCan)
4	SARM-39	Kimberlite	MINTEK, Randburg, Republic of South Africa
5	JLK-1	Lake Sediment	Geological Survey of Japan, Tsukuba, Ibaraki, Japan
6	JSD-1	Stream Sediment	Geological Survey of Japan
7	JG-2	Granite	Geological Survey of Japan
8	BHVO-1	Basalt	United States Geological Survey, Denver, CO, USA

plasma (20). All commonly used analytical atomic emission techniques in general suffer from various kinds of interferences and MP-AES is no exception. But MP-AES has relatively less interferences. The nitrogen plasma is inert when compared to the chemical reactivity of various other flames used, particularly in atomic absorption spectrometry. Also the high temperature of the microwave plasma helps to reduce chemical interferences. The temperature is high enough to break down most species into atoms or ions for excitation and subsequent emission.

Effect of Major and Minor Element Concentrations on the Signals of Trace Elements

The vast majority of crustal rocks contain about 10 major and minor elements, namely (in decreasing order of abundance) Si, Al, Fe, Ca, Na, K, Mg, Mn, Ti, Fe, Ca, Mg, Na, K, Mn, and P. Very high concentrations of these elements will have enhancement/suppression (matrix) effects on the signals of various trace elements. In order to understand these effects in MP-AES, a systematic study was carried out and the results are presented in Figure 2. A few trace elements (Bi, Tb, Sc, Y, In, Cu, Co, Mo, and Li) across the periodic table were selected and the effects of different major and minor elements on each trace element were studied. The concentration of different trace elements was kept at 2 µg/mL and the concentrations of various major and minor elements were varied from 25 to 500 µg/mL. These are the concentrations of the elements normally encountered in real rock sample solutions (after the required dilutions) used for chemical analysis. The effect of Si was not studied since most rock decomposition procedures involve elimination of Si by adding HF. From the results presented in Figure 2 it is evident

that alkali and alkaline earth elements showed severe enhancement effects in general on the MP-AES signals of different trace elements as these easily ionizable elements can improve vaporization and atomization conditions in the plasma. Aluminum, iron, titanium, and manganese also behaved in a similar way. The enhancement effects are also increasing with the concentrations of different major and minor elements. Phosphorous is an exception since its concentration generally has very little effect on the signals of different trace elements. These results indicate that the major and minor element concentrations will have enhancing effects on the signals of different trace elements and it is very difficult to quantify these effects on a particular trace element or a set of trace elements. The matrix effects in high-power nitrogen MIP were extensively studied by Zhang and Wagatsuma (21) under a variety of conditions. Based on the matrix effects, and the results of the excitation temperature and the electron number density measurements, it was concluded that the effects of Na and Ca were primarily attributed to the shift in the atom/ion ionization equilibrium resulting from a decrease in plasma temperature and an increase in electron number density. Similar effects were also noticed in the analysis of geological materials by ICP-MS recently (22)

Effect of Acid Concentration on the Signals of Trace Elements

The effect of acid concentration on the signals of some elements was also studied and the results are presented in Figure 3. These studies were carried out on 2 µg/mL multi-element solution (Li, Na, Ba, Cr, Ni, Mn, B, Fe, Ga, Bi, Zn, In, Mg, Cd, Ca, Sr, Cu, Ag, Co, Tl, Al, K, Pb) prepared in different acid concentrations (1 – 10%). Some interesting observations were made. Up to about 5% HNO₃ concentration,

there is no effect on the signals for the different elements. Above 5% HNO₃ concentration, there is a slight enhancing effect, and afterwards a gentle depression in the signal was observed for the majority of the elements. On the other hand, the HCl and HClO₄ concentrations show a slight enhancement effect with an increase in the acid concentration on the signals of all elements studied. H₃PO₄ has a slight depressing effect on the signals of several elements with an increase in acid concentration. It is possible that anions such as SO₄²⁻ and PO₄³⁻ will react with analytes to produce a species of low volatility in the plasma and this can significantly reduce ion/atom population of the analytes. As a result, there will be depression in the signals of the analytes. The effect of H₂SO₄ was not studied as it was causing precipitations when added to the multi-element solution. These studies indicated that HNO₃ is the best acid for use in sample preparations for MP-AES work.

Calibration Strategies and Linearity of Calibration Curves

One of the major considerations in any analytical spectroscopy is the method of calibration. In general, all the acids studied here have shown considerable influence on the signals of the individual elements. The effects related to acid concentrations can only be minimized and not totally eliminated as the acid concentration can be controlled during the sample preparation as well as the analysis. On the other hand, there is no control on the concentrations of different major and minor elements in individual sample solutions. Hence, it will be difficult to eliminate these interference effects. In order to overcome these types of matrix effects generally observed during the analysis of geological samples, several methods can be used. Use of identically prepared matrix

Fig. 2. Effect of concomitant (matrix) elements on the MP-AES signals of some elements.

Fig. 3. Effect of acid concentration on the MP-AES signals of some elements.

matching certified reference materials (CRMs) for calibration is one of the ways to minimize the matrix interferences as described above and to obtain reasonably accurate data in geochemical studies. This study also suggests that the major and minor element composition of the CRMs used for calibration and the sample must match as closely as possible. A few CRMs should also be analyzed as control samples to monitor the accuracy of the determinations. This is a convenient and safe approach, especially when a few other reference materials are being analyzed as unknowns, although it is difficult to obtain

more than one rock certified reference material (CRM) of the same chemical composition.

It has been observed that MP-AES calibration curves are in general linear over four orders of magnitude for several elements. Figure 4a presents calibration curves for the elements In and Bi which are linear for a wide range of concentrations. A similar calibration curve obtained for Co is not very much linear. It may be a good idea to use the most sensitive wavelengths for determining very low concentrations and the other wavelengths for the determination of different elements at appropriate

higher concentration levels (Figure 4b). The analytical wavelengths for different elements in this study were selected by considering the sensitivity and the interference effects from other concomitant elements present in different sample solutions. Earlier studies (17) have also indicated that MP-AES provides good linear calibrations for elements such as Au and Ag; hence, a single calibration standard is sufficient for the accurate measurement of trace and ultra-trace elements in geological materials. In this study, the instrument was calibrated with SO-1 for the analysis of soils and sediments; SY-2 was used for cali-

Fig. 4a. Calibration curves for few elements at different wavelengths in MP-AES.

Fig. 4b. Calibration curves for several elements at different wavelengths in MP-AES.
 Zn (213.857 nm) and Zn (481.053 nm).
 Cu (324.754 nm) and Cu (578.213 nm).
 Fe (259.940 nm) and Fe (440.475 nm).

bration for the analysis of rock samples, and the NIST 1640a reference water sample for water analysis (National Institute of Standards and Technology, Gaithersburg, MD, USA). Figures 5a and 5b are the sin-

gle-point calibration curves obtained for some elements by using SY-2 and SO-1. As discussed earlier, this is a safe approach particularly when some international reference materials with known

values for different elements are also analyzed as unknowns. Concentrations (wt% or $\mu\text{g/g}$ or ng/mL) of the elements were measured in the sample solutions after applying blank corrections.

(a) Calibration curves using SY-2

(b) Calibration curves using SY-2

Fig. 5a and b. Several practical examples of calibration curves used for obtaining concentrations of different elements in rock, soil and sediment reference material samples in this study.

Analytical Performance in the Analysis of Geochemical Samples

Most of the rocks are made up of SiO₂, Al₂O₃, Fe₂O₃, FeO, MnO, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅, and H₂O. Several other elements such as Cu, Co, Li, Rb, Sr, and U are present at extremely low concentration levels and they are trace elements. These major, minor, and trace element concentrations reveal different primary and secondary processes that these rocks have undergone (23). Therefore, accurate determination of these compositions is necessary to develop and refine models for different physico-

chemical processes operating through time and space.

In order to understand the potential of MP-AES in geochemistry, a variety of international geological reference materials comprised of basalt, gabbro, kimberlite, soil, stream and lake sediment were analyzed by MP-AES after the samples were digested by a well-tested closed sample decomposition procedure (18). Geochemical data of major, minor, and trace elements as listed in Tables III and Table IV reveal that there is very close agreement with the data obtained in this study and the reported values. These data also show that the preci-

sion obtained for major and minor elements was ≤3% RSD with comparable accuracy. The determinations were carried out at more than one wavelength for certain elements such as aluminum, manganese, and potassium. The data obtained at different wavelengths also very closely agree for different elements showing that these elements can be determined at all of these wavelengths and are accurate. Some geochemically important trace elements (Zn, Be, Ta, Nb, Cu, Hf, Zr, Ni, Sc, Mo, Pb, Sr, Ga, Cr, Ba, Li, and Rb) were also determined with a precision of ≤6% RSD and the data (Table V) compare very well with the certified values.

TABLE III
Major and Minor Oxide Data (wt %) in International Geochemical Reference Materials
Obtained by MP-AES in Comparison With Certified Values

Sample	P2O5		Al2O3		MnO		MgO		TiO2		Al2O3		Al2O3	
	213.618 nm		237.312 nm		257.610 nm		279.077 nm		307.523 nm		308.215 nm		309.271 nm	
	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value
MRG-1	0.07	0.08	8.54	8.47	0.18	0.17	13.67	13.55	3.67	3.77	8.55	8.47	8.80	8.47
SARM-39	1.43	1.46	4.22	4.29	0.16	0.17	26.12	26.24	1.41	1.58	3.97	4.29	4.24	4.29
JLK-1	0.27	0.26	16.79	16.86	0.23	0.27	1.76	1.76	0.68	0.67	16.99	16.86	16.33	16.86
JSD-1	0.10	0.12	14.78	14.66	0.11	0.09	1.86	1.85	0.66	0.65	13.93	14.66	14.22	14.66
SO-1	0.18	0.15	17.61	17.59	0.14	0.11	3.89	3.83	0.85	0.87	18.21	17.59	17.11	17.59
JG-2	0.01	0.01	11.99	12.41	0.04	0.02	0.05	0.04	0.06	0.04	12.33	12.41	12.44	12.41
BHVO-1	0.28	0.27	14.11	13.80	0.02	0.02	7.25	7.23	2.55	2.71	13.89	13.80	13.81	13.80
Sample	Fe2O3		MnO		CaO		Fe2O3		Na2O		K2O		K2O	
	400.524 nm		403.307 nm		429.899 nm		440.475 nm		568.263 nm		766.491 nm		769.897 nm	
	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value	This Study	*Reference Value
MRG-1	18.65	17.94	0.15	0.17	13.20	14.70	18.15	17.94	0.77	0.74	0.23	0.18	0.20	0.18
SARM-39	9.25	9.29	0.16	0.17	9.25	9.69	8.90	9.29	0.54	0.50	1.10	1.04	1.10	1.04
JLK-1	6.94	6.84	0.27	0.27	0.71	0.68	6.55	6.84	0.96	1.00	2.74	2.77	2.74	2.77
JSD-1	4.99	5.11	0.09	0.09	2.98	3.07	4.86	5.11	2.47	2.73	2.26	2.19	2.17	2.19
SO-1	8.23	8.58	0.11	0.11	2.32	2.46	8.28	8.58	2.56	2.70	3.16	3.18	3.08	3.18
JG-2	0.89	0.92	0.02	0.02	0.79	0.80	0.86	0.92	3.51	3.55	4.44	4.72	4.55	4.72
BHVO-1	12.63	12.23	0.17	0.17	11.24	11.40	12.40	12.23	2.27	2.26	0.65	0.52	0.59	0.52

SY-2 was used for calibration.

* (26). n = 6, Precisions ≤3% RSD.

TABLE IV
Concentrations ($\mu\text{g/g}$) of Selected Trace Elements in Some International Geological Reference Materials Obtained by MP-AES in Comparison With Recommended Values

Element	Wavelength	MRG-1		SARM-39		JLK-1		JSD-1		SO-1		JG-2		BHVO-1	
		This Study	RV	This Study	RV	This Study	RV	This Study	RV	This Study	RV	This Study	RV	This Study	RV
Zn	213.857 nm	204.08	191	74.71	70	159.64	151	105.86	99	146.65	144	12.39	12.7	109.03	105
Be	234.861 nm	ND		ND		ND		1.61	1.3	2.01	1.98	2.51	2.5	ND	
Ta	268.517 nm	ND		ND		ND		ND		ND		1.87	1.9	1.55	1.23
Nb	309.418 nm	21.77	20	ND		ND		ND		ND		18.22	15	20.1	19
Cu	324.754 nm	141.66	134	60.69	58	ND		14.58	22	55.99	61	ND		150.54	136
Hf	339.980 nm	3.74	3.76	ND		ND		ND		ND		4.38	4.7	11.41	4.38
Zr	343.823 nm	111.76	108	234.83	239	151	146	ND		82.49	84	97.01	101	177.27	179
Ni	352.454 nm	ND		ND		ND		7.51	6.9	ND		1.4	2.1	ND	
Sc	361.383 nm	ND		ND		ND		ND		ND		3.08	2.47	ND	
Mo	379.825 nm	1.07	0.87	5.61	5	ND		ND		ND		0.12	0.23	1.66	1.02
Pb	405.781 nm	ND		ND		47.02	45	ND		22.87	20	34.88	32.8	ND	
Sr	407.771 nm	267.67	266	1388.8	1400	67.46	69	287.26	323	315.48	331	14.63	16	393.67	403
Ga	417.204 nm	15.97	17	24.61	10	ND		ND		30.33	24.1	14.03	18.6	23.44	21
Cr	425.433 nm	422.93	430.59	1278.9	1300	64.41	69	19.21	22	174.39	170	7.29	7.6	275.7	289
Ba	455.403 nm	57.08	61	1677.8	1700	ND		ND		850.57	870	56.31	67	122.58	139
Li	670.784 nm	4.88	4.2	ND		49.59	54.7	26.83	24.2	45.28	48	42.55	43.4	4.63	4.6
Rb	780.027 nm	10.6	8.5	48.53	52	137.91	144	66.79	65	133.84	141	303.11	297	12.55	11

ND = not determined. *(26) Precisions $\leq 6\%$ RSD. n = 6

TABLE V
MP-AES Results (wt%) of Some Major and Minor Elemental Oxides in International Geological and Environmental Reference Materials Following the Lithium Meta-borate Fusion Sample Digestion Procedure in Comparison With Certified Data

Sample	Al ₂ O ₃		TiO ₂		Fe ₂ O ₃		MnO		K ₂ O		SiO ₂	
	237.312 nm		307.523 nm		400.524 nm		403.307 nm		769.897 nm		251.611 nm	
	This study	RV*	This study	RV*	This study	RV*	This study	RV*	This study	RV*	This study	RV*
MRG-1	8.03	8.47	3.56	3.77	18.73	17.94	0.17	0.17	0.16	0.18	39.55	39.12
SARM-39	4.59	4.29	1.47	1.58	9.74	9.29	0.16	0.17	1.2	1.04	33.78	33.44
JLK-1	16.22	16.86	0.62	0.67	6.8	6.84	0.25	0.27	2.85	2.77	56.97	57.09
JSD-1	14.02	14.66	0.63	0.65	4.83	5.11	0.09	0.09	2.29	2.19	64.78	66.42
JG-2	12.51	12.41	0.02	0.04	0.81	0.92	0.01	0.02	4.61	4.72	77.44	76.95
BHVO-1	12.2	13.8	2.75	2.71	11.88	12.23	0.16	0.17	0.6	0.52	49.78	49.94

SO-1 was used as a calibration standard. Reference Values (RV) are from (26)
n = 6; Precision < 6% RSD

When acid dissolution procedures are adopted to dissolve geological samples, Si is normally expelled by the addition of HF. As a result, it is not possible to determine silica from those solutions. Therefore, a fusion digestion method was employed using lithium metaborate for the determination of Si. In addition to Si, six other elements were also determined in terms of their oxides from these solutions. SO-1 was used as calibration standard. Very dilute solutions (0.6% wt) were analyzed and the data obtained agree very well with the reported data for all these elements (Table V). The data on the international geological reference material BHVO-1 (USGS, India) presented in Figure 6 exhibits very good agreement between the certified values ($\mu\text{g/g}$) and the values obtained in this study by MP-AES for the various major, minor, and some trace elements. In addition, the data of selected major, minor, and trace elements determined in tap water (ng/mL) from the Mulgrave area, Victoria, Australia, were also analyzed by MP-AES with a precision of $\leq 6\%$ RSD. The results are presented in comparison with permissible limits set by WHO in Table VI.

Detection Limits

The limit of detection (LOD) will suffer especially when different metals at trace concentration levels are present in a high matrix of easily ionizable elements such as Na and Ca. Zhang and Wagatsuma (20) found enhancement effects at most of the atomic lines tested and suppression effects at all of the ionic lines in the presence of Na and Ca with very high background. Naturally, in an emission spectroscopy technique, the detection limits of different elements would suffer from high background in geological and environmental matrices. The major advantage of MP-AES is its high sensitivity compared to the FAAS technique. The LOD is usually defined as the analyte concentration that produces an analytical signal equivalent

Fig. 6. Agreement between certified values ($\mu\text{g/g}$) and the values obtained in this study by MP-AES for various major, minor and some trace elements in international geochemical reference material, BHVO-1.

TABLE VI
Concentrations of Different Elements
in Tap Water from the Mulgrave
Area, Victoria, Australia, by MP-AES,
in Comparison With
Permissible Limits Set by WHO

Elements	Wavelength (nm)	Concentration MP-AES Study ($\mu\text{g/mL}$)	WHO ($\mu\text{g/mL}$)
Ca	393.366	2.68	75
Zn	213.857	0.01	5.0
Fe	259.940	0.1	0.1
Mg	285.213	1.17	50
Co	340.512	0.01	-
Ni	352.454	BDL	-
Al	396.152	0.09	-
Mn	403.076	0.003	0.05
Ba	455.403	0.01	-
Na	589.592	3.72	-
K	766.491	0.62	-

BDL = below detection limit.

n = 6, Precision $\leq 6\%$ RSD.

Synthetic multi-element solution containing Ca, Mg, Na & K (at 12.5 ng/mL), Zn, Co, Ni & Mn (at 1.25 ng/mL), Al & Ba (at 5 ng/mL) and Fe (at 2.5 ng/mL) was used for calibration.

to three times the standard deviation observed for 16 measurements of a blank solution (24). The LOD, therefore, is determined by the sensitivity of the measurement and the noise level, or stability, of the MP-AES instrument. Detection limits calculated for some elements are presented in Table VII in comparison with several other established analytical techniques. The detection limits obtained for MP-AES are much better than those reported for FAAS for several elements (25). The detection limits for all trace elements were found to be in the range of 0.1 to 33 ng/mL and are very closely approaching those of ICP-AES for several elements. MP-AES is no match to ICP-MS in terms of detection limits (Table VII), however, in terms of maintenance cost and for the determination of a set of geochemically significant elements, it compares favorably. These studies indicate that the MP-AES technique offers the required sensitivity together with a relatively higher resolution for a comprehensive analysis of geological materials.

Accuracy and Precision

Overall, precisions better than $\pm 6\%$ RSDs were obtained for most determinations with comparable accuracy for all of the results obtained in this study (Tables III - VI). However, precision was highly dependent on the absolute concentration in the material. Determinations made close to the MP-AES detection limit gave the poorest precision, as in the case of some trace elements, for example, Mo and U, where the precisions were around 5 - 6% RSD. More consistent results were obtained for elements at relatively higher concentration levels (all major and minor elements) with many yielding RSDs better than $\pm 3\%$.

TABLE VII
Detection Limits for Different Elements by MP-AES
in Comparison With Other Popular Analytical Techniques
(FAAS, ICP-AES, and ICP-MS)

Elements	Detection Limits (ng/mL)			
	FAAS	MP-AES	ICP-AES	ICP-MS
P	50,000	33	30	0.1
Zn	1	2.8	1	0.04
Au	6	1.8	20	0.005
Ag	1	0.5	1	0.005
Pt	40	4.5	-	0.005
Pd	-	3.8	-	0.01
Cd	0.5	1.4	1	0.005
Be	2	0.1	0.1	0.012
Al	30	0.6	3	0.01
B	1000	1.3	1	0.012
Mn	1	0.25	0.4	0.005
Ta	-	-	-	0.0003
Mg	0.1	0.12	0.1	0.020
Bi	20	24.4	-	-
Ti	50	7.9	0.5	0.004
Nb	-	-	-	0.001
Cu	1	0.6	1	0.005
Hf	-	-	-	0.001
Zr	-	10	-	0.007
Ni	4	1.3		0.01
Sc	-	-	5	0.009
Y	-	0.4	-	0.003
Mo	30	1.5	3	0.08
Fe	5	1.6	2	0.500
Pb	10	2.1	10	0.0012
Sr	-	0.1	0.06	0.001
Ga	-	-	-	0.002
Cr	2	0.4	2	0.005
Ca	1	0.05	0.02	0.4
Na	0.2	0.12	3	0.05
Ba	-	0.2	0.1	0.01
Li	0.5	0.01	0.3	0.01
K	1	0.65	20	0.5

ICP-MS detection limits (27).

ICP-AES detection limits (28).

FAAS detection limits (25).

MP-AES detection limits by this study.

CONCLUSION

The results obtained in this study clearly indicate that MP-AES (microwave plasma atomic emission spectrometry) is a suitable atomic emission spectrometry technique for the accurate determination of major, minor, and selected trace elements required in geochemical studies. This study also proves that by utilizing matrix matched calibration, potential sample matrix effects can be mini-mized in MP-AES studies. So far, expensive analytical techniques such as XRF, ICP-AES, and ICP-MS are being used to generate precise geochemical data. This study carried out on several international geological reference materials proves that MP-AES is a more economical alternative analytical tool for the generation of precise data of major, minor, and some selected trace elements in geological samples.

The major advantages are that the microwave plasma, generated from nitrogen taken from direct air, does not involve handling any gas cylinders, is relatively less expensive, and can be operated with improved laboratory safety. This technique provides detection limits for several elements approaching that of an ICP-AES and is much superior to flame AAS. The linear dynamic detection range is of immense importance for any analytical technique because of the wide range of elements and concentrations to be analyzed in a single analysis. Better linear dynamic range achieved by MP-AES as compared to FAAS will enable the rapid determination of trace elements in different matrices and eliminate the need for time-consuming dilutions required for elements present at higher concentrations. Further investigations in the near future will include the accurate determination of other important trace elements such as As and Se, and especially the rare earth elements (REEs) in different kinds of geologi-

cal and environmental materials such as rocks, soils, sediments, industrial effluents, and water.

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