Flame Atomic Absorption Determination of Rubidium in Different Rocks Using Acetylene-Air as Excitation Source

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Summary: The present work discloses a complete investigation of parameters affecting rubidium determination by flame atomic absorption technique. Acetylene-air flame is used during the course of this study. The instrumental conditions (flame composition and the observation height) has been examined and optimized. The obtained data declares that, the optimum conditions at 780 nm are 16 mm observation height and flame composition of 2.03 (relative stoichiometric units RSU) i.e. the oxidized ratio. The effects of different concentration of mineral acids on the sensitivity of rubidium absorption are studied. The results show that nitric acid solutions up to 2.5 M do not affect the absorption of rubidium. The interference effects of coherent cations that are present in the matrix solution on the absorbance of rubidium are also studied and no effects are observed. The detection limit of 0.01 µg mL^{-1} is obtained in the presence of 0.2% w/V of potassium as ionization buffer; the accuracy is assessed by comparing the obtained results of international standard rock samples with their reference values. The RSD obtained is of 0.4-2%.

Introduction

The determination of trace and ultra trace elements is part of an ongoing task to establish compositions of various geological materials for their petrological, geochemical and mineralogical studies[1]. Also very accurate analysis data for alkali metals are required for limestone and related materials before end use in ferrous metallurgy[2]. The main significance of the Rb-Sr pair for geologists is related to the dating of rocks and minerals by the Rb-Sr radioactive clock, which is one of the few reliable and commonly used geochronological methods[3]. Determination of traces of rubidium has been carried out using ICP-MS,[4] neutron activation analysis [5] and flame emission.[6,7] Neutron activation analysis and plasma-based techniques like ICP-MS offer good sensitivity for rubidium and the possibility of simultaneous determination of other elements. Plasma based techniques like ICP-MS requires analyte–matrix separation to get rid of matrix related suppression on ion intensities. Further, those techniques are very expensive and not widely available [8]. Calibration of emission

methods and X-ray fluorescence (XRF) spectrometry requires the use of reference materials (RMs) that are well characterized with respect to the analytes of interest. The accuracy of measurement is directly related to the quality of the selected RMs. Suitable certified RMs covering a wide range of concentrations must be simultaneously processed with the unknown samples to monitor the analytical accuracy and assure the quality of data. When the matrix of the incoming samples is not known, then the XRF method is never preferred[2]. Electrothermal atomic absorption spectrometry has been utilized for the determination of rubidium in biological fluids [9] and in erythrocytes [10]. However, halides, especially alkali metal chlorides have been reported to have serious interferences in ETAAS analysis [11]. AAS is a much cheaper and also suitable analytical method for determination of trace elements [12]. It was frequently applied in analysis of rubidium in geological samples. Since the technique is liable to matrix interference effects, parameters should be carefully optimized for reliable determination of rubidium in complex matrices such as geological matrices. Flame atomic emission/absorption spectrometry is a fast and simple method for rubidium determination [6]. It is the most preferred technique for measurement of the alkali metals [13-17]. Alkalis are better determined by flame rather than by plasma atomic emission spectrometry (AES) due to the reduced sensitivities and stabilities in much hotter plasma source. Rubidium is easily excited and ionized in acetylene- air flame due to its low excitation and ionization energies, of 1.54 and 4.16 eV, respectively. Consequently rubidium exhibits both ionic and atomic spectra. Intensity of rubidium absorption is enhanced by adding a K salt to the standard and samples solution as ionization suppressor [18]. The aim of our work was to optimize the analytical procedure and measurement parameters for the determination of rubidium in rock sample solutions by FAAS.

Experimental

Materials

All chemicals used were of the analytical grade. A stock standard rubidium solution (1000 ppm) was obtained from (Inorganic Ventures). Hydrochloric acid (Sigma and Alderish), orthophosphoric and sulfuric acid (Adwic), nitric acid (Poleskie), perchloric acid (Chemie Loba). Standard stock solutions were prepared by dissolving accurately weighted amounts of their materials, and finally diluted to

appropriate volumes and stored in clean polyethylene bottles. Double distilled water was collected from (Kottermann1034).

Apparatus

Rubidium was determined by FAAS on A UNICAM Atomic absorption spectrometer model 929 in an air–acetylene flame. The light source was a rubidium hollow cathode lamp (UNICAM) operating at 7mA current at 780 nm resonance line. The spectrometer was provided with deuterium hollow cathode lamp based background correction. The AAS set up is outlined in Table (1).

Table1. Operating conditions of AAS for Rb element

Element parameters	Rubidium (Rb)
Wavelength	780.0 nm
Alternative wavelengths	794.8, 420.2 nm
Lamp current	100%
Band width	1.0 mm
Flame type	Air -acetylene
Flame chemistry	oxidized
Fuel flow	1.1 L/min

Procedure

Sample dissolution

In a teflon beaker, 0.5 g of powdered sample (- 200 mesh) was subjected to total dissolution by digestion in 10 mL of hydrofluoric acid and 5 ml nitric acid solutions. Digest the mixture on a hot plate and evaporate the solution to dryness. Dissolve the residue in a minimum amount of diluted nitric acid (2.5 M), warm gently then dilute to 50 mL standard flask.

Calibration

After adjustment of the parameters to give maximum absorbance, Working standards of rubidium were prepared by dilution of the stock solution with water and addition of an appropriate amount of potassium, so that the final concentration was 2 g K L^{-1}.

Results and Discussion

The optimal flame and instrumental parameters were optimized in three steps, as follows: (1) determination of the absorption spectrum of rubidium in the acetylene-air flame; (2) determination of the optimal values of flame parameters (flame composition, observation height over the burner head (h)) in the flame. Then, the detection limit was determined under the optimized conditions. The interference effects from the presence of various concentrations of acids and some major and minor elements normally present in rocks were investigated.

1. Optimization of parameters

Rubidium in rock samples was determined in an air–acetylene flame at 780.0 nm. At this wavelength the background is insignificant [19]. Non-specific absorption does not contribute to the atomic absorption signal, so background was not corrected. To compensate interferences arising from ionization and to obtain a linear calibration curve, 2 g L^{-1} of K was added to each sample and standard solution.

The optimum conditions that give the highest absorbance intensity are investigated. The effect of change of observation height (1 - 25 mm) on the absorption signal intensity of Rb was investigated. The change in the height of observation has a marked effect on the analyte absorption. The highest signal value is observed at 16 mm burner height. The influence of the flame composition, on the absorption signal value of rubidium is studied. Various acetylene air ratio [stochiometric, oxidized and reduced] ratios are examined. The optimum setting is found to be oxidized condition.

Observation height and flame composition

To select the optimum conditions for an analytical measurements the two parameters mainly, observation height and flame composition are tested together. Their influences on the absorption intensity of Rb at 780.0 nm were studied. The optimum setting is found at the oxidized ratio and at 16 mm burner height, Fig (1). In FAAS, the fuel/oxidant and observation height are chosen to provide the maximum number of free atoms. The concentration of unexcited and excited atoms in a flame is determined by the fuel/oxidant ratio. It varies in different parts of the flame. Studies

of atomic and molecular distributions within the flame have been made by measuring absorption as the flame is moved vertically relative to the light path.
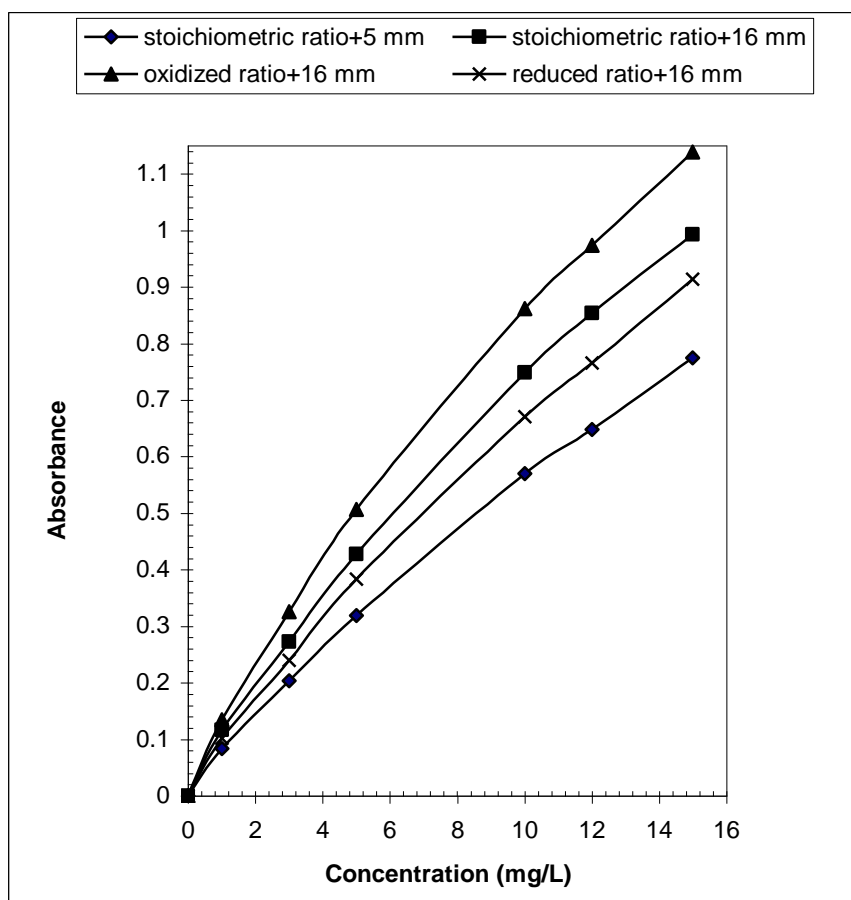

Fig. 1. Effect of flame height and flame composition together on Rb signal

Form the above study; it is declared that the maximum intensity is obtained at the following parameters: oxidized ratio, 16 mm burner height.

2. Calibration graph, limit of detection and repeatability

The calibration graph for aqueous standard solutions was proved to be linear till 15 µg L^{-1} of rubidium with a correlation coefficient better than 0.9899. The repeatability of measurement (RSD) was tested in standard sample of Rb by 10 parallel determinations. It was found to be 0.7 %.

The detection limit for an element is the minimum amount or concentration that can be detected by a given analytical procedure. There are various ways in which a detection limit can be calculated. In spectroscopy, the detection limit[20] is defined as

the smallest signal(s) that can be distinguished from random fluctuations of the background at a predetermined level of confidence. The smallest signal (s) is equalized to k times the standard deviation of the back ground (d).

$$s = k \cdot d$$

$$D.L = \frac{3 \times S.d^* \times concentration}{net\ signal} \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

S.d* standard deviation of back ground

It follows that, in order to minimize the detection limit (DL) the sensitivity must be maximized and standard deviation of the back ground must be minimized. At the condition giving higher sensitivity the detection limit of 0.01 µg mL^{-1} is obtained under the optimized conditions.

3. Interference study

Interferences were monitored by observing whether the signal produced from a standard rubidium solution is influenced by the presence of various species in the matrix solution. The concentration of Rb used throughout this study is 3 µg mL^{-1}, which is equivalent to 300 µg g^{-1} in the studied rock. The concentration ranges of the major elements studied were chosen to be similar to those normally found in rocks solution. All of the interference studies are carried out on solutions that were also 0.2% in potassium as ionization buffer.

Effect of acids

The effect of added mineral acids used in an analytical procedure on 3 ppm rubidium absorption signal is estimated at various molarities (0.25 - 2.5 M). A depressive effect is observed due to the presence of sulfuric, hydrochloric, perchloric and phosphoric acids solutions. The depressive effect is in the order ($H_3PO_4 > HClO_4 > HCl > H_2SO_4$). The obtained results are shown in Fig (2). The depressive effect of these acids may be attributed to the formation of less volatile (stable) compounds with analyte and these compounds are stable at the flame temperature. Physically due to the viscosity difference which affects the rate of nebulization.
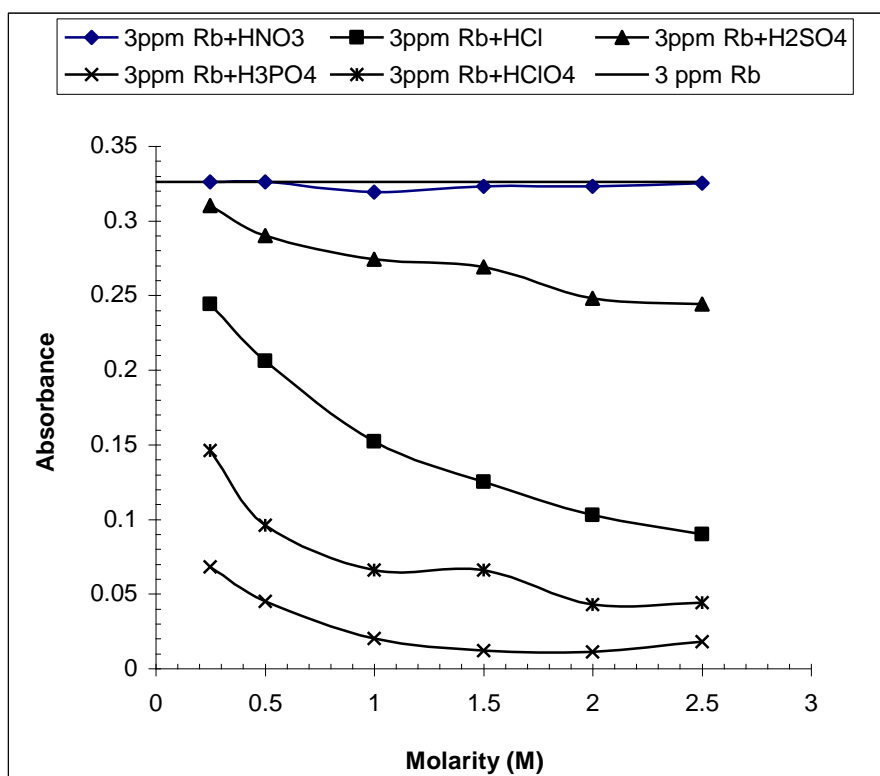
Fig. 2. Effect of common acids on rubidium absorption signal

Nitric acid has no effect on the absorption signal of rubidium. Hence it should be used for sample dissolution and rock samples attack.

Effect of diverse cations

The effect of interfering elements on the determination of 3 μg mL^{-1} Rb by FAAS is examined. An ion was considered to be an interferent when it caused a variation greater than 5% in the absorbance of the sample. Evidently, [Al, Ca, Mg, Na, K, Ti and Fe] elements have no influence on the absorbance of rubidium. These foreign cations do not interfere in the determination of rubidium over the ranges investigated in this work.

Some other cations are common to exist in sample solutions of some rocks and minerals. It may present in detectable amounts. Their presence effects on the absorption intensity of 3 μg mL^{-1} Rb are studied. The results confirm that, most of cations examined do not interfere with the determination of as indicated in Table (2).

Table (2): Tolerance limit of diverse ions on the determination of 3.00 μg mL^{-1} rubidium ion

Ion	Tolerance Limit (μg mL^{-1})
Al^{3+}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Ti^{3+}, Fe^{3+}	1000
Sr^{2+}, Ba^{2+}, La^{3+}, Y^{3+}, Th^{4+}, U^{6+}	800
Ni^{+2}, Cd^{+2}, Co^{+2}, Cu^{+2}, Cr^{+6}	800

4. Application

The proposed method is tested by applying it to the analysis of some international standard rock samples (JB-1, JB-1a, and JG-3)[21]. Other international Egyptian standard [St.4 (Granite), St.5 (Granodiorite), St.6 (Basalt)] [22] and Ph.2 (phosphate) [23] are also analyzed and compared with their certified values. The results of these determinations are given in Table (3). The obtained data are agreed well with those indicated in literature values and reducible. It demonstrates that the procedure could be successfully applied for the analysis of rubidium in different variety of samples with satisfactory accuracy and precision. Precision is approximately 0.4-2 percent.

Standard addition method is also applied to assess accuracy. Amounts of Rb added to the sample solution (phosphate) are recovered. It shows that the complete recovery of the added Rb. Fig (6) illustrates that there is no matrix interference in the determination of Rb in phosphate rock sample opened by HNO_3.

Table 3. Atomic absorption determination of rubidium in some rocks

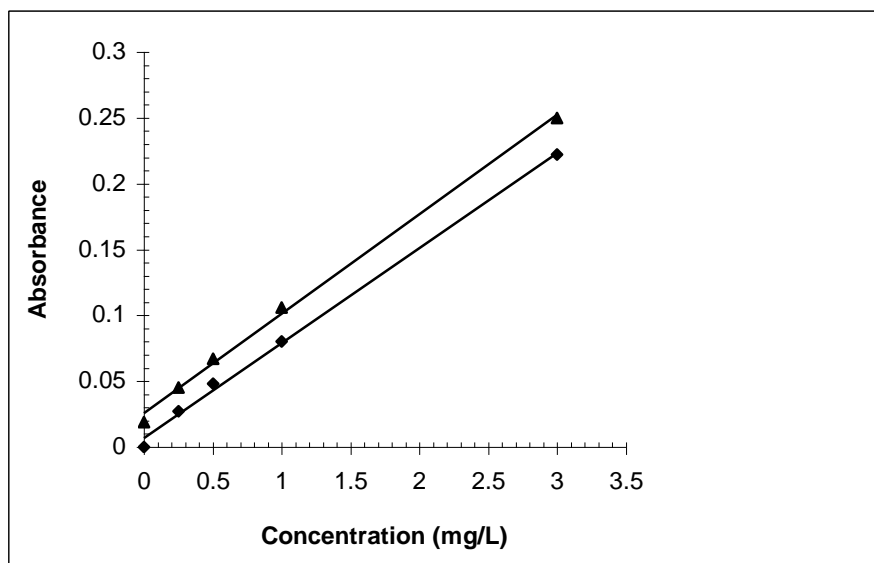| Sample	μg/mL certified values	μg/mL Present work	RSD %
JB-1	41.3	42	1
JB-1a	39.2	38	0.42
JG-3	67.3	66.4	1.3
Ph.2	20	19	1.7
St.4	99	100.6	0.51
St.5	73	72.9	0.43
St.6	33	33	1.42

Fig. 3. Standard addition method illustrate the absence of interference

♦   **Calibration with aqueous solutions**

▲   **Standard additions. Calibration graph – no interference observed from the matrix (HNO$_3$)**

Conclusion

The FAAS method described for the determination of Rb in geological materials is rapid and simple. It is found to be sufficiently and interference free. Nitric acid is chosen for the preparation of rock solution because it has no effect on the absorbance of rubidium. The rubidium determination is performed directly without masking agent. The procedure showed excellent reproducibility and accuracy consequently FAAS determination of Rb can be suitable for routine geochemical analysis.

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