Analysis of Rock Samples by Atomic Absorption and X-ray Fluorescence

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Summary: Geological investigations are usually made by a number of techniques. The purpose of present work was to explore the chemical composition of the samples under study and also to see the reliability of the different instrumental techniques used for rock and mineral analysis. Chemical tests were performed prior to the use of any other technique in order to determine the nature of these rocks. The chemical analysis indicated the silica dominance in the rock composition, hence the acidic nature of the rock. The major, minor and trace elements were determined by employing X-ray fluorescence and atomic adsorption spectroscopic methods

Introduction

The importance of chemical analysis of rocks and minerals to geological and related studies is now well established. The systematic analytical scheme underwent continuous modification in the light of the increasing knowledge of the principles of analytical chemistry. The classical methods are still widely used, various rapid analytical schemes have been proposed as an alternative [1-5]. These schemes are only adaptation of the classical scheme and still retain many of the characteristics of the latter. These in turn are being replaced by the instrumental methods.

The present work deals with the analysis of silicate rocks by both classical and instrumental techniques. The Mansehra granitic complex was selected for investigation (Location - Susalgali, Cnanser and Karakorum Highway, Northern Pakistan).

Results and Discussion

Gravimetry

Among major elements Si, Fe, Al, Ca and P were estimated as their oxides and the most abundant oxide was found to be SiO_2 which confirmed their silicate nature. The gravimetric results are tabulated in Table 1.

The moisture content was determined by drying the samples at 100°C. At this temperature, hydroscopic water, (H_2O^-) was lost. No appreciable loss occurred upto 1000°C, indicated the absence of carbonatges. As air dried samples were ignited, therefore, loss on ignition gave only the total water content *i.e.* H_2O^- and H_2O^+, latter was the water of constitution.

The chemical analysis indicated that silica was the dominant component of all the samples which could be mostly located in quartz, feldspars, chlorite and other silicates minerals.

The separation and gravimetric determination of silica (the first step in chemical analysis) was not necessarily done just to determine this chief constituent, it also permitted the subsequent determination of other major constituents with which the silica would interfere seriously if not first removed.

Atomic absorption spectroscopic (AAS) method

The major and the trace/minor elements were determined with the help of AAS. The results in % are given in Table 2. Among the major elements Na, K, Ca, Mg and Fe were estimated. The precision and accuracy of the determination of silicon (reported as silica) by AAS is still subject of some disagreement [7-9], that is why it was not determined by AAS. The problems raised are due to the polymerization of SiO_2 in both standard and sample solutions, and interference caused by the mineral acids.

Table 1: Percentage of different oxides in rock samples

Weight %	1	2	3	4	5
Water	0.21	0.5	0.3	0.4	0.05
Loss on ignition	0.4	0.5	1.0	0.48	0.08
SiO_2	87.36	89.96	88.35	90.62	85.94
CaO	0.56	0.45	0.33	0.13	0.11
Fe_2O_3	1.74	1.06	1.76	1.01	3.14
Al_2O_3	3.59	1.89	0.62	0.73	1.17
P_2O_5	0.18	0.20	0.28	0.19	0.03

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Table 2: Percentage concentration of major and trace elements determined by AAS.

Elements	1	2	3	4	5
Na	1.444	0.0919	0.0032	0.1263	*
K	0.18	*	0.0524	*	*
Ca	0.24	*	*	*	*
Mg	*	*	*	*	*
Fe	1.13	0.6228	1.106	0.6087	2.118
Hg	0.0835	*	0.0080	0.0154	*
Cd	0.0126	0.0025	0.0015	0.0028	0.0030
Zn	0.2347	0.1338	0.2372	0.0887	0.0375
Cu	0.0096	0.0026	0.8297	0.1593	0.1535
Ni	0.0164	0.0030	0.0115	0.0023	0.0145
Cr	0.0129	0.0023	0.0113	0.0027	0.0242
Pb	0.7797	0.0134	0.0441	0.0243	0.0210
Mn	0.1309	0.0232	0.0305	0.0201	0.0565
As	**	0.1646	0.2458	0.017	0.3782
Co	0.0121	**	**	**	**

*Below detection limit **Not determined

Calcium was not indicated by AAS except in one sample. It might be due to the interference caused by Al and Fe which form compounds with Ca in the flame. Magill and Svehla [10] have investigated Ca by AAS. In air-acetylene flame, the interference was caused by the formation of refractory compounds by cations and anions. Magnesium estimation is also affected by the presence of Al, Si, PO_4 and silicates [11-13].

The AAS gave indication of K only in two samples, it might be due to spectral interferences or incomplete decomposition of K minerals.

Trace and minor elements

The trace elements e.g. As, Cu, Zn, Cd, Cr, Pb etc. were indicated by AAS. The determination of As using flame techniques suffers from the fact that the three absorption lines exhibited by As are all below 200 nm and sensitivity is decreased because of absorption of the radiation by the optics, air and flame gases. The 193.70 nm was preferred because it is more sensitive [14-15]. The sensitivity of AAS techniques is very high for Cd, silicon is reported to decrease the Cd signal to some extent, but there are few other chemical interferences observed in the air-acetylene flame [16]. There are few interferences in the determination of Cu by AAS using air-acetylene flame [17]. Barnett [18] concluded that, in air-acetylene, HCl and HNO_3 gave the least interference.

X-ray fluorescence spectroscopic method

The major and the trace elements were determined quantitatively by using the XRF spectrometer. In the case of WD-XRF, concentrations were obtained with respect to Zr, used as internal standard and the values are given in Table 3. Since, Cr-tube was used for excitation for the determination of lighter elements such as excitation for the determination of lighter elements such as Al and Si. These elements were not detected, as analysing crystal was LiF which could diffract the wave length upto 0.25 nm. The heavier elements such as Nb, Y, Zr, Rb etc. were detected. For lighter elements, crystals with large interplaner 'd' spacing were necessary. The scintillation counter detector was used which was adequate only for wavelength shorter than about 0.18 nm because of the absorption of longer wavelength X-ray by the casing of NaI.

Table 3: Percentage - concentration of trace metals by WD-XRF

Elements	1	2	3	4
Cu	0.2049	0.1805	0.7544	0.4053
Ni	-	-	0.0211	0.0374
Zn	0.11044	0.0324	0.7145	0.1038
Pb	-	0.0547	0.2907	-
Sr	0.3580	0.4063	2.1060	2.1885
Rb	0.9132	0.6011	2.8452	-
Y	0.5027	0.3199	1.0468	-
Zr	1.00	1	1	1
Nb	-	0.1812	-	-
Mo	0.1806	0.1061	-	0.0872
Co	0.0258	-	-	-
Cr	0.2364	0.0200	0.1665	-

Conclusion

The low concentration of Fe by AAS may be due to the presence of Al and Si which depress the Fe signal [19]. As acid dissolution technique was used for AAS analysis, some minerals were resistant to such attack and therefore, low results will be encountered for elements present in such minerals. As mostly HCl was used for decomposition, therefore, silicates having high proportion of Fe were not completely decomposed.

Cadmium, manganese and mercury were not indicated by WD-XRF but detected by AAS. In the determination, AAS gave better results than XRF, in which the possible interference is K1.3 line of Cr at 0.2085 nm if Cr is present as a major

constituent [20-23]. But Cr was present at trace level as indicated by AAS, therefore, it would not interfere in Mn determination by XRF. Phosphorus was not detected by XRF, but estimated as P_2O_5 gravimetrically. There is no interference likely to be encountered in the XRF determination of P.

Experimental

The rock samples, after being crushed and ground, were stored in labeled bottles. These were studied by gravimetry, atomic absorption and X-ray fluorescence methods.

Gravimetry

The classical procedure for the estimation of Si, Fe, Al, Ca and P were performed [6]. These elements were estimated as their oxides. Moisture content was also determined.

Atomic absorption spectroscopic method

One percent solution of the rock samples was prepared after digesting in aqua-regia and run on AAS. Shimadzu Atomic Absorption Spectrophotometer Model AA-670 was used under standard analytical conditions.

Estimation of Hg and As by AAS

The cold-vapor mercury estimation method was used, employing a mercury analyzer reduction unit interfaced with the atomic absorption spectrophotometer. Also, arsenic in all samples was analysed through the hydride generation unit interfaced with the AAS. These techniques not only furnish a much lower detection limit of the elements under working conditions, but also yield better reproducibility, within ±2-3% for replicate measurements.

X-ray fluorescence spectroscopic method

The spectrometers utilized for these purpose were either WD-spectrometer SRS-200, M/S Seimens, Germany or ED-XRF spectrometer XR-500, M/S Links System, England. In the first case samples were directly taken in polyethylene bottles while in the second case polyethylene cups were used.

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