IBN AL- HAITHAM J. FOR PURE & APPL. SCI VOL.22 (1) 2009

Mass Spectrometric Determination OF Radioactive Decay OF ^{87}Rb TO ^{87}Sr IN Some Iraqi Geological Minerals

K. I. Hussain
Department of Chemistry , College of Education Ibn-Al-Haitham, University of Baghdad

Abstract

Determination of isotopic composition of strontium and Rubidium in some geological samples was performed by using thermal ionization mass spectrometry. The optimum evaporation and ionization currents were determined for each of strontium and Rubidium, employing double rhenium filament by using faraday cup as detector. The results were compared with reference materials (NBS Standards) of Sr and Rb. The radioactive decay of ^{87}Rb to ^{87}Sr was also determined.

Introduction

Thermal ionization mass Spectrometry is an internationally recognized method for isotope abundance measurements of different elements (1).

The importance of the strontium and Rubidium to earth sciences lies in two facts. First, one of the naturally occurring isotopes of rubidium ^{87}Rb is radioactive and decays to a stabile isotope of ^{87}Sr. Therefore, the amount of Sr in a mineral or rock containing rubidium increases continuously as a function of time. This phenomenon is employed for the determinations of rocks and mineral by the Rb – Sr method. Secondly, radiogenic Sr can be treated as a geological "tracer" to study certain geological processes which are of interest to pathologists (2).

Rubidium has two naturally occurring isotopes: ^{85}Rb (72.15%) and ^{87}Rb (27.85%). In addition a large number (about 20) of short – lived radioactive isotopes of Rubidium were produced by nuclear reactions under laboratory conditions. Strontium has four stable isotopes: ^{88}Sr (82.56%). ^{87}Sr (7.02), ^{86}Sr (9.86%). And ^{84}Sr (0.56%). In addition, 14 short – lived radioactive isotopes of strontium were made artificially, among these is ^{90}Sr, which is a product of anuclear fission of uranium. The isotopic composition of strontium in nature is not constant, but depends on strontium which is extracted and, on the length of time, it has been associated with rubidium (3).

^{87}Rb decay to stable ^{87}Sr beta emission is shown in equation 1:

$$^{87}Rb \longrightarrow {}^{87}Sr + \beta + \gamma + Q \ldots\ldots\ldots [1]$$

Where β = beta particle having or electronic charge of -1, γ = neutrino, and Q= decay energy. Measuring their energies is in units of million electron volts (MeV). The value of Q for the decay of ^{87}Rb is 0.275 MeV, which is unusually low for beta – decay processes. The beta particles emitted by the decaying ^{87}Rb nuclei have Kinetic energies ranging from essentially zero to a maximum of 0.275 MeV (2).

Experimental

Instrumentation: Thermal ionization quadruples mass spectrometer (THQ), Finnegan Mat Co. (W. Germany) is provided for isotope ratio determination. It is controlled by a computer system which allows manual operation of. Semi – automatic and automatic operation.

Reagents: NBS, 987. $SrCO_3$: this standard is certified for use as an assay and isotopic standard.

NBS, 984. RbCl: this lot of rubidium chloride was prepared to ensure material of intermediate purity and high homogeneity.

Separation Procedure:

1. Mineralization of rock Sample : (2g) of powder sample is placed in a platinum crucible, $HClO_4$ and HF (50 ml of each) were added. After evaporation to dryness another

portion of $HClO_4$ (50 ml) was added, and the solution was evaporated to decompose fluoride. The residue was dissolved in 10 ml of 6.2 M HCl and the resulting solution was evaporated to dryness. The residue was then dissolved in 2.5 M HCl and the solution was evaporated to dryness. This step was repeated twice.

Separation of Sr/ Rb from astandard solution : A standard solution contains Sr and Rb (2000ppm of each)was evaporated as described above .A sample was then taken in small amount of 2.5M HCl ,quantitatively transferred in to asmallcolumn (13cm *5 cm) filled with cation exchanger [(dowe *50*8)(200-400mesh)],previously equilibrated with 2.5M HCl. After the feed soaked in to the resin bed, the walls of the column were washed with few small portions of the eluent bringing each time the level of the liquid in column to the upper level of the resin bed. The column was then connected to the burette with the supply of the eluent, and the elution was performed in aconstant flow rate under external pressure from paretic pump.

The column was eluted with 2.5MHCl .Rb was eluted first and then Sr.The concentration of Rb and Sr were measured with the help of x-ray fluorescence. Separation of Sr and Rb from real samples rock was performed by using the above procedure (4).

Results and Discussion

The results showed that the presence of other alkali metals in rubidium samples do not generally interfere with the rubidium isotopes measurements. Therefore, no attempt is made to obtain pure rubidium by using an appropriate chemical procedure (5).

Table (1A) shows the results of analysis of NBS Rubidium standard (984) and the reproducibility of Rubidium isotopes measurements. The measured ratio of ^{85}Rb / ^{87}Rb are in agood agreement with the theoretical value (R det./R theo.= 1.007). Rubidium signals (^{85}Rb , ^{87}Rb) are easy to obtained and are stable. However, they are very susceptible to small changes in filament current (temperature), and it is easy to overheat the sample in the early stages of an analysis. Overheating subsequently leads to too-rapid growth and/or premature decay. Both of which necessitate

aborting the run. Analysis should be made on slowly or moderately growing signals (6). The best intensity of the ^{85}Rb and ^{87}Rb signals are measured at an accelerating voltage of 10 KV and required currents of (0.4: 2.4Amp) for the evaporating and ionizing filament respectively. Table II. A. shows the isotopic ratio and St. Deviation of, NBS strontium carbonate standard 987. The mean isotopic ratios of strontium were determined after normalizing to internal standard (^{88}Sr / ^{86}Sr = 8.375209) by the Instrument.

Tables (1B): II, B, Summarize the results of analysis of isotopic ratios and St. Deviation, for Rb and Sr in some minerals. The stability of peak intensity for Strontium carbonate (NBS 987) has the lowest time stability of the ion current in comparison with Sr extracted from the investigated samples. This is due to isotope fractionation occurred in the ionic emission process.

The best intensity of the strontium isotopes signals required currents of 0.7 and 2.8 Amp, for the evaporating and ionizing filaments respectively. The observed ratios were constant over data – taking period of (20-25) minutes and any fast signal decay was rejected.

The percentage values of ^{87}Sr produced by radioactive decay of ^{87}Rb in the siltstone and shale minerals (differences between natural and determined values). were found 0.10912: 0.19542 respectively. It was noticed that these amounts were affected by the nature of the rocks which was mentioned above.

Conclusions

The investigations of isotopic ratios composition of two minerals rocks containing both, Sr and Rb were carried out by using mass spectrometer type (THQ).The values of radiogenic of ^{87}Sr were measured and calculated for siltstone and shale. The measurements were standarised by using NBS standards for Sr and Rb.

References

1- AGGARWAL, S.K., ALMAULA, A. (1984), J. Nucl. Chem., letters, 87:163-169.

2- Faure, G. and Powell, J.L. (1972) "Strontium Isotope Geology" Speringer – Verlag, p.1-11.
3- Audi, Bersillon, Blachot, Wapstra (2003). The Nubase evaluation of nuclear and decay properties, Nuc .phys, A 729:103-128.
4- Smale, A.A.;Hughes, T.C. and Mapper, D.(1964), Geochim. Cosmochim. Acta , 27, 209.
5- Shields, W. R. (1966), Analytical mass Spectrometry Section Instrumentation and and Procedures for Isotopic Analysis, NBS-277, July 25.
6- SHIELDS. W.R,(1969), Analytical mass Spectrometry section, NBS-506, July .
7- David R. lide , Norman E .Holden (2005) Handbook of chemistry and physics , 85 th Edition , CRC press , Boca Raton , Florida.

Table(1A):Mass Spectrometric Analysis of NBS Rubidium Isotopes Standard 984.

Mean Ratio ($^{85}Rb/^{87}Rb$)	Standard deviation
* 2.615897	4.9×10^{-4}
2.615162	2.5×10^{-4}
2.614271	2.0×10^{-4}
2.614392	1.8×10^{-4}
2.613924	1.0×10^{-4}
2.610021	2.5×10^{-4}
2.611503	3.7×10^{-4}
2.614264	3.0×10^{-4}
2.613052	4.4×10^{-4}
2.612024	1×10^{-5}
2.613006	3.0×10^{-4}
2.612234	1.9×10^{-4}
Mean= 2.613312	1.6×10^{-4}

- Each value is a mean value of 10 reading.
- Correction factor = 2.6133/2.5930 = 1.007

Table (1B): Mass Spectrometric Analysis of Rubidium Isotope for Siltstone and Shale.

Silt stone (red clay marly)		Shale (blower carbonic)	
Mean Ratio ($^{85}Rb/^{87}Rb$)	Standard deviation	Mean Ratio ($^{85}Rb/^{87}Rb$)	Standard deviation
* 2.688345	7.3×10^{-3}	2.598873	2.6×10^{-5}
2.687450	3.2×10^{-3}	2.592516	1.9×10^{-4}
2.690264	9.8×10^{-3}	2.591813	2.8×10^{-4}
2.698203	6.8×10^{-3}	2.600131	1.2×10^{-4}
2.696473	3.7×10^{-3}	2.597071	2×10^{-4}
2.704983	1.1×10^{-3}	2.594166	5.4×10^{-4}
2.692792	2.3×10^{-3}	2.594673	4.8×10^{-4}
Mean= 2.694073	6.25×10^{-4}	2.595292	2.9×10^{-4}

*Each value is a mean of 10 reading.

Table (2A): Mass Spectrometric Analysis of Strontium Isotopes Standard 987.

Mean Ratio ($^{87}Sr/^{86}Sr$)	Standard deviation	Mean Ratio ($^{84}Sr/^{86}Sr$)	Standard deviation
0.709934	4.6×10^{-4}	0.0445	5.0×10^{-4}
0.708011	4×10^{-4}	0.045019	3.8×10^{-4}
0.716531	4.9×10^{-4}	0.042212	4.6×10^{-5}
0.715022	3.9×10^{-4}	0.041694	1.3×10^{-4}
0.714160	3.5×10^{-4}	0.041582	2.7×10^{-5}
0.713641	4.5×10^{-4}	0.041612	8.8×10^{-5}
0.713002	2.2×10^{-4}	0.041425	7×10^{-5}
Mean=0.712508	2.9×10^{-4}	Mean=0.042579	1.5×10^{-4}

Table (2B): Mass Spectrometric Analysis of Strontium Isotopes for Siltstone and Shale.

Siltstone (red clay marly)				Shale (blower carbonic)			
$^{87}Sr/^{86}Sr$	St. dev	$^{84}Sr/^{86}Sr$	St. dev	$^{87}Sr/^{86}Sr$	St. dev	$^{84}Sr/^{86}Sr$	St. dev
0.729953	4.8×10^{-4}	0.048011	4.9×10^{-4}	0.735365	2.1×10^{-4}	0.043541	4.2×10^{-4}
0.723800	8.5×10^{-4}	0.047889	5.6×10^{-4}	0.734316	1.1×10^{-4}	0.043211	5.9×10^{-4}
0.722368	7×10^{-4}	0.047228	6.2×10^{-4}	0.732513	4.9×10^{-4}	0.042371	7.9×10^{-4}
0.724624	3.5×10^{-4}	0.046613	5.3×10^{-4}	0.732819	2.4×10^{-4}	0.042570	1.5×10^{-3}
0.723140	1.2×10^{-4}	0.046869	7.7×10^{-4}	0.734338	1.1×10^{-3}	0.042724	8.8×10^{-4}
Mean=0.724777	3×10^{-4}	Mean=0.047322	6.15×10^{-4}	Mean=0.733870	1.1×10^{-4}	Mean=0.042883	4.8×10^{-4}

قياسات تحليلية نظائرية لنظير السترونتيوم 87 المتولد بالتحليل الإشعاعي من نظير الريبديوم 87 في بعض الصخور الجيولوجية العراقية.

خليل إبراهيم حسين
قسم الكيمياء ، كلية التربية –أبن الهيثم ، جامعة بغداد

الخلاصة

تضمنت خطة العمل قياس النظائر المستقرة لكل من السترونتيوم والريبديوم باستخدام المطياف الكتلي ذو التأين الحراري. حيث تم قياس هذه النظائر لمجموعة من الصخور الجيولوجية العراقية ، كذلك يجري قياس دقة النتائج باستخدام نماذج قياسية للريبديوم و السترونتيوم من NBS. كما تم قياس نظير السترونتيوم 87 المتولد بالتحليل الإشعاعي من نظير الريبديوم 87.