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**Experimental study on oxygen and water removal from
gaseous streams for future gas systems in LHC
detectors**

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I-Abstract

An experimental gas system dedicated to test the gas purification efficiencies is presented, as well as details on solid state adsorbers used for tests, gas analyzers, calibrations and related procedures. The gas system is conceived to mix different gases at established conditions of pressure and flow-rate, to introduce and control pollutants (oxygen and water) and to measure the purification effects using different types of cleaning agents.

Oxygen and water adsorption data were obtained for a BASF R-3-11 copper catalyst. Measurements were done for Argon and Nitrogen as carrier gases with a pollution range between 140vpm to 0.3% for oxygen and between 1% to 73% relative humidity at 20°C. The working pressures were in a range of 1.6-3 bar abs at room temperature.

II-Introduction

Gas particle detectors need purification and recirculation of the gaseous mixtures in order to eliminate the impurities (mainly oxygen and water) that appear during normal operation, due to air leaks and air diffusion. Recirculation with purification is more advantageous than constant fresh gas supplying since it reduces significantly the operating costs and assures the purity in the gas supply.

To eliminate the impurities mentioned, the gas flow is passed through cartridges filled with cleaning agents, such as molecular sieves and highly dispersed metallic copper, called catalyst.

Molecular sieves are high porous synthetic alumino-silicates that can adsorb molecules from gases or liquids small enough to enter their pores. By other words, it can take up in internal cavities or hold on the surface such molecules by chemisorption. The forces involved in the adsorption are Van der Waals forces. Besides the kinetic diameter of the adsorbate, molecular sieves adsorb preferentially based on polarity and molecular unsaturation degree. The partial pressure of each component of the gaseous mixture as well as the temperature influences the amount of adsorbed species.

Besides the copper catalyst is generally used as a catalyst, in our tests it is not acting as a promoter of reactions in its active sites, but as a chemical absorption agent. The copper is oxidized by oxygen molecules present in the gas stream, forming a copper oxide and thus removing oxygen from the gas flow. The catalyst, as supplied, is composed of approximately 30% copper oxide [3] in highly dispersed form deposited on a high specific surface molecular sieve. The activation (or regeneration) of the catalyst, as received from the supplier, is realized before its use. The process consists in the chemical reduction of copper oxide to copper (cf eq. 1).



During the gas purification, copper is oxidized through the following reaction (cf eq. 2).



Therefore the theoretical capacity to absorb oxygen for 1 kg catalyst is 60g, which corresponds to 47nℓ O₂.

III-Experimental Set-up

III.1-The gas system

A special gas system was built for the present work. It offers the possibility to introduce and use controlled pollution degrees of oxygen and water in different mixtures.

The gas system is designed to mix up to three different gases through three flowmeters (Vögtlin TYP V100) each one with a different range (2.5-25ℓ/h; 14-140ℓ/h; 80-800ℓ/h). The main gas is also supplied to a binary gas analyzer, as reference gas, and by a flowmeter (Vögtlin TYP V 100; 2.5-25ℓ/h) to a gas saturation device (Lauda RM6). Besides the water pollution there is also the possibility of oxygen pollution realised by adding a flow of compressed air or pre-contaminated gas, regulated by a flowmeter (Vögtlin TYP V100; 0.3-3ℓ/h). The gas mixture, after pollution, passes through the purifier (a cylindrical cartridge filled with the cleaning agent).

In fig 1 it is shown the gas system for the purification tests.

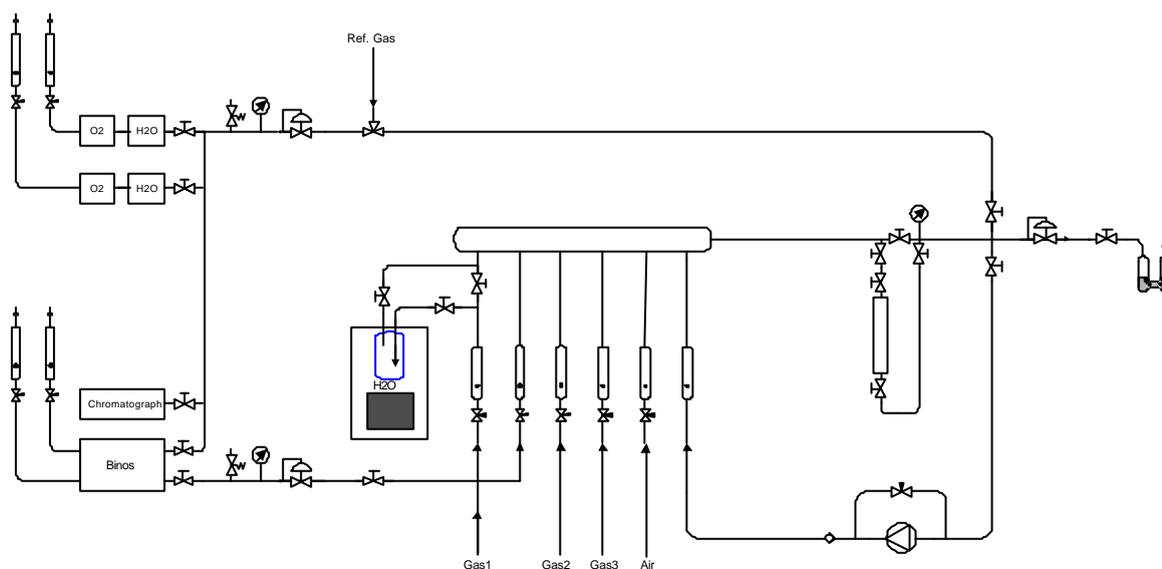


Fig1: Gas system for purification tests

The gas system can be operated in two modes: first in an open circuit, where the gas is sent to vent via a bubbler and secondly in a closed circuit. The circulation is maintained by a membrane pump (Neuberger KNF 145.2ANE) and monitored by a large flowmeter (Vögtlin V1375-3; 0-3m³/h).

The pressure in the system is regulated by a backpressure reducer (Dräger Tescom 26-2320-24, P_{max} = 3.5bar). A small fraction of the gas mixture passes via another pressure reducer (Air Liquide A7 1934) into the different analyzers in order to keep a constant overpressure of 100mbar. The different analyzers connected to the system are oxygen analyzers (Orbisphere, Arelco TEC,

Panametrics O2X1), water analyzers (SHAW-TR, Xentaur LPDT) and a binary gas analyzer (Orthodyne AL2R). The system is able to receive a reference gas for the apparatus calibration without affecting the gas mixture. It is also prepared to supply an output to a gas chromatograph in order to check the analyses and to detect other impurities than oxygen and water.

The monitoring devices are connected to a PC through an interface (National Instrument SCXI-1000 with a card AT-M10-16E-10). The software Labview receives and records the data.

The gas system was initially checked with a helium leak detector giving a leak rate of approximately 10^{-8} mbar ℓ /s. With this leak rate an oxygen and water contamination of less than 1 vpm is achieved.

III.2-Purifiers

All measurements were performed using a copper catalyst (BASF R-3-11). These cleaning agents are dark green cylindrical pellets, 5mm diameter and 3mm long. Its bulk density is 0.9g/cm³. It were used four cartridges all with the same dimensions (D=15mm; L=350mm \Rightarrow 62cm³) and filled with the same amount of catalyst (44.5g).

III.3-Gases

The gases used in the measurements were argon(46), nitrogen(45), compressed air and Noxal3 (6% H₂ in argon), supplied by Carbagas.

The pre-mixed bottles, prepared by us, had an oxygen content of 3000vpm and 2375vpm.

III.4-Procedure

Cartridges Regeneration

At the beginning of a measurement, the purifiers have to be regenerated. The reaction involved in this process is the chemical reduction of copper oxide to copper (cf eq. 1).

Hydrogen is supplied in a mixture of Noxal3, instead of pure hydrogen. The different steps of regeneration are summarized :

- The Noxal gas is passed through for at least two hours while the temperature is gradually increased to 150°C.
- After this step, the temperature is increased to 215°C and the cartridge is fed with Noxal at nominal flow;
- After the reducing process the Noxal is interrupted and the temperature is decreased at room temperature in an inert gas flow (e.g. argon).

Appropriate tests were carried out to optimize the regeneration process. The optimal flow of Noxal3 was established to 30nl/h and the reducing time to 6 hours.

Purification Measurements

To start the oxygen capacity measurements, an oxygen contaminated gas flow is passed through the gas system while bypassing the purifier, in order to measure the oxygen content. After stabilization (≈ 30 min) the gas flow is passed through the purifier. Within 60 sec the oxygen concentration drops drastically (< 1 vpm), meaning that almost all oxygen is retained right from the beginning.

Concerning the water capacity measurements, the flow goes immediately to the purifier to avoid water adsorption on internal walls of the metal pipes between the cartridge and the analyzer, therefore permitting a better control of the measurement. The dew point shown a value of -79°C (< 1 vpm) till the beginning of saturation, showing that almost all water is adsorbed since the starting of the measurement.

The saturation time is defined as the time from the start of the measurement until the time when the gas coming out from the purifier has an oxygen or water content of > 5 vpm.

Measurements were performed for oxygen capacity, oxygen capacity for previously water saturated cartridges and water capacity.

The oxygen pollution was done either with a compressed air bottle and a pre-mixed bottle of air in nitrogen. The water pollution is made using an argon flow saturated at 15°C , giving a relative humidity of 73% at 20°C . In order to obtain a lower relative humidity, additional dry gas can be added to the wet gas flow.

IV-Experimental Data

IV.1-Cartridges Regeneration

In order to test the influence of regeneration parameters on the catalyst adsorption capacity measurements, it were used several regeneration programs as function of the Noxal3 flow and the regeneration time.

In fig 2 it is shown the influence of the Noxal quantity on the capacity.

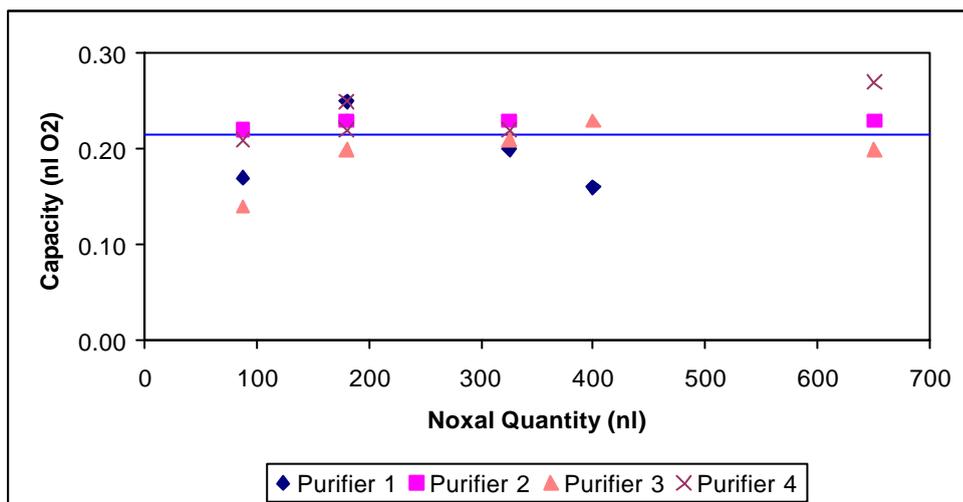


Fig 2: Influence of the catalysts regeneration program on the capacity

It can be seen that within the statistical and systematical uncertainty the variation of the noxal quantity between 90nl and 650nl does not influence the capacity for O₂. For practical reasons a flow of 180nl is chosen to perform further measurements, which corresponds to 30nl/h during 6 hours.

IV.2-Oxygen Capacity Measurements

Oxygen capacities were measured at 1.6 bar abs for gas velocities between 7.6 and 12 cm/s and oxygen content from 140vpm to 0.3%.

The oxygen capacity (C_{O_2}) is calculated taking into account the calibrated total flow (ϕ_T), the saturation time (t) and the average between the oxygen content at the beginning and at the end of the measurement (c) (cf eq.3).

$$C_{O_2} = j_T \cdot t \cdot c \quad \text{Eq. 3}$$

An oxygen measurement for an argon mixture with 282vpm oxygen content is shown as an example in fig 3.

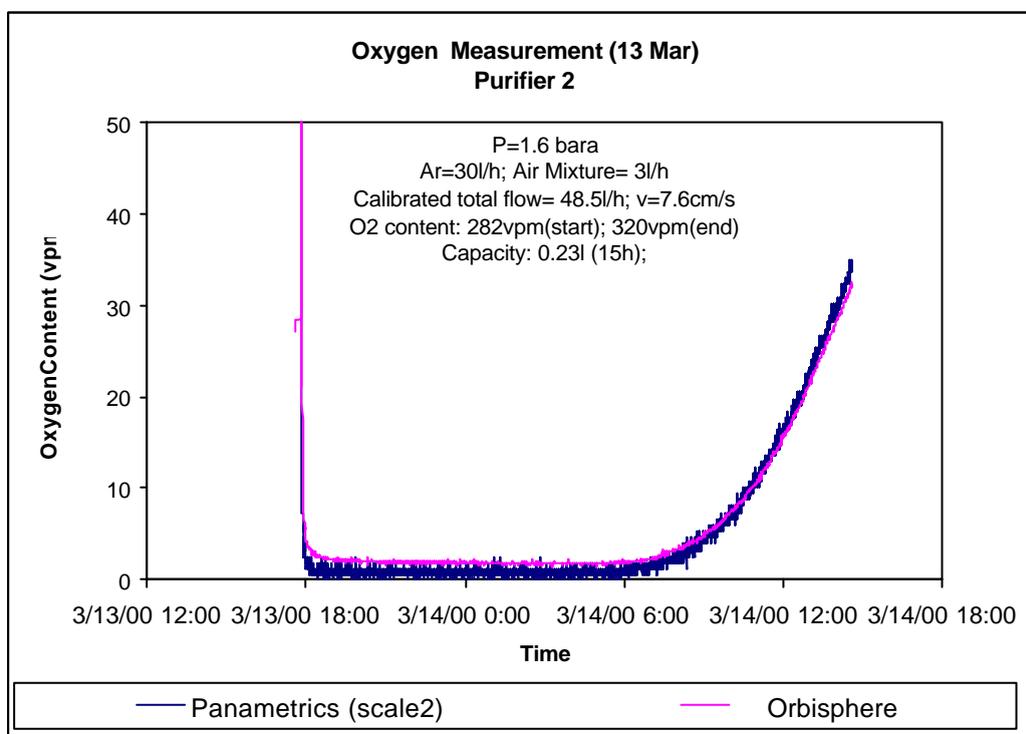


Fig. 3: Oxygen capacity measurement for an argon mixture with 282 vpm oxygen content.

As it can be seen in figure 3, the initial oxygen content of 282vpm drops abruptly within a few minutes below 2 vpm. The same behavior was observed when interrupting the oxygen supply in a gas flow. Therefore it can be concluded that the purifier reacts immediately with the oxygen in the gas.

Table 1 presents the process parameters and the correspondent oxygen capacity results. It can be seen that there are some differences on the oxygen content in the beginning and at the end of the measurement due to the fluctuations in the flow rates.

Purifier	Date	P (bara)	Ar flow (ℓ/h)	Air flow (ℓ/h)	Cal.Total flow (nℓ/h)	velocity (cm/s)	O2 vpm start	O2 vpm end	C (nℓ O ₂)	Time
1	14-Feb	1.6	40	0.4	56.3	8.9	2750	2650	0.25	100min
1	16-Feb	1.6	40	0.4	56.3	8.9	2510	2550	0.20	85min
1	24-Feb	1.6	40	0.4	56.3	8.9	2580	2550	0.17	73min
1	10-Mar	1.6	40	2*	59.4	9.3	150	199	0.23	22h
									0.20	Average
2	17-Feb	1.6	40	0.4	56.3	8.9	2500	2080	0.23	110min
2	21-Feb	1.6	40	0.4	56.3	8.9	2800	2950	0.23	87min
2	24-Feb	1.6	40	0.4	56.3	8.9	2550	2380	0.22	94min
2	13-Mar	1.6	30	3*	48.5	7.6	282	320	0.23	15h
									0.23	Average
3	14-Feb	1.6	40	0.4	56.3	8.9	2480	2220	0.20	89min
3	17-Feb	1.6	40	0.4	56.3	8.9	2470	2560	0.21	88min
3	22-Feb	1.6	40	0.4	56.3	8.9	2560	2390	0.20	86min
3	24-Feb	1.6	40	0.4	56.3	8.9	2420	2070	0.14	69min
3	8-Mar	1.6	40	2*	59.4	9.3	141	***	0.23	28h
3	25 May	3.0	20**	3*	70.1	11	315	290	0.18	8h
									0.20	Average
4	15-Feb	1.6	40	0.4	56.3	8.9	2120	1950	0.22	115min
4	18-Feb	1.6	40	0.4	56.3	8.9	2710	2780	0.22	85min
4	22-Feb	1.6	40	0.4	56.3	8.9	2530	3150	0.27	103min
4	24-Feb	1.6	40	0.4	56.3	8.9	2580	2950	0.21	83min
4	16-Mar	1.6	40	2*	59.4	9.3	159	***	0.25	26h
4	14-Apr	3	30	3*	71.2	11.4	307	318	0.22	9h
									0.23	Average
	*Pre mixed bottle: O2=3000vpm **Nitrogen flow ***It was not possible to read O2content at the end								0.21 +/- 0.03	Total Average

Table 1: Oxygen Capacity measurements

The obtained results are consistent for the different measurements and give an average oxygen capacity of $0.21 \pm 0.03\text{nℓ}$ ($4.72 \pm 0.67\text{nℓ/kg}$). This result corresponds to an effective capacity of about 10 %, regarding the theoretical capacity. However, it is a satisfactory result when compared with the capacity given by the supplier – 4nℓ/kg .

The oxygen capacity was also measured at 3 bar abs giving a result similar with those at lower pressures confirming that the retention of oxygen is a purely chemical reaction and thus independent of the pressure.

In table 2 it is presented the oxygen capacity measurements for the determination of the maximum flow through the cartridge.

Purifier	Date	P (bara)	Ar flow (ℓ/h)	Air flow (ℓ/h)	Cal.Total flow (nℓ/h)	velocity (cm/s)	O2 vpm start	O2 vpm end	C (nℓ O ₂)	Time
1	29 may	1.6	120	25*	200.1	31.4	522	523	0.02	13min
2	29 may	1.6	60	25*	123.1	19.3	855	842	0.06	34min
1	25-Feb	1.6	60	0.3	81.8	12.9	1630	1540	0.16	72min
4	29 may	1.6	30	20*	76.4	12	1120	1100	0.18	90min
1	30 may	1.3	30	20*	76.4	12	1065	1060	0.08	60min
*Pre mixed bottle: O2=2375vpm										

Table 2: Oxygen capacity measurements

As it can be observed in table 2, the oxygen removal capacity of the catalyst decreases for velocities higher than 12 cm/s (76.4nℓ/h). Above this value, the increase of velocity causes the diminution of the mass transfer zone, leading to a decrease on the absorption efficiency. However, if the velocity is decreased the cartridge is able to continue its oxygen removal.

The maximum flow corresponds to a space velocity of 1500:1 (ℓgas / ℓcopper catalyst / 1hour), at 1.6 bar abs. Applying this space velocity to the three standard cartridges used in CERN gas systems, it can be forecast the maximum operating flow (see table 3).

Cartridge dimensions [Diam.(mm)xLength(mm)]	Maximum operating flow (nℓ/h)	Oxygen capacity (nℓO ₂)
“small” 15x350	75	0.2
“medium” 34x450	580	1.6
“big” 65x650	2.5x10 ³	7.0

Table 3: Maximum operating flows and oxygen capacities for the three standard cartridges used at CERN gas systems.

In order to evidence the influence of water adsorption on the oxygen capacities, measurements were done for previously water saturated cartridges. It was used a wet stream of oxygen in order to avoid water desorption. The results are summarized in table 4.

Purifier	Date	P (bara)	Ar flow (ℓ/h)	Water Sat. flow (ℓ/h)	Air flow (ℓ/h)	Cal.Total flow (nℓ/h)	velocity (cm/s)	Water content(%)	O2 vpm start	O2 vpm end	C1 O2(nℓ)	C1 (time)
4	4-Apr	1.6	20	10(15°C)	3*	51	7.9	0.3	280	289	0.47**	33h
2	28-Mar	1.6	20	10(15°C)	3*	51	7.9	0.3	233	265	0.43**	34h
1	24-Mar	1.6	20	20(15°C)	2*	63	9.9	0.45	148	130	0.44**	50h
*Pre mixed bottle: O2=3000vpm												
**Previously saturated with water												

Table 4: Oxygen Capacity measurements using water saturated catalyst.

The results obtained were in average, $0.46 \pm 0.02n\ell$ ($10.4 \pm 0.5n\ell/kg$), which represents around twice the capacity for oxygen in dry conditions. This interesting effect can be explained as follows: the activated copper is deposited on a molecular sieve. When it is saturated with water its highly porous structure is filled with molecules of water, therefore covering the copper. The water improves the oxygen access to the copper surface, due to the diffusion through water, and also improves the electrons exchange during the reaction, due to the water good conductive properties, thus leading to a higher efficiency of the copper oxidation.

IV.3-Water Capacity Measurements

Water capacities were measured at pressures between 1.3–3 bar abs for velocities between 4.9 and 11.5 cm/s and relative humidity from 1% to 73% at 20°C.

The water capacity (C_{H_2O}) is calculated from the partial pressure of water vapor (which for our measurements was the saturation pressure at 15°C, $p_{H_2O} = 16.86\text{mbar}$), the total pressure of the system (P_T), the calibrated water saturated flow (ϕ_1), and the saturation time (t) (cf. eq.4).

$$C_{H_2O} = \frac{P_{H_2O}}{P_T} \cdot \dot{j}_1 \cdot t \quad \text{Eq 4}$$

The ratio between the partial pressure and the total pressure corresponds to the water content in the saturated flow. The relative humidity at 20°C is equal to the ratio between the water vapor partial pressure (p_{H_2O}) and the water saturation pressure at 20°C (p_{sat}). Both the water content and the relative humidity (rh) are multiplied by a conversion factor ϕ_1/ϕ_T to obtain the correspondent value in a mixed flow, being ϕ_T the calibrated total flow (cf. eq.5).

$$rh = \frac{P_{H_2O}}{P_{sat}} \cdot \frac{\dot{j}_1}{\dot{j}_T} \quad \text{Eq 5}$$

As an example it is shown in figure 4 a water measurement, in terms of dew point, for an argon mixture with 73.1% relative humidity, monitored by a Shaw device. Figure 5 corresponds to the same measurement but the data was converted for vpm water content, through the exponential equation - valid for dew point between -80°C and -20°C (cf eq.6).

$$Y(\text{vpm}) = 16531 \cdot \exp^{0.126D(^{\circ}\text{C})} \tag{Eq 6}$$

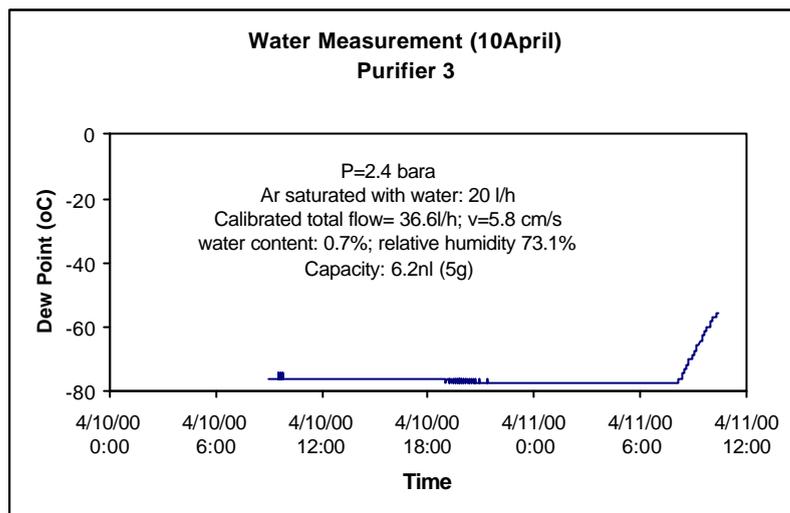


Fig 4: Water capacity measurement for a water saturated argon flow with 73.1% relative humidity

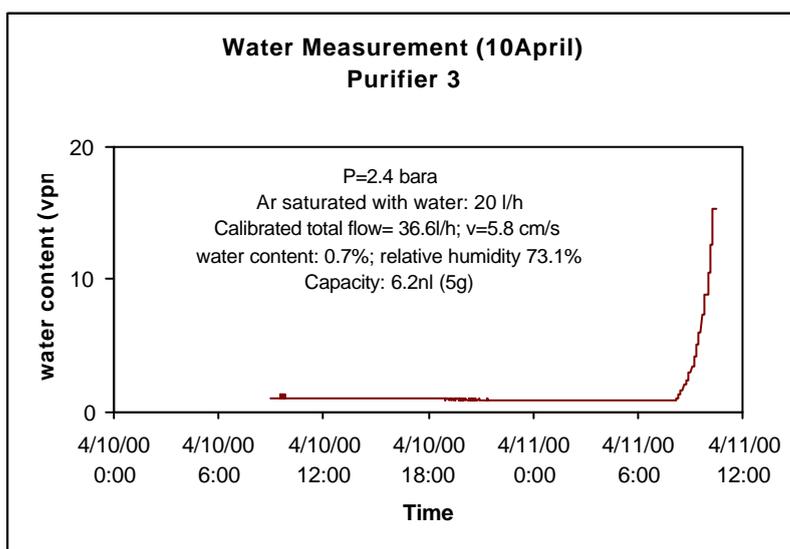


Fig 5: Water capacity measurement for a water saturated argon flow with 73.1% relative humidity. Values are converted for vpm water content.

Table 5 presents the process parameters and the corresponding water capacity measurements.

Purifier	Date	P (bara)	Ar flow (ℓ/h)	Water Sat. flow (ℓ/h)	Air flow (ℓ/h)	Cal.Total flow (nℓ/h)	velocity (cm/s)	Water content(%)	rh (%)	C nℓ H ₂ O	C g H ₂ O	C g H ₂ O/kg	Time (h)	Time for a 36 nℓ/h flow
2	19-Apr	1.3	0	25(15°C)	0	31	4.9	1.30	73.1	5.0	4.0	90	12	10
2	11-May	1.6	30	0.4(15°C)	0	43	6.8	0.0145	1	2.1	1.7	38	317	379
1	8-May	1.6	50	2.5(15°C)	0	73	11.5	0.07	4.9	2.5	2.0	45	49	100
4	4-May	1.6	30	3(15°C)	0	48	7.6	0.12	8.6	2.7	2.2	49	45	61
1	5-Apr	1.6	20	10(15°C)	3*	51	7.9	0.31	21.8	3.5	2.8	63	22	31
3	2-May	1.6	20	20(15°C)	3*	52	8.2	0.58	40.5	3.8	3.0	68	13	19
1	23-Mar	1.6	0	25(15°C)	0	36	6.3	1.05	73.1	4.9	3.9	88	13	13
2	27-Mar	1.6	0	25(15°C)	0	36	6.3	1.05	73.1	5.1	4.1	92	13	13
4	31-Mar	1.6	0	25(15°C)	0	36	6.3	1.05	73.1	5.4	4.3	97	14	14
1	18-Apr	2	0	20(15°C)	0	33	5.2	0.84	73.1	5.6	4.5	101	20	18
3	10-Apr	2.4	0	20(15°C)	0	37	5.8	0.70	73.1	6.2	5.0	111	24	24
2	11-Apr	3	0	20(15°C)	0	41	6.4	0.56	73.1	6.1	4.9	110	20	23
*Pre mixed bottle: O ₂ =3000ppm														

Table 5: Water capacity measurements

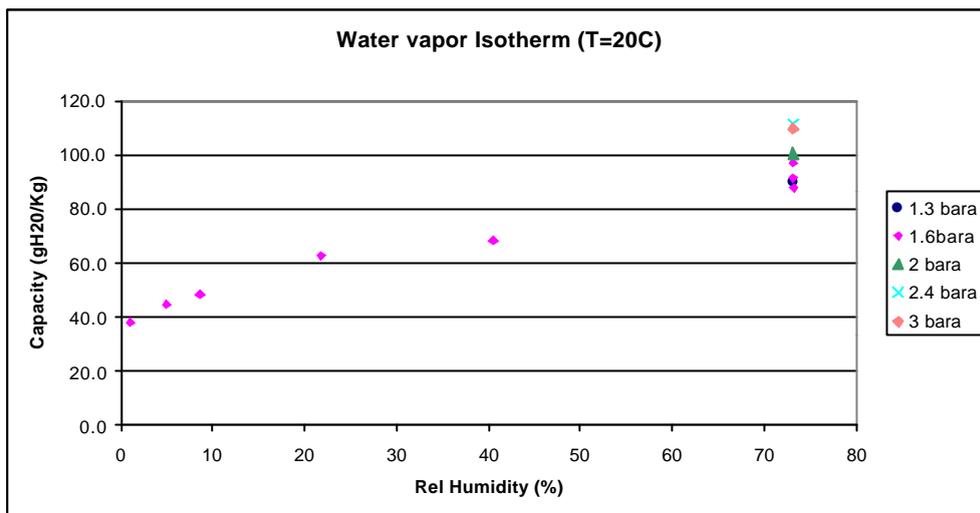


Fig 6: Water vapor adsorption isotherm for activated copper at room temperature

As it can be seen from figure 6, the water capacity is clearly dependent on the relative humidity and, at lower degree, on the total pressure, which demonstrates the physical character of the adsorption process.

Despite the fact that water capacity decreases with relative humidity, in terms of saturation time the cartridge will always withstand more time when the relative humidities are lower, since the decrease of its capacity is less important when compared to the decrease in relative humidity. The effect on saturation time is presented in figure 7, where the values at 1.6 bar abs were normalized to a flow of 36 nℓ/h.

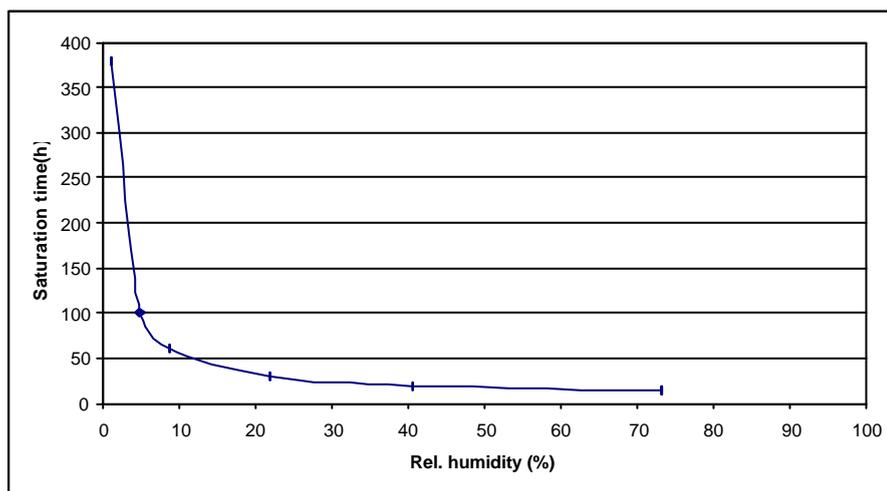


Fig 7: Water vapor saturation time, at 1.6 bar abs, for a normalized flow of 36 nℓ/h

V-Conclusions

Activated copper is able to purify a gas stream polluted with oxygen and water. The capacity for oxygen ($4.72 \pm 0.67 \text{ n\ell/kg}$) is independent on pressure indicating that oxygen retention is a purely chemical reaction. The reaction is more efficient if the cartridge is already saturated with water ($10.4 \pm 0.5 \text{ n\ell/kg}$), due to the water effect on improving the access of oxygen to copper and to the better interfacial electron transfer. The maximum flows, for an efficient oxygen retention, for the three standard cartridges used in CERN gas systems are 75 n\ell/h , 580 n\ell/h and $2.5 \times 10^3 \text{ n\ell/h}$, respectively.

The capacity for water is dependent on relative humidity (45-97g/kg, $P=1.6 \text{ bar abs}$) and, at a lower degree, on the total pressure, showing the physical character of adsorption.

To purify a stream contaminated with air is enough one catalyst cartridge, since there is 21% O_2 and around 1.7% H_2O ($hr=70\%$, $T=20^\circ\text{C}$) in air. Thus the oxygen capacity is the limiting factor for the saturation of the cartridge. Special attention has to be paid if a component in the mixture can be more adsorbed than water (higher polarity, lower size, etc). Further studies should be done using gas mixtures containing CO_2 to see the influences on water capacity, since CO_2 is usually easily adsorbed and has a dimension similar with water (H_2O kinetic diameter: 2.65 \AA ; CO_2 kinetic diameter: 3.3 \AA [1]).

Appendix 1 –Flowmeters Calibration

- flowmeter 0.3-3ℓ/h (Vögtlin TYP V 100);
- flowmeter 2.5-25ℓ/h (Vögtlin TYP V 100);
- flowmeter 14-140ℓ/h (Vögtlin TYP V 100);
- flowmeter 80-800ℓ/h (Vögtlin TYP V 100);

As the flowmeters are calibrated for air at 15°C and 1.013bar by factory, it was necessary another calibration for the working gases at different pressures with a digital flow calibrator Ion Science-Saga. For the 80-800ℓ/h flowmeter the flow calibrator could not measure flows above 280ℓ/h at a pressure of 1.2 abs bar, due to the insensitiveness of the device.

0.3-3l/h flowmeter

flow(l/h)	calibrated flow (l/h)			
	1.2 bar abs	1.6 bar abs	2.0 bar abs	3.0 bar abs
0.3	0.42	0.54	0.72	0.78
0.5	0.54	0.78	0.96	1.20
1.0	1.44	1.86	2.22	3.06
1.5	1.92	2.88	3.84	4.98
2.0	2.70	3.78	4.92	6.42
2.5	3.30	4.92	5.88	7.20
3.0	4.02	5.58	6.96	8.82

Table A.1: 0.3-3l/h flowmeter calibration for compressed air.

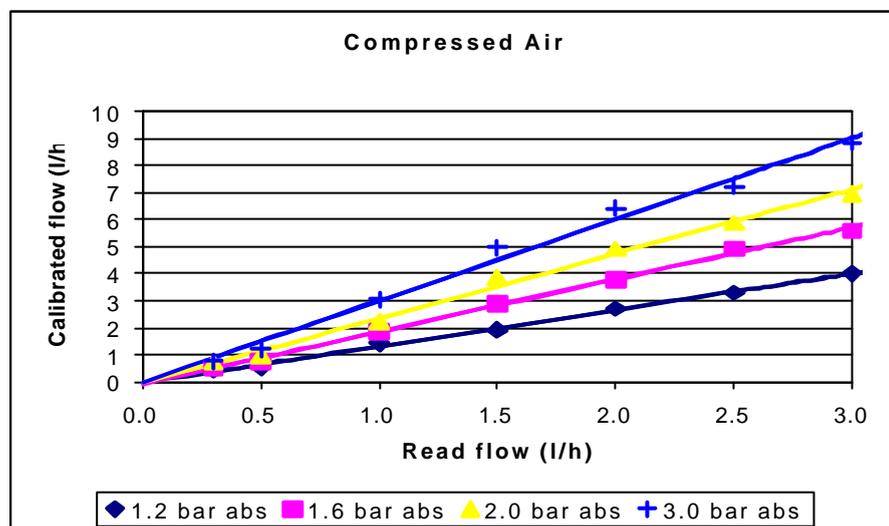


Figure A.2: 0.3-3l/h flowmeter calibration for compressed air.

$$\varphi_{\text{cal}}(\ell/h) = a + b\varphi_{\text{read}}(\ell/h)$$

P (bar abs)	a	b
1.2	-0.02 ± 0.06	1.34 ± 0.03
1.6	-0.08 ± 0.08	1.93 ± 0.04
2.0	-0.04 ± 0.14	2.39 ± 0.08
3.0	0.00 ± 0.26	3.01 ± 0.14

Table A.3: Linear regression parameters

2.5-25 ℓ/h flowmeter

flow (ℓ/h)	calibrated flow (ℓ/h)		
	1.6 bar abs	2 bar abs	3 bar abs
2.5	4.4	5.4	7.3
3	6.2	7.2	8.9
5	7.8	9.1	13.1
10	15.6	19.2	24.1
15	22.2	25.3	31.9
20	29.5	32.8	41.2
25	35.1	40.6	50.5

Table A.4: 2.5-25 ℓ/h flowmeter calibration for water saturated Argon.

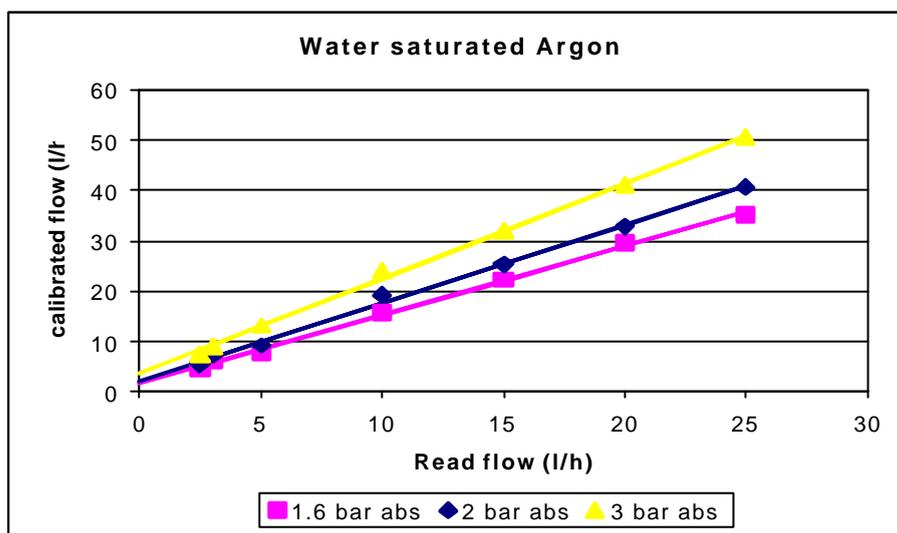


Figure A.5: 2.5-25 ℓ/h flowmeter calibration for water saturated Argon.

$$\varphi_{\text{cal}}(\ell/h) = a + b\varphi_{\text{read}}(\ell/h)$$

P (bar abs)	a	b
1.6	1.52 ± 0.40	1.37 ± 0.03
2.0	2.19 ± 0.57	1.54 ± 0.04
3.0	3.50 ± 0.58	1.89 ± 0.04

Table A.6: Linear regression parameters

14-140ℓ/h flowmeter

flow (l/h)	calibrated flow (l/h)		
	1.6 bar abs	2.0 bar abs	3.0 bar abs
14	20.2	24.3	31.3
20	30.0	33.9	47.2
30	44.4	49.0	64.2
40	55.2	62.4	80.7
50	68.0	75.7	97.8
60	81.6	89.9	115.2
70	93.8	102.4	130.7
80	108.8	117.2	148.9
90	121.2	129.1	165.0
100	132.0	141.0	178.8
140	182.4	195.2	244.2

Table A.7: 14-140 ℓ/h flowmeter calibration for Argon.

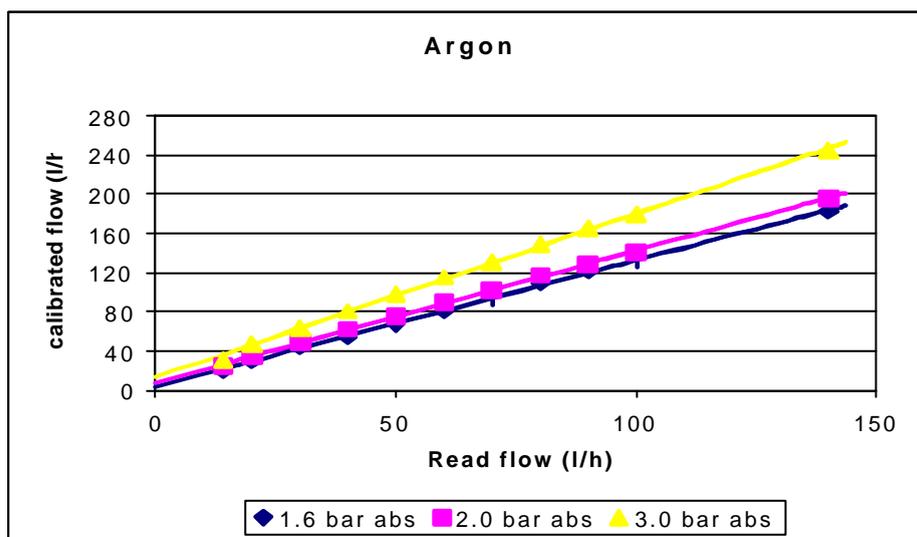


Figure A.8: 14-140 ℓ/h flowmeter calibration for Ar.

$$\varphi_{\text{cal}}(\ell/h) = a + b\varphi_{\text{read}}(\ell/h)$$

P (bar abs)	a	b
1.6	4.34 ± 0.80	1.28 ± 0.01
2.0	7.80 ± 0.80	1.35 ± 0.01
3.0	13.28 ± 1.43	1.67 ± 0.02

Table A.9: Linear regression parameters

80-800ℓ/h flowmeter

flow(l/h)	calibrated flow (l/h)		
	1.2 bar abs	1.6 bar abs	2.0 bar abs
80	82.8	104.4	123.0
100	99.6	128.4	151.2
120	126.6	152.4	178.2
140	146.4	177.0	202.2
160	165.6	198.0	229.8
180	185.4	222.0	253.2
200	204.0	245.4	270.6
220	225.6	268.2	
240	244.2	290.4	
260	264.0		
280	286.2		

Table A10: 80-800 ℓ/h flowmeter calibration for Argon.

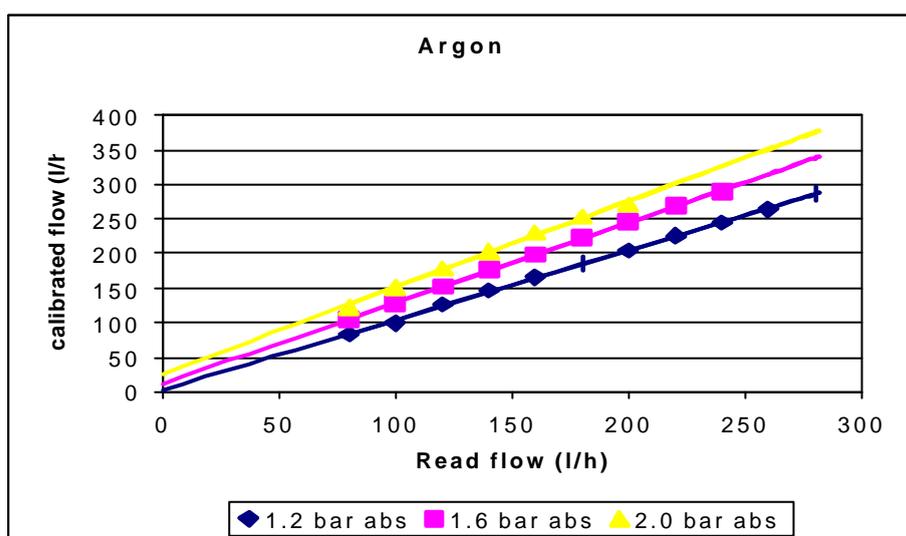


Figure A.11: 80-800 ℓ/h flowmeter calibration for Ar.

$$\varphi_{\text{cal}}(\ell/h) = a + b\varphi_{\text{read}}(\ell/h)$$

P (bar abs)	a	b
1.2	2.6 ± 1.8	1.011 ± 0.009
1.6	12.6 ± 1.0	1.162 ± 0.006
2.0	26.6 ± 4.9	1.247 ± 0.003

Table A.12: Linear regression parameters

Appendix 2 –Oxygen analyzers

Orbisphere device 2611 (sensor 2118; flowchamber 2112)

This device consists in a electrochemical sensor made by two noble metal electrodes immersed in a electrolyte of 1 molar potassium hydroxide. The sensor is separated from the gas sample by a gas-permeable membrane.

This sensor is of polarographic type. An applied electrical potential between the electrodes reduces the oxygen during measuring, producing a current proportional to the partial pressure throughout the range from 10^{-6} bar to 0.3 bar. The signal is displayed in vpm or percentage according to the different scales in which it is working. The range selection is automatically made from the 5 available scales (0-30%; 0-19.99%; 0-1.999%; 0-1999vpm; 0-199.9vpm) except for the most sensitive range which must be selected manually.

Calibration is made each time that the membrane is changed (most of the times due to the electrolyte refilling) since the sensitivity of the instrument depends on the membrane tension. After changing a new membrane it should be waited at least 30min for the relaxation of it. The calibration is performed in air saturated with water vapor. To have an air saturated with water vapor, the sensor is hold in a way that the membrane is 1 cm above the surface of clean water. According with the room temperature and pressure, the device is calibrated for the correspondent partial pressure, which is assumed as being the % by volume.

Arelco TEC and Panametrics O2X1

Both devices are made of a galvanic fuel-cell oxygen sensor inside a flow chamber. The fuel-cell works using a fuel (potassium hydroxide), which is inside the cell, and oxygen supplied by the gas stream to produce water and an electrical signal proportional to the oxygen content. The signal is converted and displayed on Labview. Arelco TEC has two ranges of which the range from 0-227.4 vpm was used. Panametrics has 6 ranges, which permit to measure oxygen from 0 to 25%. In the measurements the range 0-1000vpm was used. These devices were calibrated with mixtures with different oxygen contents checked by the Orbisphere device.

Both sensors need a long period of stabilization (24 hours), after exposing the sensor to the air, for the correct oxygen measurement in the lowest scale, while orbisphere reacts faster. Nevertheless Orbisphere needs several membrane exchanges and electrolyte refilling compared with the no-maintenance fuel-cells.

Because of the water production during the running of these sensors, it must be installed always afterwards the water sensor in order not to influence the water measurement.

Appendix 3 –Water analyzers

Shaw-TR (Red Spot)

The water analyzer sensor is made of a thin dielectric layer which adsorbs or releases water molecules within its pores, depending on the water vapor content on the gas stream. This dielectric layer is connected to a porous conductive gold layer, enabling to measure the electrical capacitance between the two layers. The capacitance changes caused by the water entering the pores are direct proportional to dewpoint temperature (DP).

Shaw device has an automatic calibration needing only a pre-set adjustment for the maximum of the scale. This is made exposing the sensor to atmospheric air, which is wetter than the maximum of the scale (DP = -20°C).

Appendix 4 –Binary gas analyzer

Orthodyne AL2R

This device measures the composition in a binary mixture by comparison of their thermal conductivity. Taking one gas of the mixture as reference, the difference of thermal conductivity between that and the binary mixture will give an electrical signal that will be proportional to the gas composition.

For calibration it is necessary to pass through the device the reference gas as well as the calibration gas with a content higher than those from the further gases to analyze. Putting the button in zero position it is adjusted the digital indicator to zero. Setting the button to analyze position and passing the calibration gas, it is adjusted the maximum of the scale. After verifying again the zero, the device is ready to read a content of a certain mixture.

Appendix 5 – Technical data concerning the three standard cartridges

Cartridge	Small	Medium	Big
Diameter (mm)	15	34	65
Length (mm)	350	450	550
Volume (dm ³)	0.062	0.41	1825
Catalyst amount (g)	44.5	350	1500
Flow max.(nl/h)	75	580	2500
Oxygen capacity (nl)	0.2	1.6	7.0
Water capacity (g) 73.1% r.h., 1.6barabs, 20°C	4.1	32	138

Table A.13: Technical data concerning the three standard cartridges

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