

Rapid Determination of Minor and Trace Metals in Indigenous Nonmetallic Minerals

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Summary: Using flame atomic absorption techniques, a rapid and sensitive method was developed for determination of minor and trace contents of copper, cobalt, nickel, zinc, lead, manganese, silver chromium and gold in indigenous non-metallic minerals (phosphorite and bauxite). Different mineral acids (HCl, H₂SO₄, HNO₃) were used for the decomposition of the samples and HNO₃ was found to be more suitable for digestion as compared to other acids. The instrumental conditions and other working parameters were optimised. The results obtained by the present method are found to be more reliable as compared to the other existing methods.

Introduction

The geochemical laboratory is usually faced with the need to evaluate substantial specimen of the mineral, ores, and rocks with a proper balance between the accuracy and precision on the one hand and speed and cost of the analyses on the other. A problem may arise when analyzing some of the metals like gold through the flame atomic absorption analysis the preferable technique even after the use of well established procedure of concentration of gold by extraction into MIBK [1-2].

A number of methods have already been in use for the trace elemental analysis [3-13], but these methods are laborious and time consuming. We have developed a simple sensitive and rapid method for the determination of minor and trace content of the associated metals for complete chemical evaluation of the above mentioned minerals. The present investigations were undertaken in continuation of our earlier studies on geochemical evaluation of the phosphate rock samples of Lambidogi and Batakna (Hazara) [14-15] and Bauxite of (Khushab and Attock) [16-17].

Results and Discussion

Effect of mineral acids

The effect of different mineral acids i.e HCl, HNO₃ and H₂SO₄ was studied on the decomposition and subsequent leaching of the samples of bauxite and phosphorite. Efforts were also made to

study the effect of mixtures of these acids as well. It was revealed that the decomposition of the samples through leaching with HNO₃ alone gave satisfactory results. As analytical grade and chloride free HNO₃ was used in these studies, the addition of Hg(NO₃)₂ to hinder the interference of chloride was avoided. Moreover, the samples under investigations were free from antimony and bismuth, therefore, the use of tartaric acid to suppress the formation of antimonic and bismuthic acids was also abstained. These studies are shown in Table-3.

Effect of HNO₃ concentration

The acid leaching studies were carried out with different molar concentrations (0.5-5.0 M) of HNO₃. It was noted that leaching with 1.00-1.1 M (6.5-7.0 ml/100 ml) of pure and concentrated HNO₃ gave maximum recovery of the metals under investigations. These observations are shown in Fig. 1A.

Effect of temperature

To optimise the effect of temperature, the acid leaching studies of the samples were performed at different temperatures (25-75°C) on a steam bath. It is observed that 60-70°C is the optimum temperature for the completion of acid leaching of the samples. These studies are depicted in Fig. 1B.

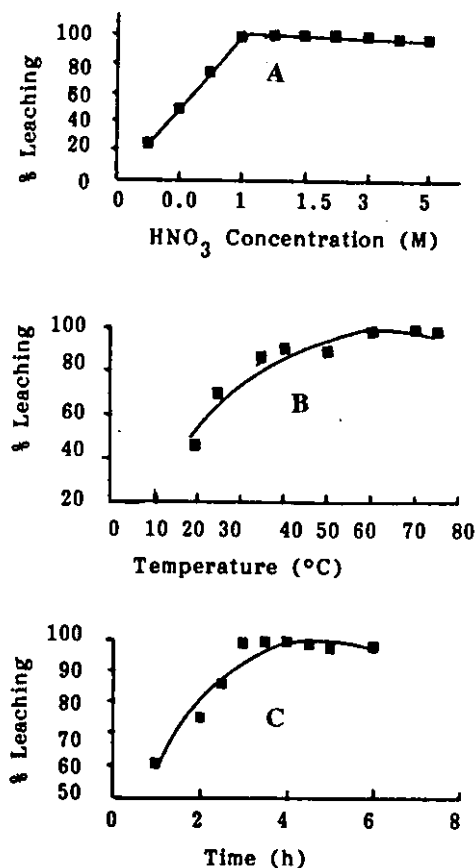


Fig. 1: Effect of (A) HNO₃ concentration (B) temperature (C) time on % leaching

Effect of time

Having optimised the above mentioned parameters, efforts were also made to study the effect of time (1.0-6.0 h) on the overall acid leaching studies. The investigations reveal that 3.0-4.0 h. is the optimum time. The effect has been presented in Fig 1C.

Calibration, precision, sensitivity, etc.

The statistical data of each element are shown in Table-2.

Experimental

Instrumentation

A Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer (Model Z-8000) was used for absorbance measurements. The elements

copper, cobalt, zinc, nickel, chromium, manganese, lead, silver and gold in the samples were analysed on Zeeman flame mode. Standard burner was used for acetylene-air flame. The instrumental conditions for Atomic Absorption Spectrophotometer and the results are summarized in Table-1 and Table-3 respectively.

Reagents

All the chemicals used in present studies were reagent grade/analytical grade and were tested for the presence of any interfering materials. Unless otherwise specified all solutions were prepared by dissolving 1g each of the pure metal by appropriate addition of HNO₃ (usually 1:1) followed by dilution to 1l with distilled deionised water and stored in polyethylene bottles as stock solutions. Each solution contained 1000 µg/ml of the respective metal. Further dilutions were made from the stock solutions, so that the resulting standard solutions contain 1 µg/ml of the metals (Cu, Co, Mn, Cr, Ni, Zn, Pb, Ag and Au) under investigations.

Procedure

0.1-0.2 g of the powdered and well agated samples (either phosphorite or bauxite) were leached with 6.5-7.0 ml (1.0-1.1M) of nitric acid over stem bath at 70-75°C for 3-4 h. The leached solution was cooled down at room temperature and using decantation technique the residue was washed two to three times with distilled deionized water. The matrix was then filtered through a 5 cm Whatman filter paper and the filtrate was diluted to 100 ml with distilled deionized water in a volumetric flask.

Conclusion

The present article describes a rather easy, sensitive, precise and rapid method for the determination of minor, trace and value-added metals in bauxite and phosphorites. The method developed can be applied for the evaluation of other indigenous non-metallic minerals for simultaneous determination of a number of trace metals after dissolution of the specimen at the same acid concentration. The extragenous addition of mercuric nitrate, to hinder or mask the interference of chloride ion was avoided. As the samples were

Table-1: Instrumental conditions for elements

Conditions	Cu	Co	Zn	Ni	Cr	Mn	Pb	Ag	Au
Lamp current (mA)	7.5	10.0	10.0	10.0	7.5	7.5	7.5	7.5	10.0
Wavelength (nm)	324.8	240.7	213.8	232.0	359.3	279.6	283.3	328.1	242.8
Slit (nm)	1.3	0.2	1.3	0.2	1.3	0.4	1.3	1.3	1.3
Oxidant pressure (kg/cm ²)	1.60	1.60	1.60	1.60	1.60	1.60	1.6	1.6	1.60
Fuel pressure (kg/cm ²)	0.30	0.35	0.20	0.25	0.40	0.30	0.30	0.30	0.20
Burner height (mm)	7.5	10.0	7.5	10.0	7.5	7.5	7.5	7.5	7.5

Table-2: Stastical calculation value for 10 data of 1.00 µg/ml of the elements.

	Cu	Co	Zn	Ni	Cr	Mn	Pb	Ag	Au
Mean (µg/ml)	1.03	1.04	1.32	1.05	0.99	1.0	0.99	0.98	1.10
SD (µg/ml)	0.05	0.02	0.04	0.08	0.02	.02	0.02	0.03	0.04
% RSD	5.18	1.89	3.04	7.94	1.88	2.08	1.81	3.06	3.64
r	1.000	0.9980	0.9928	0.9970	0.9798	0.9965	0.9975	0.9936	0.9993

SD = standard deviation, for better precision SD should be less than 0.1 µg/ml [19]

RSD = relative standard deviation.

r = correlation coefficient.

Table-3: Element contents as % of ore sample using various composition of mineral acid

Sample	Acids used	Cu	Co	Mn	Cr	Ni	Pb	Zn	Ag	Au
Bauxite	HNO ₃	0.0028	0.0011	<0.0004	0.0033	<0.0004	0.0005	0.0014	<0.002	<0.001
Attock	HNO ₃ -HCl	0.0026	0.0009	<0.0004	0.0030	<0.0004	0.0005	0.0012	<0.002	<0.001
	HNO ₃ -H ₂ SO ₄	0.0025	0.0009	<0.0004	0.0028	<0.0004	0.0004	0.0010	<0.002	<0.001
Bauxite	HNO ₃	0.0035	0.0010	<0.0004	0.0055	<0.0004	0.0005	0.0013	<0.002	<0.001
Khushab	HNO ₃ -HCl	0.0029	0.0085	<0.0004	0.0050	<0.0004	0.0005	0.0012	<0.002	<0.001
	HNO ₃ -H ₂ SO ₄	0.0030	0.0070	<0.0004	0.0048	<0.0004	0.0005	0.0010	<0.002	<0.001
Phosphorite	HNO ₃	0.0052	0.0034	0.0280	0.0040	0.0092	0.0170	0.0139	<0.002	<0.001
Bataknaia	HNO ₃ -HCl	0.0049	0.0033	0.0260	0.0039	0.0090	0.0150	0.0136	<0.002	<0.001
	HNO ₃ -H ₂ SO ₄	0.0050	0.0030	0.0200	0.0037	0.0085	0.0150	0.0134	<0.002	<0.001
Phosphorite	HNO ₃	0.0044	0.0033	0.0070	0.0072	0.0016	0.0055	0.0068	<0.002	<0.001
Lambidogi	HNO ₃ -HCl	0.0040	0.0032	0.0067	0.0070	0.0015	0.0050	0.0067	<0.002	<0.001
Detection	HNO ₃ -H ₂ SO ₄	0.0038	0.0029	0.0006	0.0068	0.0013	0.0050	0.0059	<0.002	<0.001
Limit		0.0004	0.0010	0.0004	0.0016	0.0004	0.0014	0.0008	0.0020	0.0010

Table-4: Comparative results of element contents as % using different methods

Sample	Methods	Cu	Co	Mn	Cr	Ni	Pb	Zn	Ag	Au
	AAS ¹	0.0028	0.0011	nil	0.0033	<0.0002	0.0005	0.0014	<0.002	<0.001
Bauxite										
Attock	Colorimetric ²	0.0020	0.0009	0.0001	0.0029	0.0001	nil	0.0010	nil	nil
	AAS ¹	0.0035	0.0010	nil	0.0055	<0.0002	0.0005	0.0013	<0.002	<0.001
Bauxite										
Khushab	Colorimetric ²	0.0040	0.0008	nil	0.0060	0.0002	nil	0.0010	nil	nil
	AAS ¹	0.0052	0.0034	0.0280	0.0040	0.0092	0.0170	0.0139	<0.002	<0.001
Phosphorite										
Bataknaia	Colorimetric ²	0.0055	0.0035	0.0300	0.0035	0.0100	0.0200	0.0100	nil	nil
	AAS ¹	0.0044	0.0033	0.0070	0.0072	0.0016	0.0055	0.0068	<0.002	<0.001
Phosphorite										
Lambidogi	Colorimetric ²	0.0050	0.0028	0.0065	0.0075	0.0009	0.0050	0.0060	nil	nil

n.d. = not determined

¹Atomic Absorption Spectrometry (Present Method)

²Colorimetric method [18].

free of bismuth and antimony, the addition of tartaric acid to prevent the precipitations of these elements as their acids were also abstained. The data obtained by evaluation of the minerals for the determination of trace metals using the present method was also compared with the already established and standard methods (Table-4), and it

was found that the results obtained from the present method were comparatively more precise.

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