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CARBON DIOXIDE PURIFICATION SYSTEM

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УСТАНОВКА ДЛЯ ОЧИСТКИ CO_2

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Аннотация

В работе рассматривается описание установки для получения двуокиси углерода (CO_2) высокой чистоты (лучше 99,99 %) из исходной CO_2 чистотой 99.8 – 99.96 %. В установке реализовано сочетание нескольких методов очистки: криогенного (вымораживание CO_2 с последующей откачкой примесей), адсорбционного (осушка цеолитом) и хемосорбционного (поглощение кислорода активной медью, нанесенной на силикагель). Применение криосорбционного насоса для откачки на стадии вымораживания гарантирует отсутствие в конечном продукте следов масла. Описан процесс очистки и регенерации основных блоков установки. Для экспресс-анализа результатов очистки CO_2 использован метод газовой хроматографии.

Abstract

Carbon dioxide (CO_2) purification system intended to produce CO_2 with the high purity (better than 99.99 %) from 99.8 – 99.96 % initial gas is considered. The combination of different purification methods is applied: cryogenic (freezing of CO_2 with the subsequent pumping of impurities), adsorption (drying by zeolite) and chemo sorption (oxygen sorption with activated copper carried by silica gel). The use of a cryopump at the freezing stage for evacuation allows producing oil free carbon dioxide. The purification procedure and regeneration of set-up basic units are described. Gas chromatography method for fast CO_2 analysis is used.

Introduction

The tests of new detectors created by PNPI for the CMS [1], Atlas [2] and others projects [3] required the use of carbon dioxide with purity about 99.99 %. The best CO_2 from available in Russia standard grades has the purity of 99.96 %. Pure carbon dioxide delivered from abroad has a high cost. Therefore we decided to solve the problem of pure CO_2 production using Russian cheap standard Carbon Dioxide and the combination of different methods for its purification. The purification process of standard (99.96 % or 99.80 %) CO_2, or even less qualitative (< 99 %) gas is described below.

1. System design

The CO_2 purification system gas scheme is shown in Fig. 1. The system includes: 40 l Measuring cylinder, preliminary dryer (Dryer), multifunction unit consisting of dryer and oxygen purifier (H_2O&O_2 Purifier), two 2 l freezers (Freezer and Additional Freezer), Cryopump, mechanical roughing pump with a liquid nitrogen trap (Vacuum pump), Freezer-Storage, 50 l Dewar for Cryopump and Freezer, manual valves MV1 – MV11b, bypass manual valve MVB, pressure indicators PI0 – PI2, ionization vacuum gauge BT-2A, pressure-vacuum indicator PVI1. There are several additional units not shown in Fig. 1: a blower equipped with an electric heater for freezers heating and 500 l liquid nitrogen tank. Unrefined liquid Carbon Dioxide is delivered in 40 l standard steel cylinders (Unrefined CO_2 in the scheme). Equilibrium gas pressure inside the unrefined cylinder is about 5.0 MPa (it depends on the room temperature). Refined gas is accumulated to a specially prepared 40 l stainless steel cylinder (Pure CO_2). The gas scheme of installation may be conventionally divided by two parts. On the left of the MVB valve a preparation part (dosing and preliminary drying) is shown. On the right of the MVB valve the fine purification part is located.

A scheme of H2O&O_2 Purifier unit is shown in Fig. 2. The unit includes two cartridges (dryers). The dryers are made from the stainless steel tube with 35 mm outside diameter, 3 mm wall thickness and 330 mm length. Each dryer contains 170 grams of molecular sieve adsorbent (zeolite NaX). This amount enables the system to remove about 35 grams of water vapor and to dry the gas down to 1 – 2 ppm level at the room temperature.

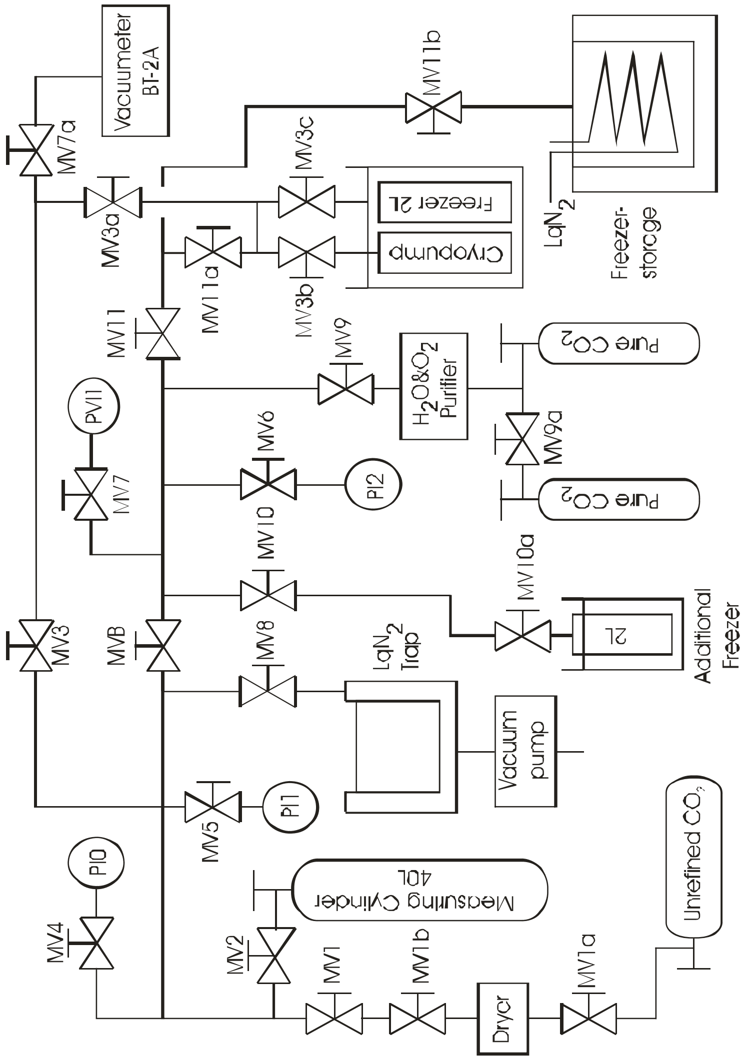

Fig. 1. Simplified flowchart of the system

The filters are installed upstream and downstream of the adsorbent to prevent entering of the particles to the gas flow. The heating elements are placed outside of the dryers. As the thermal insulation a fiberglass tissue is used.

The dryers are regenerated by heating to 350 °C simultaneously with the purging of Nitrogen. A temperature transmitter (TT) is installed outside of the dryer. It is connected to the temperature controller TC2 that supports the dryer temperature at the set point during the regeneration process.

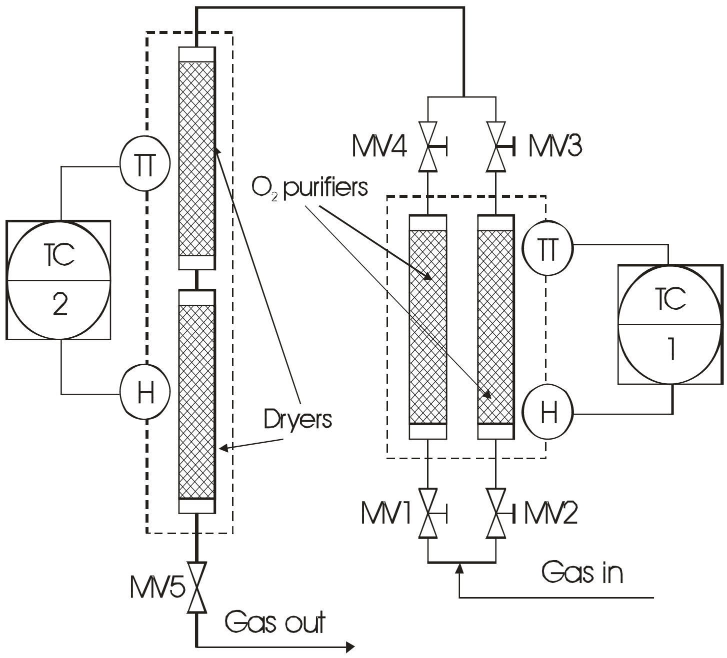

Fig. 2. Simplified flowchart of H2O&O_2 Purifier

There are two purifiers in the system. First one operates while the second one is a spare. They are combined into single unit because their operating and regenerating temperatures are equal (200 °C). Temperature of the unit is handled with the temperature controller TC1.

The Purifiers design is similar to the dryers. Both of them are filled with the pure copper applied on Silica gel granules. Thus Oxygen removal in the Purifiers is provided with the copper oxidation. After saturation the heated Purifiers are regenerated with Hydrogen purging.

Preliminary Dryer (similar to the H2O&O_2 Purifier unit) is the cartridge filled with NaX zeolite. This unit is regenerated with dry nitrogen at 350 °C temperature supported by the purifier unit temperature controller TC2.

To provide the more deep regeneration of the dryers and the purifiers, they are pumped with the roughing pump down to 10 Pa at their regenerating temperature.

The design peculiarities of Cryopump are shown in Fig. 3. The pump is a stainless steel cartridge filled with adsorbent (CKT activated carbon). Cryopump is constantly cooled with liquid Nitrogen. The cooling provides better adsorption capability of the adsorbent.

To increase the cooling efficiency the copper heat exchanger is placed inside the cartridge. Additionally the cartridge is equipped with 6 longitudinal channels to extend the heat-exchange surface. Cryopump regeneration is carried out at 473 K and 10 Pa vacuum.

Freezer-Storage (Fig. 4) is used to accumulate purified Carbon Dioxide and keep it in the solid state. Up to 6 kg of frozen CO_2 can be accumulated in this unit. Freezer-Storage is manufactured from thick-walled stainless steel tube to sustain up to 10 MPa pressure. It has inner copper coiled heat exchanger and surrounded by a foam coating for good thermal insulation. Liquid Nitrogen is used as the coolant.

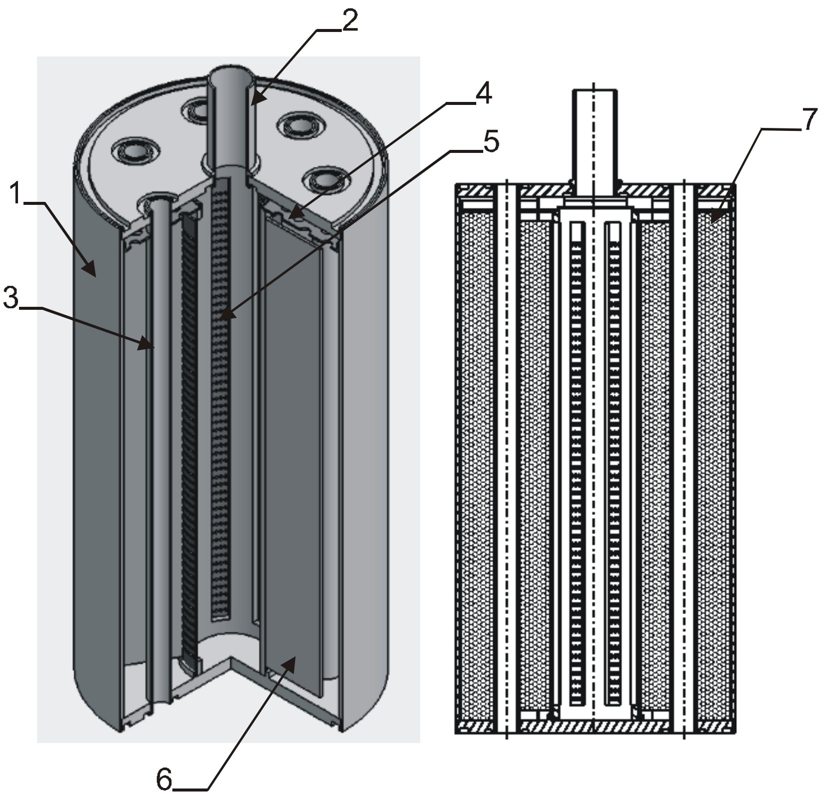

Fig. 3. Cryopump layout. 1 – cartridge; 2 – manifold; 3 – pipe; 4, 5 – wire meshes (dust filters); 6 – heat distributor; 7 – adsorbent (activated carbon)

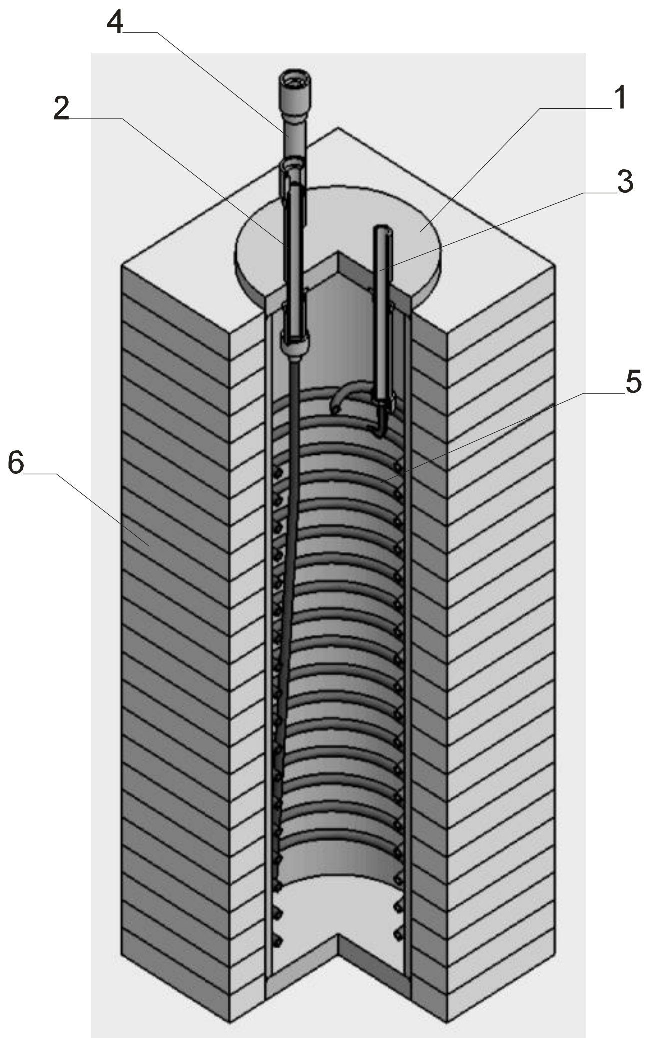

Fig. 4. Freezer-storage layout. 1 – thick-walled shell; 2 – inlet liquid nitrogen connector, 3 – liquid nitrogen vented steam connector; 4 – connector for pure CO_2; 5 – coil pipe; 6 – thermal insulation (expanded foam)

2. Purification process

The process of purification consists of three main stages. On the first stage the gas from Unrefined CO_2 cylinder is transferred to Measuring Cylinder through Preliminary Dryer. The volumetric amount of dried gas can be estimated with PI1 pressure in 40 l measuring cylinder. The Measuring Cylinder and the Unrefined Cylinder pressures have to be similar. At these conditions Measuring Cylinder is capable to contain up to 2 m^3 of CO_2 at the room temperature.

The filling rate of Measuring Cylinder should not exceed 1 bar/min to prevent the water breakthrough downstream of Preliminary Dryer. This rate is adjusted with MV1 manual valve.

On the second stage CO_2 gas is transferred by portions of 240–280 l to Freezer cooled with the liquid Nitrogen where it is sublimated to the solid state. The saturated vapor pressure of CO_2 is below 10^{-4} Pa [4] at the liquid nitrogen temperature. It permits us to assume that the main gas is fully frozen at the described conditions.

The amount of frozen CO_2 can be estimated with the pressure drop in the Measuring Cylinder measured by PI1. The presence of gaseous impurities with the boiling point below the liquid Nitrogen temperature increases the residual pressure in Freezer. Initially these gases are pumped out with Vacuum Pump and then with Cryopump. Vacuum Pump is only used at the pressure more than 10 Pa (forevacuum) in Freezer. Cryopump reduces the residual gases pressure down to 10^{-1} Pa. The forevacuum and high vacuum are measured with PVI1 and BT-2A gauges.

On the third stage CO_2 is purified from O_2 and H_2O traces down to the level of 1 – 2 ppm by passing it through H_2O&O_2 Purifier. The blower equipped with the electric heater is used to pressurize the Freezer vessel. The pressure in Freezer is measured with PI2 pressure indicator. Freezer can be pressurized up to 10MPa. The pure CO_2 is accumulated in one of 40 l Pure Cylinders. The flow rate of CO_2 through H_2O&O_2 purifier should not exceed 30 l/min. It is estimated by averaging the PI2 readings.

3. Purification efficiency

The purification efficiency can be estimated by the gas chromatography method. Carbon dioxide quality during the production is controlled with “Tsvet-800” gas chromatograph. One meter column filled with CKT activated carbon is applied for the analysis. Helium is used as a carrier gas. Chromatograms are processed by inner normalization [5] method. The difference between the chromatograms of unrefined gas and CO_2 after the purification is illustrated by Fig. 5 and Fig. 6. Each chromatogram shows two peaks. The large one is the main component (CO_2) and the small one is the impurities (principally air components – $N_2 + O_2 + Ar$). Presented diagrams are corresponded to “very dirty” sample of gas with 98.65+/–0.05% purity and the purified one with 99.98 +/– 0.01%.

The unrefined and purified samples are analyzed by different approaches. A one-pass measurement is good enough for a “dirty” sample. For the more precise estimation of treated gas purity, a set of repeated measurements with consequent exponential approximation is preferable. An instance of refined gas test is shown in Fig. 7. The change of measured concentration is explained by purging of chromatograph inner lines. The exponential fit gives an estimation of clean gas purity.

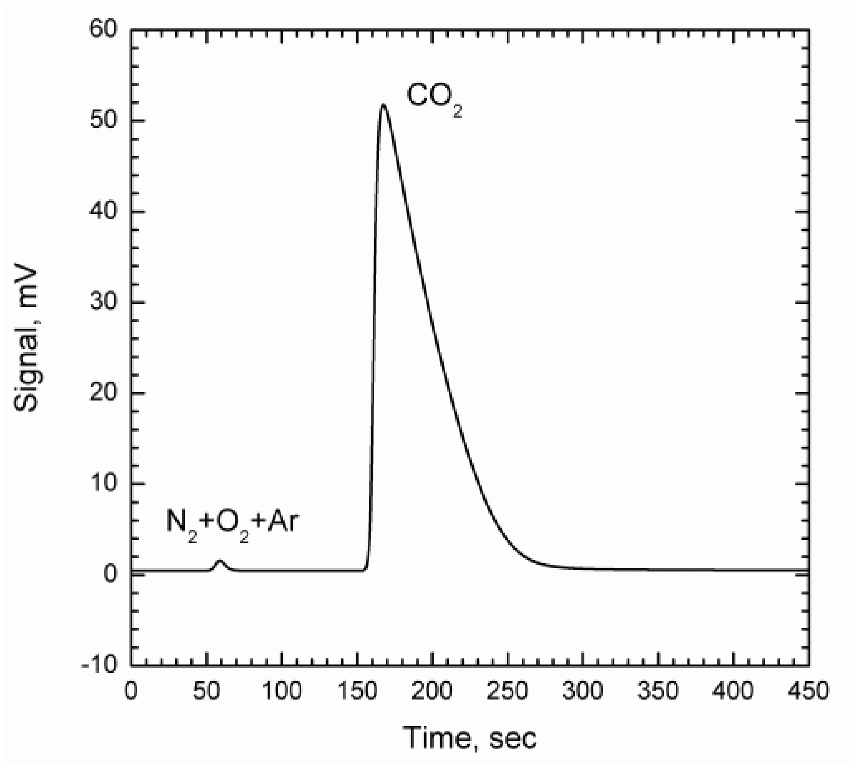

Fig. 5. The chromatogram of CO_2 before the purification

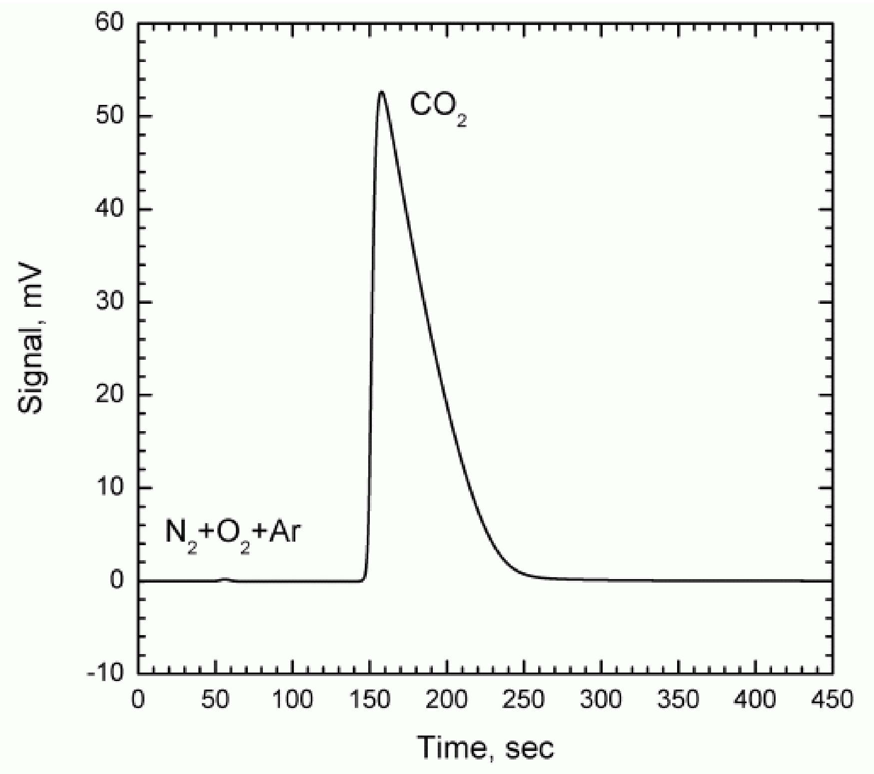

Fig. 6. The chromatogram of CO_2 after the purification.

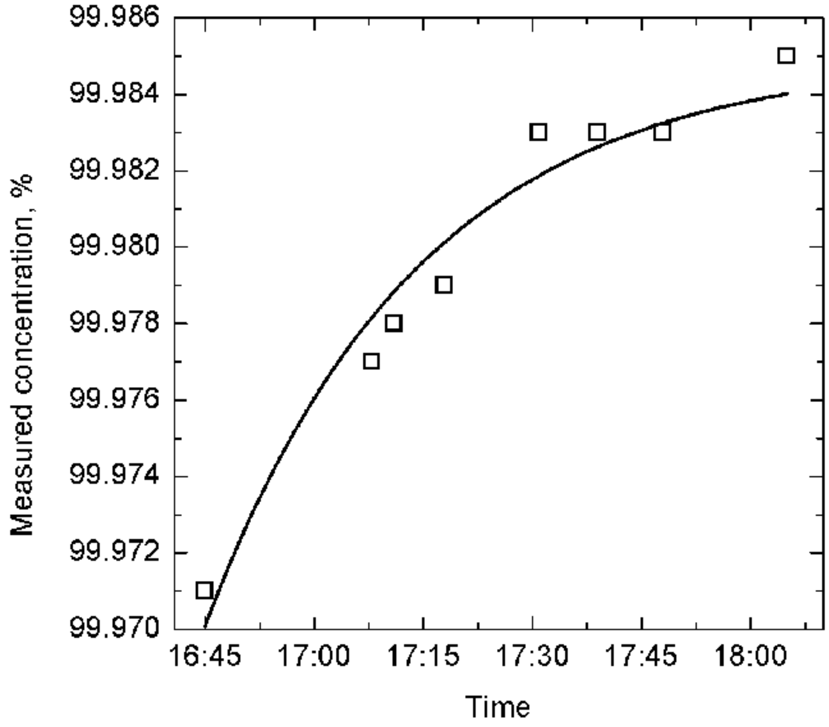

Fig. 7. The variation of the measured CO_2 concentration during the process of purging. Solid line shows the exponential fit

The quick test is suitable for analysis of samples taken from regular industrial cylinders. For more precise measurements and detailed analysis of the obtained product a big sample of purified gas was taken to a specially treated stainless steel cylinder. The complex analysis of this sample was carried out by the Laboratory of State Standards in the field of analytical measurements at Mendeleyev Institute of Metrology [6]. The results of analysis are presented in Table 1.

The results of the complex analysis of purified CO_2.

Number	Description	Method	Value, %
1	Content of CO_2	Chromatography	> 99.998
2	Content of N_2	Chromatography	0.00011
3	Content of O_2+Ar	Chromatography	< 0.00004
4	Content of CO	Chromatography	< 0.0001
5	Content of hydrocarbons	Chromatography	< 0.0001
6	Content of CH_4	Chromatography	< 0.00008
7	Content of H_2O vapor	Coulometric analysis	< 0.0004

Conclusion

The system showed good purification efficiency. 99.998 % purity of Carbon Dioxide was achieved. It was confirmed by the results of the complex analysis carried out by the Laboratory of State Standards in the field of analytical measurements. Productivity of the system can reach 0.5 m^3 (at normal conditions) per working shift. It is sufficient to satisfy the needs of PNPI in CO_2. Also, the system can be used for the Freon-14 purification.

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