Development of a high vacuum sample preparation system for helium mass spectrometer

P Kumar, N K Das, C Mallik and R K Bhandari
Variable Energy Cyclotron Centre, 1/AF, Bidhan Nagar, Kolkata – 700064
Email: pradeep_vecc@yahoo.co.in

Abstract. A high vacuum sample preparation system for the $^3\text{He}/^4\text{He}$ ratio mass spectrometer (Helix SFT) has been developed to remove all the gaseous constituents excluding helium from the field gases. The sample preparation system comprises of turbo molecular pump, ion pump, zirconium getter, pipettes and vacuum gauges with controller. All these are fitted with cylindrical SS chamber using all metal valves. The field samples are initially treated with activated charcoal trap immersed in liquid nitrogen to cutoff major impurities and moisture present in the sample gas. A sample of 5 ml is collected out of this stage at a pressure of $10^{-2}$ mbar. This sample is subsequently purified at a reduced pressure of $10^{-7}$ mbar before it is injected into the ion source of the mass spectrometer. The sample pressure was maintained below $10^{-7}$ mbar with turbo molecular vacuum pumps and ion pumps. The sample gas passes through several getter elements and a cold finger with the help of manual high vacuum valves before it is fed to the mass spectrometer. Thus the high vacuum sample preparation system introduces completely clean, dry and refined helium sample to the mass spectrometer for best possible analysis of isotopic ratio of helium.

1. Introduction
The $^3\text{He}/^4\text{He}$ ratio provides useful information on the origin of helium (primordial or radiogenic). It is also an important indicator to the study of magmatic volatiles\cite{1}. The most vital part of any mass spectrometric analysis is the sample preparation. Several sample extraction and cleaning techniques\cite{2}\cite{3} have been used for helium isotopic analysis using high vacuum sampling systems. The mass spectrometer requires completely clean and dry samples at a pressure lower than $10^{-7}$ mbar for precise measurements. Helium bearing gas samples collected at atmospheric pressure from different geothermal field stations contains impurities like N$_2$, O$_2$, Ar, CH$_4$ etc. This paper describes the fabrication, design and operational details of cleaning of field samples at a vacuum of the order of $10^{-7}$ mbar for helium isotope analysis.

2. Design, Fabrication and Operation
The sample preparation system is fabricated with all stainless steel components (316L) and cleaned prior to use on the system. The cleaning is done by boiling the fabricated parts in 5% HNO$_3$ followed by cleaning with acetone and alcohol followed by drying. Conflate flanges with OFHC copper gasket are used to assemble various components of the sample preparation system.
2.1 The Pretreatment stage

The samples are collected from geothermal field stations in pre-evacuated stainless steel sampling cylinders (500 cc, double ended) for analysis. These sample gases were first treated with liquid nitrogen cooled activated charcoal trap for removal of most of the impurities like moisture, nitrogen, oxygen, hydrocarbons and argon. The schematic of the assembly of the charcoal trap is shown in figure 1.

![Fig. 1. Schematic of pretreatment stage charcoal trap assembly.](image)

The pretreatment stage consists of two turbo molecular vacuum pumps along with two charcoal traps with interconnected tubings, valves and vacuum gauges. All the interconnected tubings are ¼” SS tubes and the valves are Swagelok SS 4L valves. The vacuum gauges used are compact full range gauges (Pfeiffer).

Sample collected from the pretreatment stage in a cylinder that was evacuated to a vacuum level of $10^{-6}$ mbar using TMP 2 with V8, V9 and V10 valves open. The charcoal traps were first evacuated to a vacuum level of $10^{-5}$ mbar with use of TMP 1 and V4, V5 and V6 open. While evacuating the charcoal traps V3 and V7 are kept closed. When the vacuum level in the charcoal traps reached to the desired level, liquid nitrogen was poured to the containers followed by closing of V4 and V6. Valve V5 was kept close and sampling bottle (S2) is evacuated to $10^{-6}$ mbar. After a time of about 10 minutes allowed for cooling the charcoals, valve V2 and V3 and V5 are opened and the field sample was allowed to pass through the first trap and vacuum decreases. After few minutes valve V6 was opened to allow the sample gas to pass the second charcoal trap. With liquid nitrogen cooled charcoal, most of the impurities like moisture, nitrogen, oxygen, hydrocarbons present in the sample get trapped up on the charcoal leaving relatively pure helium sample. At this stage vacuum inside the charcoal trap was of the order of few mille-bar. After done this valve V7 and V8 was opened while V9 and V10 were kept closed and the helium sample was collected in a 5 ml SS sample cylinder for further cleaning. 5 ml of the relatively pure helium sample was collected at a vacuum pressure of $10^{-2}$ mbar from the pretreatment stage.

2.2 The Sample Preparation system

Figure 2 shows the schematics of the high vacuum sample preparation system. The interconnecting vacuum tubes are fabricated from ¾” SS pipes. The whole system is assembled on a table top for easy access and operation.
The sample preparation system is an all metal high vacuum system consists of the following components:

1: Turbo-molecular drag vacuum pump (Pfeiffer, 60 l/s) with two stage diaphragm backing pump
2: StarCell Ion pump (Varian, 20l/s) for clean vacuum
3: SAES NP10 zirconium getter pumps (Zr 84 wt%, Al 16 wt%) in jackets that can be water cooled
4) Ultra low volume micro ion gauge (Granville Phillips)
5: Liquid nitrogen cooled cold finger (0.5" dia, 4" long)
6: All metal UHV valves (Varian)
7: SS manifold (volume 355 cc). The turbo molecular drag pump has a DN63CF inlet port and the ion pump has a DN40CF inlet port. The all metal valves have DN16CF connections. The pumps, gauges, cold finger were connected to the SS manifold using the all metal valves. The total volume of the gas preparation line including the getters is 355 cc. There are two inlets lines to enable admission of the sample gas to final clean up line. Each of the inlets are pumped by turbo molecular pump backed by diaphragm pump and are fitted with NP10 getter pump.

Sample from the pretreatment stage collected at a pressure of \( \sim 10^{-2} \) mbar and expanded in a 1000 cc SS cylinder. The cylinder was first evacuated using a turbo molecular pump to a vacuum pressure \( \sim 10^{-7} \) mbar and isolated from the pump by closing valve V19. The vacuum pressure was monitored using a pirani vacuum gauge. The sample gas from the 5 ml cylinder transferred to the 1000 cc cylinder by opening valve V18 and allowed to expand and the sample gas pressure decreases from \( 10^{-2} \) mbar to \( \sim 0.5 \times 10^{-4} \) mbar.

Helium sample from the 1000cc cylinder at a pressure \( \sim 10^{-4} \) bar was introduced through one of the inlet port using a 0.1 cc pipette with valve V16 open. The sample gas exposed to the four getters, the ion pump and the cold finger at a vacuum pressure of \( \sim 10^{-8} \) mbar via opened valves V1, V4, V11 and V17. Since the internal volume of the sampling system including the getters is 355 cc the pressure will reach to \( 1 \times 10^{-6} \) mbar. At this time the turbo pump was isolated from the manifold via closed valves V2, V10 and V14. Expansion of 0.1 cc of the sample in the manifold occurs and pressure of the sample gas drops to \( \sim 1 \times 10^{-6} \) mbar. Sample gas at a pressure of \( 10^{-6} \) mbar is not suitable to inject into the mass spectrometer. The valve V9 was closed to trap the sample in two getters (volume 103 cc) and the remaining manifold was evacuated by opening valve V2, V10 and V17 by turbo pump. Again on improvement of vacuum pressure to an order of \( 10^{-5} \) mbar, the turbo pumps are then isolated from the manifold and V9 was opened to expand the trapped sample gas further. By this time the sample gas pressure further drops to \( \sim 2 \times 10^{-7} \)
mbar. As the sample gas exposed to the four getter pumps remaining active gases are caught in to it. With the cold finger the remaining moisture etc. are cleaned up. At this stage the sample gas in the gas preparation system is ready for inject into the mass spectrometer for analysis. The mass spectrometers flight tube with inlet pipe has a volume of 1275 cc, and kept at a vacuum of \( \sim 10^{-9} \) mbar. With opening of the inlet valve V3 sample get injected to the mass spectrometer. Prior to injection of the sample: turbo pump, ion pump, cold finger and the getters are isolated from the manifold with closing respective valves. The injected sample expands into the mass spectrometer and final vacuum pressure during analysis was of the order 5 X \( 10^{-8} \) mbar. Figure 3 shows the enlarged view of the sample preparation system along with the assembly with the mass spectrometer. Figure 4 illustrates the relative intensities of helium - 3 and helium - 4 of air sample analyzed with the mass spectrometer.

Fig. 3. The sample preparation system

Fig. 4. Intensity of helium -3 and Helium -4 in air sample
3. Conclusion
Several helium samples collected from various geothermal fields in West Bengal, Jharkhand, Bihar and Odisha were analyzed successfully for helium isotope ratio. The developed sample preparation system is efficient to deliver clean samples of helium at a suitable vacuum pressure for representative isotopic ratio analysis.

Acknowledgement
We are thankful to Department of Atomic Energy, Government of India, for supporting this research work.

References
[1] Das N K, Ghose D, Bhandari R K, Sen P and Sinha B 2009 Current Science 96 pp 1031-1032
[2] Beyerle U, Hertig W A, Imboden D M, Baur H, Graf T and Kipfer R 2000 Environ. Sci. Technol. 34 pp 2042-2050
[3] Jenkins W J, Lott D E, Cahill K, Curtice J and Landry P 2010 The Go-Ship Repeat Hydrology Manual: A Collection of Expert Reports and Guidelines 134 14