ENRICHMENT OF OXYGEN-18 ISOTOPE BY FRACTIONAL DISTILLATION

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FRAKSİYONEL DİSTİLASYON İLE OKSİJEN - 18 İZOTOPUNUN ZENGİNLEŞTİRİLMESİ

Abstract:

In the scope present study, fractional water distillation column operating under vacuum, with a height of 200 cm and a diameter of 3 cm, was designed and manufactured from Pyrex glass. Column was operated at an evaporation/condensation rate of 120-140 ml/min and a feed flow rate of 0.5-10 ml/min at 52 °C under -0.8 bar vacuum pressure. Oxygen-18 isotope ratios were determined using Isotope Ratio Mass Spectrometry (IR-MS). Results of the IR-MS analysis indicated that maximum relative O-18 isotope enrichment in distilled natural water was 28-90 ppm. The data gathered from the fractional water distillation column designed in this study was not available in the literature. The operation parameters of such fractional water distillation column has not been reported before due to the fact that the column system designed in this study is much smaller in scale than the similar column systems reported in literature.

Özet:

Bu çalışmada, vakum altında çalışan 200 cm yüksekliğinde ve 3 cm çapında fraksiyonel su destilasyon kolonu tasarlanmış ve pyrex camdan imal edilmiştir. Kolon; -0.8 bar, 52° C'de 120-140 ml/dk buharlaşma/yoğunlaşma ve 0.5-10 ml/dk besleme hızlarında damıtılmış su (distilated water) ile çalıştırılmıştır. Oksijen-18 izotop oranlarının analizi İzotop Oranı – Kütle Spektrometresi (IR-MS) cihazı ile yapılmıştır. Yapılan deneyler sonucunda; damıtılmış suda ki doğal O-18 izotop miktarında 28-90 ppm aralığında artış olduğu ölçülmüştür. Bu tip bir fraksiyonel su damıtma kolonunun çalışma parametreleri daha önce literatürde raporlanmamıştır çünkü bu çalışmada tasarlanan kolon sistemi literatürde bildirilen benzer kolon sistemlerinden çok daha küçüktür.

Keywords: Stable Isotope, Oxygen-18, Fractional Distillation, Isotope Enrichment, Vacuum Distillation.

Anahtar Kelimeler: Kararlı İzotop, Oksijen-18, Fraksiyonel Destilasyon (damıtma), İzotop Zenginleştirme, Vakum Destilasyonu.

1. Introduction

As it is well known the stable isotopes are nonradioactive chemicals with no emission of ionized radiation. Oxygen is naturally composed of three main stable isotopes which are $^{16}O_2$ (99.727%), $^{17}O_2$ (0.04 %) and $^{18}O_2$ (0.20 %), atomically. Moreover, among of these, the $^{17}O_2$ and $^{18}O_2$ isotopes, are also mainly used in, climate, temperature change and medicine based researches in atmospheric studies. In addition to this; natural water is found as a composition of, $H_2^{16}O$ with a lower boiling point at 100^0C, and $H_2^{18}O$ with a higher boiling point at 100.14 ^0C, in nature (Goncharuk, 2014).

The demand for $^{18}O_2$ enriched (> 90%) water especially in medical area, has an increasing trend in recent years. For example, the $^{18}O_2$ enriched water used as a target material in proton accelerators; is preferred for the synthesis of radiopharmaceutical, Flourodexoyglucose (FDG) containing β radiating ^{18}F with a half-life of 109.8 min, which can be utilized as a diagnostic material in positron emission tomography (PET) (Khalil, 2017).

After Lewis and Cornish discovered the difference between the vapor pressures of $H_2^{16}O$ and $H_2^{18}O$, in 1933, the enrichment studies of $^{18}O_2$ with distillation were begun (Lewis and Cornish, 1933). For the first time in 1937, large-scale oxygen-18 enrichment was carried out by fractional distillation technique by Huffman and Urey. In this study, tray typed steel column with a height of 10.7 m was used. This column was filled with 200 ml of water and after being run for 70 hours, 5 times more enriched product than natural water was obtained (Huffman and Urey, 1937). Later, the enrichment of $^{18}O_2$ with the water distillation method was carried out by Thode, Smith and Walkling (1944), Dostrovsky, Hughes and Llewellyn, (1948), Dostrovsky, Llewellyn and Vromen (1952), Kistemaker, Bigeleisen and Nier (1957).

Another method used to enrich the oxygen-18 isotope is the process of enriching the oxygen and the carbon monoxide gases by thermal diffusion (Ageev and Panchenkov, 1963). In addition, the $^{18}O_2$ isotope can be enriched by water electrolysis (Ogden, 1935) and chemical exchange methods (Taylor and Bernstein, 1947).

Beside of these methods, laser enrichment of $^{18}O_2$ in oxygen gas was studied in 1994 by Tetsuro et al. (Tetsuro and Kyoko, 1994). In 2009, Takashi et al. proposed a new method that combines both distillation and laser enrichment for enrichment of $^{18}O_2$ within the ozone gas (Takashi and Hitoshi, 2009).

Among all aforementioned methods, fractional distillation is very crucial. Generally, Oxygen-18 is enriched with cold fractional distillation of nitrogen oxide (NO) and fractional distillation of water. Although the reported separation factor value, α, is 1.03 at 77 K for the fractional distillation of nitrogen oxide, these systems are not currently being operated because of the corrosive and toxic nature of NO. Furthermore, the requirement of good thermal isolation in order to keep the temperature at 77 K during operation is another disadvantage for these systems. Nevertheless, for the fractional distillation of water at T = 330 K, separation factor is 1.0037. As the operation temperatures are higher, fractional distillation of water is more economically efficient than the cold distillation of nitrogen oxides (Kim, Choi, Chang and Choi, 2008). The fractional distillation of the water is carried out in a vacuum environment. Although the vacuum systems are generally very difficult to operate, achieved separation factor values are higher in vacuum environment as compared to those at atmospheric pressure environment. Additionally, as the boiling temperature of the water is lower under vacuum, fractional distillation in the vacuum environment is preferred. In the fractional distillation columns, fillers and structural fillers of various shapes are used. The theoretical plate number in these columns

ranges from 400 to 600 (Dostrovsky, Llewellyn and Vromen, 1952). Under vacuum or atmospheric pressure, liquid isotopic mixtures that have close boiling points can be separated with these columns as a result of small differences between their boiling points. In cryogenic fractional distillation, gas isotopic mixtures are used instead of liquid isotopic mixtures, as opposed to fractional distillation (Pop et al., 2006). In the cryogenic fractional distillation column, similar fillers are used as in the case of fractional distillation column (Pop et al., 2006). These gas entrances are liquefied at very low temperatures and $^{18}O_2$ are separated using the small differences in the boiling points of the isotopes. In the cryogenic fractional distillation process, the separation factor is higher than the achieved separation factor values at fractional distillation, whereas the column height is shorter. However, the operation of such columns is considerably difficult (Pop et al., 2006).

Other than these, $^{18}O_2$ enrichment studies that combines the membrane diffusion and water distillation were carried out in 2009 (Kim, Chang and Choi, 2009).

Among all the previously mentioned processes, the distillation of water and cryogenic distillation of liquid oxygen and nitrogen oxide systems have been industrially established and are still in operation today. The water distillation method offers several advantages in terms of economic, technical and transportation along with the storage of $^{18}O_2$ in the form of water.

In this study, a laboratory-scale fractional distillation column made of Pyrex was designed and installed. The active working length of the column was 180 cm which is shorter than that of other column systems reported in the literature. The fractional distillation column, which is filled with Propack filler, was operated under vacuum. To the best of our knowledge, the designed column system has been used for the first time in our country.

2. Material and Method

2.1. Design of Fractional Distillation System

The continuously evaporated water coming from boiler passes through the column unit and goes to the condenser. In the meantime, the vapor created film layer deposited on the packing material in column, causes mass transfer. During this continuous cycle; feed of water vapor in condenser, becomes poor in terms of ^{18}O and this residual water and finally accumulates in the distillation reservoir with the help of natural gravity (Figure 1). The fractional isotope separation factor, α, in such type of columns at 20^0C is given by the following formula,

$$\alpha = \frac{(^{18}O/_{16}O)_{liquid}}{(^{18}O/_{16}O)_{vapor}} = 1.0098 \qquad (1)$$

The system seen in Fig.1 is mainly composed of the following parts:

    i.   Boiler

    ii.   Filled tray type mass transfer column made of Pyrex glass

   iii.   Chiller

    iv.   Vacuum system

    v.   Reflux system
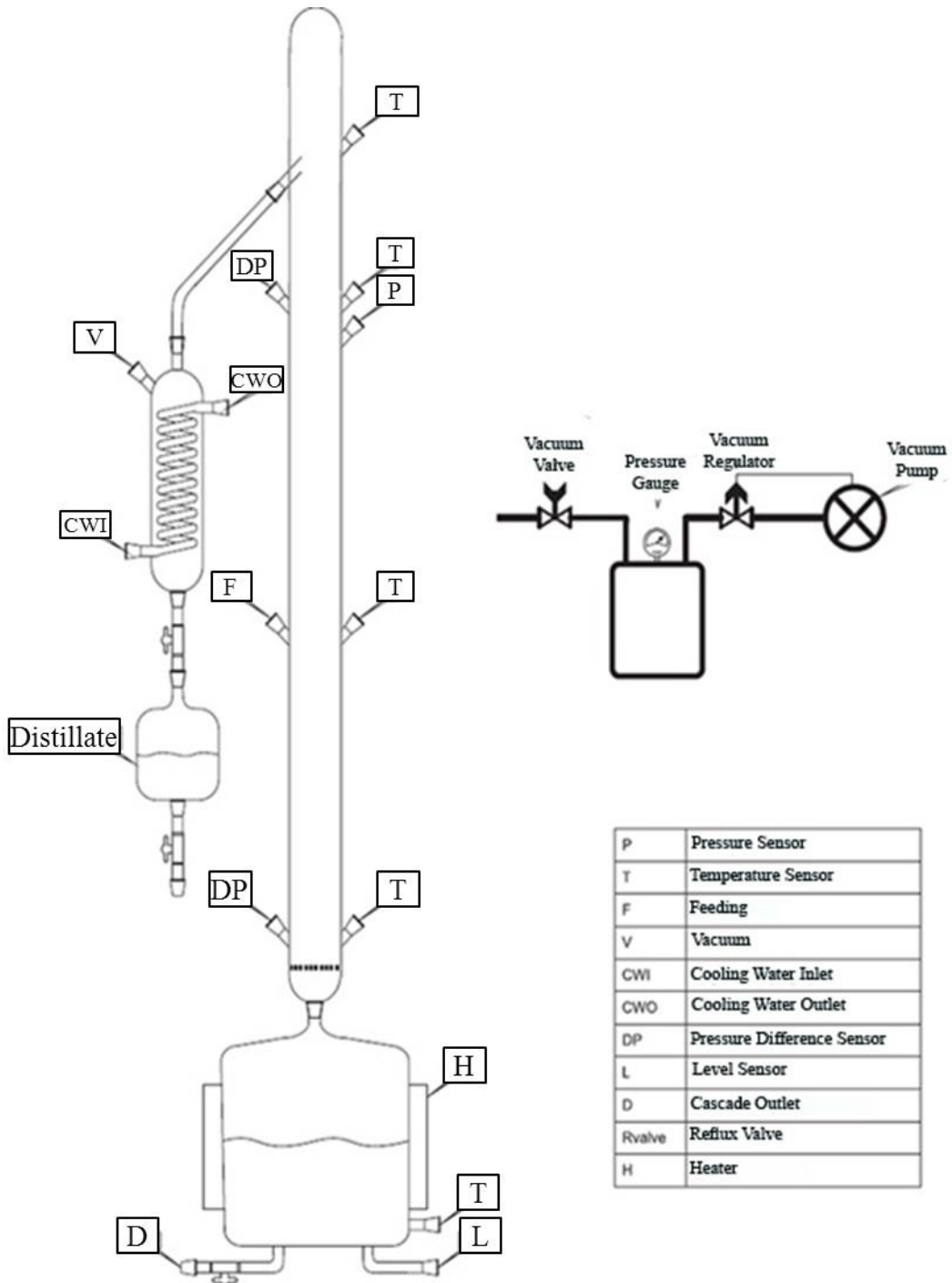
vi.   Distillation reservoir

Figure 1. Schematics of vacuum type fractional distillation column system.

As it is well known, the choice and stacking of the packing materials are extremely important points in fractional distillation process. In this study, an experimental small scale filled tray type column system working under vacuum conditions has been designed and constructed (Figure 2).

Figure 2. Filled Tray Type Column System.

2.2. Boiler and Level Control

Water level in the cylindrical boiler with 4 cm of diameter and 35 cm of height, made of tempered Pyrex glass; was controlled with PID level meter having an Efactor Model level control element, monitored via computer system. This element was placed at a certain level from the bottom of the boiler. The outer surface of the above mentioned boiler was completely wrapped with a PID controlled flexible plate type heater also. This boiler was also thermally insulated against any probable heat leakage. The volume of water within the boiler was tried to be kept stable at 300 ml during the experiments. In case of water exceeding the above this value; the excess water was drawn with PID controlled peristaltic pump to feed tank.

2.3. Filled Tray Type Transfer Column

Mass transfer in distillation processes can be realized with randomly or regularly placed packing materials according to the size of the column used. For example, randomly packing technique is preferred for columns with small diameters (< 250 mm).

In this study, a cylindrical tube type with 200 cm of height (180 cm of "active working area" height, i.e. the part where the exchange reactions take place) and 3 cm diameter made of Pyrex glass, column was designed (Figure 2). However as it can be found in literature, the most of the similar studies were realized with larger scale systems such as generally at least with approximately 10 m height and 5 cm of diameter (Dostrovsky, Hughes and Llewellyn, 1948). The system had three temperature sensors placed at bottom, middle and top sections respectively as seen in Figure 2. The bottom and the top of the distillation column were equipped with two vacuum sensors. The bottom and the upper parts of the active working area

were filled with the size of $\dfrac{1''}{4} \times \dfrac{1''}{4}$ Propack packing material with 5 cm of height and, another 5 cm of Propack materials with $\dfrac{1''}{8} \times \dfrac{1''}{8}$ in size were also added following the previous filling materials. The rest of this column i.e. the middle part of it, was filled via $\dfrac{1''}{16} \times \dfrac{1''}{16}$ of steel braided type Propack fillers again.

The fractional column system working under vacuum conditions (-0.8 bar), was also wrapped with 1 kW of flexible plate type heaters which enable a considerably homogenous heating of the temperature controlled column system and also prevent the condensation of water in the inner parts of this column during the whole exchange operations.

2.4. Chiller

The water vapor passing rising and through the column in upward direction produced in boiler was condensed with the help of double glazed condenser cooled at 3-7 ^{0}C by a closed cycle chiller, and transferred to distillation reservoir (Figure 3).

Figure 3. Double glazed condenser and distillation reservoir.

2.5. Vacuum System

The column of the fractional water distillation system was evacuated from its upper section by a mechanical rotary pump, equipped with a relay controlled reservoir placed in between pump and column line, to prevent continuous run of vacuum pump itself. In case of any pressure increase in the vacuum reservoir, rotary pump starts to run to maintain the vacuum in the column to its set value (called; "on/off system"). As it's very well known, the isotope separation factor critically depends on the lowest possible absolute vacuum value which can be attained within the column. Thus, the vacuum value was tried to be kept around 0.2 bars during

the experiments. However, there are some studies in literature reported the absolute vacuum values as about 0.173 bars (Kistemaker, Bigeleisen and Nier, 1957).

2.6. Reflux System and Ratio

Reflux ratio is defined as the ratio of the liquid returned to the column to the liquid taken as product from distillation medium. If this ratio is high in liquid systems with very close boing points with respect to each other, then the separation factor i.e. enrichment tends to be higher. Huffman and Urey reported in their study that they achieved to reach to 22:1 ratio with their cascaded column system (Huffman, 1937). However, reflux rate has also an economically optimum value since an increase in reflux rate results a decrease in the amount of enriched water with heavy oxygen. In addition, the process could not be economical due to waste of energy and time, so far. Therefore, determination of an optimum reflux rate is primarily important for a dedicated system due to the above mentioned points.

The evacuated fractional system used for ^{18}O enrichment purposes have the column lengths around 10 m as can be seen in literature (Dostrovsky, Hughes and Llewellyn, 1948). Since the column length (i.e. height) used in this study was chosen as max. 2 m due to the physical limitations of our laboratory, higher reflux rates could not be attained in our results.

The system was designed and constructed as an internally controlled reflux system initially, but the "on/off system" caused an intermittent return of water to column, which braked down the steady state nature of the column system itself and expected reflux values were never reached during any stage of the experiment. Therefore, the system was redesigned as an "externally controlled reflux" type in which dosage was sustained with dosage pump running with lower flow rate. The dosage pump working under vacuum conditions was calibrated after a long term of trials during our preliminary studies. The water with light oxygen content was accumulated in distillation reservoir and used as a feedback supply to system which was held in steady state because of the nature of this continuous feedback mechanism.

2.7. Evaporation-Condensation Rate:

Another critical parameter in the enrichment is the control of the speed of the evaporation and the condensation rates. As it was indicated previously, evaporation was realized with 1 kW of PID controlled flexible heater wrapped around cylindrical boiler placed under the thermally stabilized column. Besides, the temperature profile was monitored and controlled by three thermocouples placed at different points along with the column.

The vapor obtained from the boiling distilled water at 52^0C in boiler, passing through packing materials going to the jacked Pyrex condenser at the upper part of the column, was condensed and accumulated in the distillation tank, as it was mentioned in section 2.1.3. The temperature profile was tried to be sustained as $52\text{-}46^0$C from boiler throughout the column (i.e. from bottom to the top).

While the vapor coming from boiler and passing through the fractional distillation column, it reacts with liquid film layer on the packing material and creates a mass transfer. In this study, the system was reached to steady state after 10-15 hours of running cycle. Finally, vaporization and condensation rates became steady-state by the end of this period of time, as expected.

2.8. Liquid Feeding System

Approximately a total amount of 2 liters of distilled water in the feed tank (Figure 1) was fed into the system from the top of the column (over the packing materials) at a flow rate of 0.5 - 10 ml/min with the help of an automatically controlled peristaltic pump. Small fluctuations were detected at lower feeding rates, as predicted.

3. Results and Discussion

The operation of our continuous system was realized according to the following steps;

- Filling of boiler up to 300 ml with controlled peristaltic fed pump.

- Initialization of vacuum system manually, gradually and setting it to 0.8 bars (absolute 0.2 bars)

- Setting of the temperature values in computer program and actuation of heaters

- Starting up the closed cycle chiller

- Running of the system at minimum reflux rate in order to prevent the air bubble formation of water at connectors of the distillation reservoir.

- Reflux pump is on, according to its present value.

Then the fractional distillation column reached to its steady state within 10-15 hours following the above listed procedure. In the first steps of our study, condensation rates were determined by running the system for a short period of time at different boiler temperatures. These values were listed in Table 1.

Table 1. Condensation Rates at Different Boiler Temperatures.

Boiler Temperature °C	Condensation Rates ml/hours
50	20
52	118
54	186

As it is seen from Table 1, the condensation rates were measured as 20 ml/hours at 50^0C and 186 ml/hours at 54^0C, respectively. The temperature is a critical parameter in distillation as it is well known. It was thought that, at higher condensation rates, i.e.186 ml/hours, there might be accumulation of water inside the column, so mass transfer and enrichment would decrease. Therefore, the system was kept at 52^0C during the whole experiments. Positions of the temperature sensors mounted along the column were annotated as "T" in Figure 1. Temperatures from bottom to top along with the column were measured as 52^0C (boiler), 50^0C, 48^0C and 46^0C, respectively. During the experiments, boiler temperature was set at 52^0C. After

long term of trials and operations with minimum reflux ratio at this temperature value, the condensation rate of water was determined as 120-140 ml/hour.

Five different types of main trials were realized in the scope of our study. Following each trial, samples taken from feed-water tank, boiler (heavy fraction) and distillate (low fraction) were analyzed in terms of their isotope contents by Isotope ratio Mass Spectrometer (IR-MS) and the results were given in Table 2.

Table 2. Experimental Parameters and Results

PARAMETER	RESULT OF EACH EXPERIMENT NUMBER				
	1	**2**	**3**	**4**	**5**
Average Column Pressure (bar)	-0.800	-0.800	-0.800	-0.800	-0.800
Average Feed Flow Rate (ml/min)	10	5	5	2	0.5
Boiler Temperature (°C)	52	52	52	52	52
Average Pressure Difference (bar)	-0.020	-0.021	-0.021	-0.021	-0.020
Boiler Level (ml)	300	300	300	300	300
Initial Amount of Water in Feed-Water Tank (ml)	2700	2500	1700	1700	1700
Duration of Experiment (Hours)	15	19	70	59	87
^{18}O Concentration in Distilled Water (ppm)	1984.69	1984.69	1984.69	1984.69	1984.69
^{18}O Concentration in Distillate (ppm)	1977.09	1979.01	1973.76	-	-
^{18}O Concentration in Boiler (ppm)	2012.36	2015.21	2024.71	2017.27	2075.18
Amount of Enrichment in Boiler (ppm)	28.07	30.92	40.42	32.98	90.89

In the first experiment (Experiment 1), water feed rate was set to 10 ml/min, but it is observed that this higher rate caused an excess accumulation of water in the boiler and so, low level of enrichment in O^{18} which was about 28 ppm. This low level enrichment was also due to the imbalance of liquid-vapor in column's active working area. In the following experiment (Experiment 2), feed rate was set to 5 ml/min, and feed-water tank was filled with 2500 ml of water but the achieved results were still not sufficient for an enrichment study. Following these

experiments, keeping the feed rate fixed at 5 ml/min and lowering the initial amount of water (1700 ml) in the tank resulted in an increase of ~10 ppm in the ^{18}O concentration value in boiler. As opposed of this result, it was observed that further decrease in fed rate i.e. ~2 ml/min caused a certain decrease in the enrichment. All the results obtained up to this stage were showed that liquid-water equilibrium in column could not achieved yet. To overcome this difficulty, the feed rate was lowered and set to 0.5 ml/min by holding the amount of water in boiler at 1700 ml fixed, and running the system for 87 hours. Then, all caused a three times of increase of the enrichment by comparing to the feed rate of 2 ml/min.

4. Conclusion

In the present study, column pressure, boiler temperature, amount of product and water in boiler were tried to be kept fixed throughout the experiments. As it was shown in Table 2, water was enriched with regard to ^{18}O by ~91 ppm after 87 hours of running of fractional distillation column system. Since the isotope ratio ^{18}O to ^{16}O at vapor phase was not measured, the separation factor of the existing column system could not be calculated.

5. Acknowledgments

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