

## EXPERIMENTAL PLANT FOR $^{18}\text{O}$ SEPARATION BY CRYOGENIC OXYGEN DISTILLATION

Floarea POP, Iuliana PICIOREA, Mariana ILIESCU, Mihai CULCER,  
Cornelia CROITORU, Ioan STEFANESCU

National R&D Institute for Cryogenics and Isotopes Technologies ICIT Ramnicu Vâlcea  
Uzinei no.4 Street, mail code 240050, PO 4, POB 10, Rm. Vâlcea, Romania, <http://www.icsi.ro>  
e-mail: [pop.floarea@icsi.ro](mailto:pop.floarea@icsi.ro);

**Abstract** – The paper presents cryogenic laboratory distillation plant, built in our institute for oxygen isotopes separation studies and laboratory experiments stage. ICIT Rm. Valcea research regarding  $^{18}\text{O}$  separation was begun with the water distillation. Subsequently they were directed to oxygen distillation too. This choice can be explained by higher separation factor than at water distillation, the absence of toxicity and existence of inexpensive raw material, because these plants can be grafted on the air separation plants. A very important utilization of oxygen-18 is in medicine, in positron emission tomography (PET) as precursor for  $^{18}\text{F}$  production. This utilization has increasing the worldwide demand for oxygen-18.

**Keywords:** isotope, oxygen-18, cryogenic distillation.

### 1. INTRODUCTION

Oxygen-18 is used as tracer in chemistry, in biomedical applications, for environmental and hydrology studies. A very important utilization of oxygen-18 is in medicine, in positron emission tomography (PET) as precursor for  $^{18}\text{F}$  production. This utilization has increasing the worldwide demand for oxygen-18.

Oxygen isotopes can be separated by distillation, thermodiffusion, chemical exchange or membrane diffusion processes. Just distillation and thermodiffusion were used to produce  $^{18}\text{O}$  at large scale. Because it realises with high-energy consumption, thermodiffusion is used to work with low quantities of materials. Isotope distillation can be performed at usual temperatures, the case of water distillation, or at cryogenic temperatures, the case of carbon monoxide and nitrogen oxide distillation. ICIT Rm. Valcea research regarding  $^{18}\text{O}$  separation was begun with the water distillation. Subsequently they were directed to oxygen distillation too. This choice can be explained by higher separation factor than at water distillation, the absence of toxicity and existence of inexpensive raw material, because these plants can be grafted on the air separation plants. In water distillation process simultaneously with  $^{18}\text{O}$  concentration it produces deuterium concentration (hydrogen isotope). In positron emission tomography

(PET) oxygen-18 is used like water ( $\text{H}_2^{18}\text{O}$ ). An other argument to develop oxygen distillation laboratory research is the elimination of intermediate stages necessary to break X-O chemical bonds (X = D, C, N). As a process, the cryogenic distillation is not different by the distillation at positive temperatures. However temperature conditions (90K) cause a series of particularities regarding the working techniques and equipments.

The paper presents in detail cryogenic laboratory distillation plant built for oxygen isotopes separation studies and the stage of laboratory experiments.

### 2. EXPERIMENTAL PLANT SCHEMA

Natural oxygen is a mixture of three stable isotopes with weight 16, 17 and 18, with the composition presented in Table 1 [1].

Isotope	Percentage (mol %)	Atomic weight
$^{16}\text{O}$	99,759	15,9949
$^{17}\text{O}$	0,037	16,9999
$^{18}\text{O}$	0,204	17,9991

Table 1: Oxygen isotopes

The oxygen isotopes separation by distillation is possible because the difference between vapour pressures of molecular species that hold these isotopes. The separation factor, defined as rate of vapour pressures of isotopes molecular species, is one of the quantities that characterize the separation process. A low value of this rate indicates a difficult separation. Oxygen-18 separation by distillation is more difficult than other cryogenic gas, deuterium for example, because it's separation factor is very small, table 2 [2].

	$^{16}\text{O}_2 - ^{16}\text{O}^{18}\text{O}$	$\text{H}_2 - \text{HD}$	$\text{H}_2 - \text{D}_2$
T (K)	90.18	20.39	
$\alpha$	1.0126	1.73	2.97

Table 2: Separation factor values

The experimental plant built for study oxygen isotopes separation, by distillation, is schematic presented in figure 1. This plant permits distillation column operation at constant pressure.

To ensure, at pressure  $P$ , the required vapour flow rate in column, it introduced in boiler the  $Q_{\text{boiler}}$  heat quantity. Because it is impossible to provide the total thermal insulation given to the open space, in the system penetrates the  $Q_{\text{ins}}$  heat quantity. The refrigerating capacity  $Q$  of cryogenic engine, that ensure the thermal agent in condenser, is constant. The difference between refrigerating capacity of cryogenic engine and cold quantity necessary for column,  $(Q_{\text{boiler}} + Q_{\text{ins}})$ , is compensated by the heat introduced in the condenser by means of a new

electric heat source, in accordance with the thermal balance equation:

$$Q_{\text{cond}} = Q - (Q_{\text{boiler}} + Q_{\text{ins}}) \quad (1)$$

Oxygen is a cryogenic gas that boils, in normal conditions, at 90.18 K, table 3 [1]. A condenser, cooled with liquid nitrogen provides the reflux for column. The column is operated at total reflux. In these conditions the liquid/vapour rate is known,  $L/V = 1$ .

For hydrogen isotopes separation it was used a similar distillation plant.

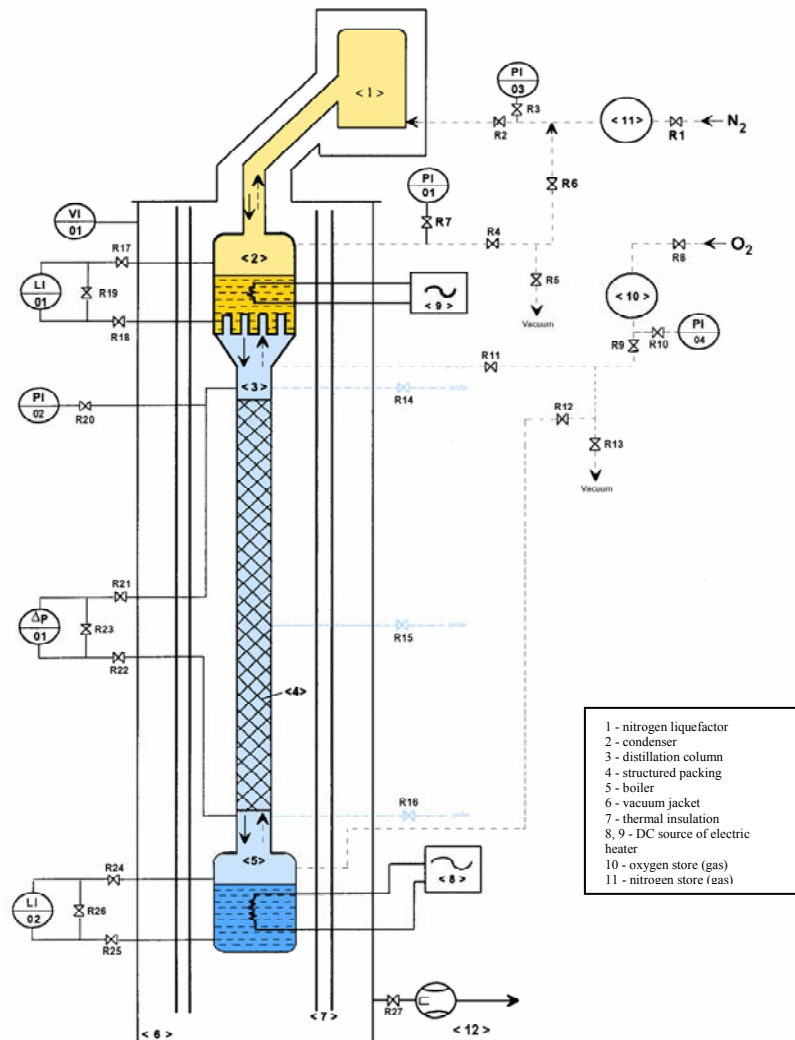


Figure 1. Schematic diagram of the oxygen cryogenic distillation plant

Characteristic quantity	Triple point		Boiling point		Critical point	
	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>
Temperature (K)	54,351	63,148	90,18	77,347	154,576	126
Pressure (bar)	0,00152	0,1253	1,01325	1,01325	50,4266	33,9996

Table 3. Fixed points of oxygen and nitrogen

### 3. EXPERIMENTAL PLANT

The experimental plant for oxygen isotopes separation is composed of cryostat, cryogenerator and control board. The cryostat is presented in figure 2. Its basic components, distillation column, condenser and boiler are presented in figure 3 and 4. These are introduced in a cold box with 465 mm diameter and a height of 1750 mm. The cold box is composed a fixed cylinder and two movable cylinders. They form the vacuum jacket of the cryogenic area. Distillation column has 37 mm inner diameter and is equipped with structured packing, on a height of 1000 mm. Structured packing introduces low pressure drop comparative with random packing. The plant has a vertical multitubular condenser that has 76 copper tubes of  $\phi 10 \times 2 \times 160$  mm. The vapours from condenser are liquefied by means of a cryogenerator with reversed Stirling cycle, at 80K level. The cryogenerator, shown in figure 5, used 99.9% helium

as working gas. Condenser jacket, of stainless steel, communicates with a liquid store, equipped with electric heater. This heated liquid store permits to maintain a constant temperature in column.

The electric boiler of plant, also of stainless steel, has a height of 230 mm and inner diameter of 55.5 mm at top and 80 mm at bottom.

The plant is operated manually, by apparatus assembled on control board, presented in figure 6.

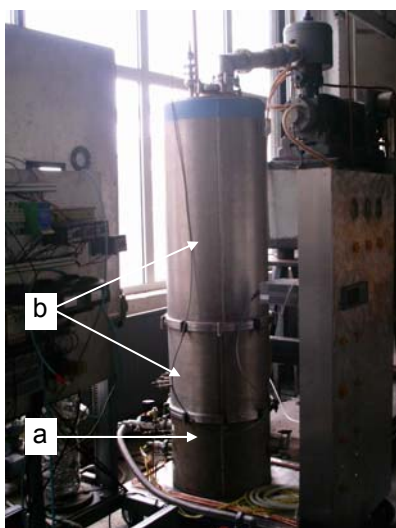


Fig. 2 Experimental cryostat  
a – fixed cylinder  
b – movable cylinder

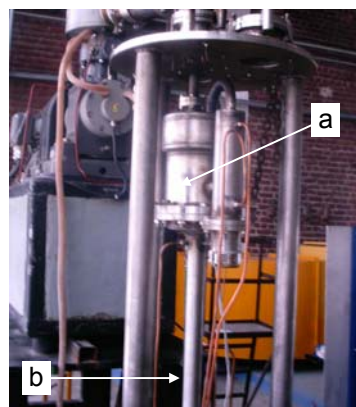


Fig. 3 Cryostat detail  
a – condenser  
b – column

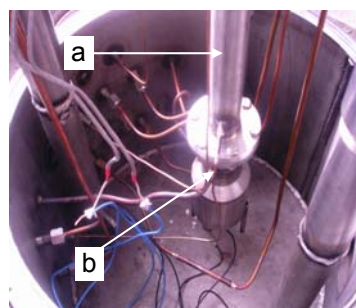


Fig. 4 Cryostat detail  
a – column  
b – boiler

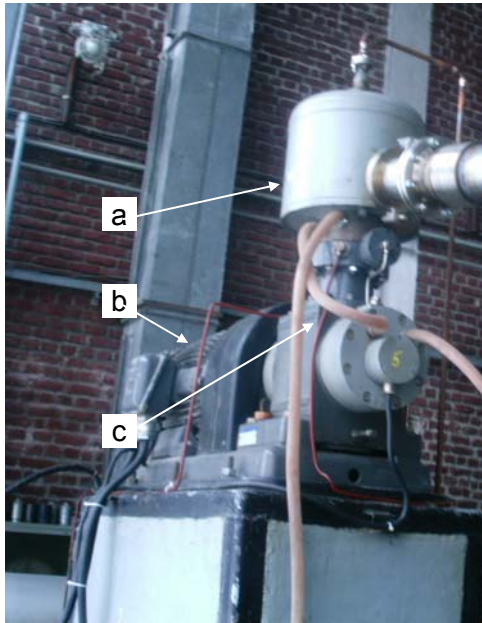


Fig. 5 Cryogenerator  
a - condenserhead  
b - motorul de antrenare  
c - carter

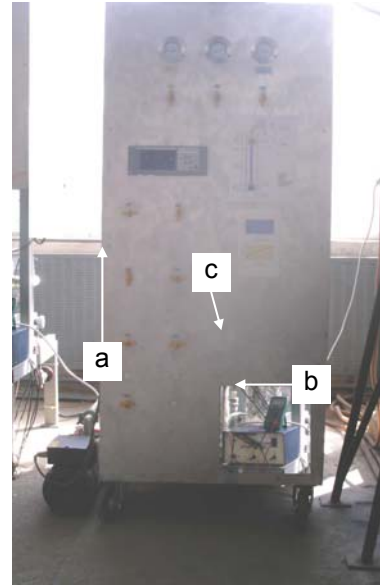


Fig. 6 Control board  
a - board  
b - supply source  
c - milivoltmeters

#### 4. RESULTS. EXPERIMENTAL STAGE

First experiments on the laboratory plant aimed at determination of useful refrigerating capacity ( $Q_u$ ). According to equation (1),  $Q_u$  is:

$$Q_u = Q - Q_{ins} = Q_{boiler} + Q_{cond}$$

At usual pressures for cryogenic distillation plants the condenser is able to work at  $\sim 25$  grade temperature differences, table 4.

Pcol	Tcol	Pcond	Tcond	$\Delta T_m$
bar	K	bar	K	K
1,0	90,1	1,0	77,2	12,9
		2,0	83,6	6,5
		3,0	87,9	2,2
		3,5	89,7	0,4
2,0	97,2	1,0	77,2	20,0
		2,0	83,6	13,6
		3,0	87,9	9,3
		4,0	91,2	6,0
3,0	102,0	1,0	77,2	24,8
		2,0	83,6	18,4
		3,0	87,9	14,1
		4,0	91,2	10,8

Table 4. Pcol = f( $\Delta T_m$ )

Because  $^{18}\text{O}$  separation factor is very low and by pressure increasing it decreases, distillation column is operated at pressure values closed of atmospheric level. To avoid the air entrance, by possible untightness, the plant work pressure will be a little bit upon atmospheric value. Water and other impurities from air solidify at column temperature and disturb condenser and column functioning. Table 5 presents the main operation parameters [3].

According to values from this table, the useful refrigerating capacity is 105.4 W. Subsequently decrease from 105.4 to 80.7 W, is caused by de solar radiation, the laboratory having large windows. Taking into consideration simplifying assumptions, 100% heat efficiency for immersed electric heater and adiabatic functioning of column, the vapour flow rate in column is calculated with relation:

$$w_v = \frac{4 \cdot Q_{boiler} \cdot v_v}{r \cdot \pi \cdot D_c^2} \quad (2)$$

where:

- $w_v$  – vapour flow rate, m/s
- $Q_F$  – introduced heat in boiler, kW
- $v_v$  – vapour specific volume at working pressure,  $\text{m}^3/\text{kg}$
- $r$  – vaporisation heat at working pressure, kJ/kg
- $D_c$  – column inner diameter, m

Time	P <sub>jacket</sub>	U <sub>boiler</sub>	Q <sub>boiler</sub>	P <sub>col</sub>	U <sub>cond</sub>	Q <sub>cond</sub>	P <sub>cond</sub>	Q
	mbar	V	W	bar	V	W	bar	W
11 <sup>58</sup>	6,8x10 <sup>-2</sup>	81,3	64,9	1,0	104	40,5	3,2	105,4
13 <sup>23</sup>	7,06x10 <sup>-2</sup>	81,6	65,4	1,4	65,4	16,0	4,0	81,4
14 <sup>00</sup>	6,8x10 <sup>-2</sup>	81,6	65,4	1,22	77,5	22,5	3,8	87,9
15 <sup>00</sup>	6,8x10 <sup>-2</sup>	81,6	65,4	1,22	755	21,3	2,6	86,7
16 <sup>00</sup>	6,8x10 <sup>-2</sup>	81,6	65,4	1,3	64	15,3	3,65	80,7
17 <sup>00</sup>	6,6x10 <sup>-2</sup>	81,6	65,4	1,2	64	15,3	3,4	80,7
17 <sup>30</sup>	6,6x10 <sup>-2</sup>	81,6	65,4	1,2	64	15,3	3,4	80,7

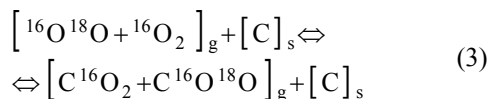
Table 5. Experimental data

In experimental conditions (table 5) the vapour flow rate was almost constant, above 5 cm/s, table 6. This value is in usual range for isotopes separation by distillation at cryogenic temperatures [4].

Time	Q <sub>boiler</sub>	P <sub>col</sub>	w <sub>v</sub>
	W	bar	cm/s
11 <sup>58</sup>	64.9	1.0	6.424
13 <sup>23</sup>	65.4	1.4	4.837
14 <sup>00</sup>	65.4	1.22	5.420
15 <sup>00</sup>	65.4	1.22	5.420
16 <sup>00</sup>	65.4	1.3	5.147
17 <sup>00</sup>	65.4	1.2	5.512
17 <sup>30</sup>	65.4	1.2	5.512

Table 6. Vapour rate in experimental column

The samples extracted from column were analysed by mass spectrometry. At the moment at these preliminary tests, <sup>18</sup>O analysis could not be done directly from oxygen samples, just from CO<sub>2</sub>. They were transformed in carbon dioxide by following chemical reaction:



In fact, from reaction between oxygen and carbon results CO too. <sup>18</sup>O from CO is not analysed. From this cause the analysis results have not true values; they will not be presented in this paper. On the basis of this analysis it was estimated a separation rate between column bottom and top of 1.2. In the second semester of 2006 year ICIT Rm. Valcea will put into service a new mass spectrometer that permit <sup>18</sup>O analysis from oxygen. Then the experiments on the oxygen distillation plant will be continued.

## 5. CONCLUSIONS

ICIT Rm. Valcea built-up an experimental plant to study <sup>18</sup>O cryogenic separation, by oxygen distillation. Preliminary tests emphasize stable functioning of the cryogenic distillation plant and possibility to growing the column vapour loading by boiler upgrading.

Isotopic concentration (<sup>18</sup>O) obtained by CO<sub>2</sub> analysis is affected by errors, introduced during chemical transformation of oxygen in carbon dioxide.

The experiments will continue in the second semestre of 2006, when ICIT Rm. Valcea will put in service a new mass spectrometer that permit <sup>18</sup>O analysis from oxygen.

## References

- [1] \* \* \*, *Encyclopedie des gaz*, Elsevier L'air Liquide, France, 1976
- [2] A. M. Rozen - *Teoria razdelenia izotopov v kolonah*, Ed. Atomizdat, Moscova, 1960
- [3] F. Pop, C. Croitoru, A. Bornea, M. Sidorencu, *Theoretical study regarding the use of cryogenic distillation at oxygen isotopes separation*, Research report, ICIT Rm. Valcea, nr. 10854/09.10.2003
- [4] F. Pop, C. Croitoru, M. Iliescu, M. Culcer, Gh. Dracea, *Preliminary tests to determine cooling capacity of the cryogenerator*, Research report ICIT Rm. Valcea, march., 2005
- [5] F. Pop, C. Croitoru, M. Iliescu, M. Culcer, Gh. Dracea, *Laboratory research regarding cryogenic separation of oxygen isotopes*, Research report ICIT Rm. Valcea, sept., 2005
- [6] Gh. Vasaru, *Tritium Separation*, Editura Dacia, Cluj-Napoca, 1987