LAWRENCE LIVERMORE LABORATORY
University of California Livermore, California 94550

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CONSTRUCTION AND OPERATION
OF A LARGE VOLUME NOBLE GAS PURIFIER

S. W. Stribling

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MASTER

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Abstract

A closed-loop, noble gas purification system capable of reducing the total active gas impurity concentration (e. g. H_2, O_2, N_2, CH_4, H_2O) of 400 dm^3 (STP) of commercially available research grade xenon to ~1.5 ppm is described. This system has reduced the total active gas contamination of 200 dm^3 (STP) of

recovered xenon from ~200 ppm to ~1.5 ppm. In addition to supplying ultrapure bottled gas to 10 MPa, the purifier may be connected directly to an experiment. In this latter mode, the experimental apparatus becomes p.. t o. the purification loop and is cleaned concurrently with the gas.

Introduction

The purpose for developing a noble gas purification system was the unavailability of extremely pure noble gases (< 2 ppm total impurity concentration of H_2, O_2, H_2O, N_2, CH_2) necessary for evaluating high-pressure molecular gas lasers and for conducting related basic physics experiments.[1-3] In addition, no appropriate purifier was readily available. The basic design of the described purifier was taken from a system reported by H. Zaklad[4] for purifying small amounts of liquid Xe. The size of the system was increased so that it would be capable of purifying, storing and delivering 400 dm^3 (STP) of Xe to experimental gas cells at a maximum pressure of 10 MPa. The system has operated successfully for more than two years. It also can readily be adapted to the other noble gases.

The purification system is a four-stage, closed-loop system using an in-line pump

to maintain a constant gas flow at an absolute pressure of approximately 340 kPa. Pressure intensification is accomplished by cryogenically condensing the purified gas into a clean 1-2 dm^3 stainless steel pressure vessel and allowing the temperature to return to ambient.

Figure 1 is a schematic representation of the system. The first stage is a molecular sieve column maintained at ambient temperature. The second stage is a hot (870 K) calcium metal reactor. The third stage is a hot (450 K) copper catalyst reactor and the fourth stage is a cold (195 K) molecular sieve column.

The first stage removes H_2O, CO_2, and hydrocarbons; the second stage removes O_2, N_2, and H_2O; the third stage removes H_2, CO, and O_2; the fourth stages removes NO, H_2O, N_2O, CO_2, NH_3 and hydrocarbons. The four stages are in series, although provisions
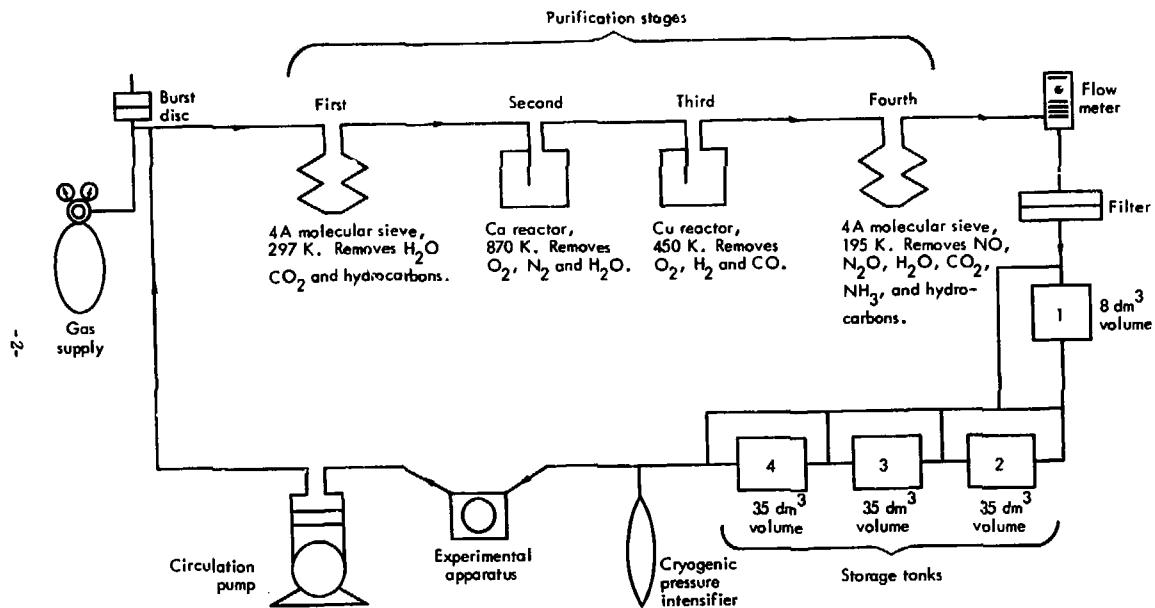
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Fig. 1. Noble gas purifier, schematic layout.

are made for bypassing any one or more of them.

Gas, as supplied by the manufacturer or recovered from previous experiments, is introduced into the system through stage 1. It is circulated through the purifier until the desired impurity concentration is reached. Impurities are continually monitored and analyzed by an inline gas chromatograph and a Beckman hygrometer.[*] The chromatograph constructed by the LLL General Chemistry Division, uses a helium ionization detector and 5A molecular sieve columns.

Commercially available research grade Xe may have high impurity levels, e.g. Kr, 50 ppm; N_2, O_2, Ar and H_2 5 ppm each; and CH_4 10 ppm. Measured levels of H_2O have been as high as 30 ppm. After 25-50 h of purification (depending on the gas volume), the impurity concentration is reduced to N_2, < 0.15 ppm; O_2, ~0.1 ppm; H_2, ~0.04 ppm; CH_4, < 0.006 ppm; and H_2O ~0.2 ppm. The concentrations of other noble gases remain unchanged. [It is possible that the concentration of other active gases may also have been reduced in the purification process, although their presence was not detected with the gas chromatograph.]

Mechanical Design

The closed loop purification system is designed for continuous flow operation. Care is taken to avoid trapped volumes, since this would greatly lengthen the purification time and render the gas analysis uncertain. Furthermore, the entire system is easy to clean before use (hot vapor degreasing and/or Diversey DS9-333 process) and the traps and filters are easy to replace. Finally, the complete system can be evacuated (total leak rate less than 2×10^{-4} mm^3/s He (S. T. P.) as measured by a helium mass-spectrometer leak detector) and can be baked out.

Figure 2 is a detailed diagram of the apparatus. The first and fourth stages

are identical and interchangeable 4A molecular sieve columns (see Fig. 3). Each contains 3 m of 10 mm o.d. × 0.9 mm wall stainless steel tube packed with 1.5 mm particle size 4A molecular sieve. In order to minimize the amount of xenon gas trapped on the surface, molecular sieve 4A (sodium-based material) was chosen over molecular sieve 5A (calcium-based material). At 0.1 MPa and 195 K, 1 g of molecular sieve 5A absorbs 0.1 dm^3 of xenon where molecular sieve 4A absorbs one-fourth of this amount (Ref. 4). The packed tubing is rolled into an 80 mm o.d. coil with 6.3 mm stainless steel "Cajon" fittings TIG welded to the ends. The fourth stage molecular sieve column is cooled (using a crushed dry-ice/Freon-11 slurry) to 195 K (liquid vapor pressure of Xe at 195 K ~0.4 MPa).[5] Operating the column at a lower temperature might seem

-3-
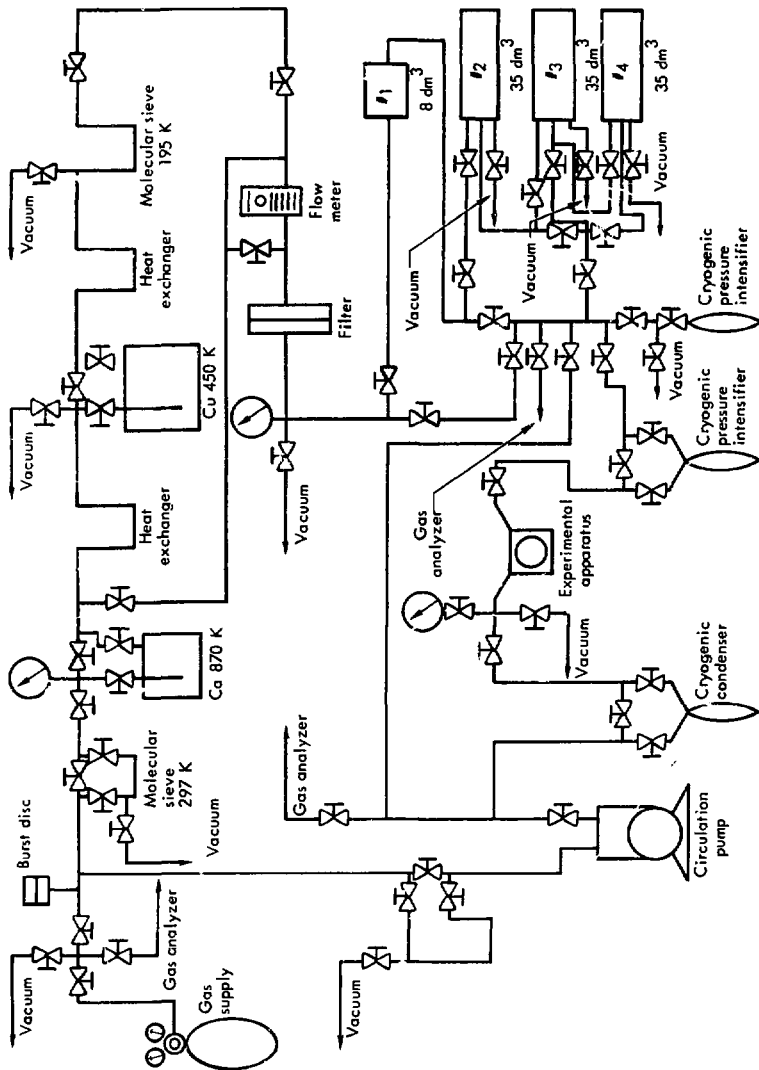
Fig. 2. Noble gas purifier, detailed layout.

Vacuum

Molecular sieve 195 K

Heat exchanger

Vacuum

Heat exchanger

Cu 450 K

Flow meter

Filter

Vacuum

v_1

8 dm³

v_2

35 dm³

v_3

35 dm³

v_4

35 dm³

Vacuum

Vacuum

Vacuum

Cryogenic pressure intensifier

Cryogenic pressure intensifier

Ca 870 K

Vacuum

Gas analyzer

Experimental apparatus

Cryogenic condenser

Burst disc

Molecular sieve 297 K

Vacuum

Gas analyzer

Gas analyzer

Circulation pump

Gas supply

Vacuum

Vacuum

Vacuum

-4-

TIG weld — 6.3 mm Cajon SS tube fitting

10 mm × 0.9 mm wall SS tube 3 m long

Fiberglass plug

1.5 mm particle size Linde 4A molecular sieve
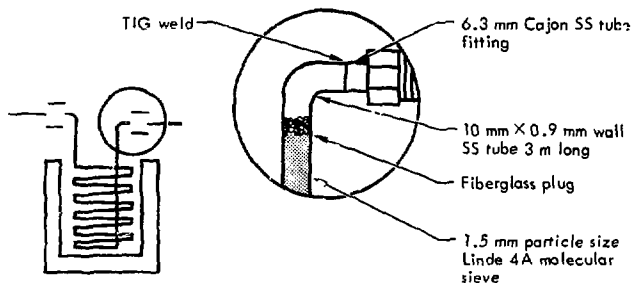
Fig. 3. Detail of 4A molecular sieve column, purifier stages 1 and 4.

advantageous from a gas purification standpoint, but at 0.3 MPa xenon will liquify at ~185.5 K.

The second and third stage reactors are of identical mechanical design (see Fig. 4). The second stage reactor is filled with 160 g of Ca metal nuggets. The third stage is charged with an equal weight of Cu catalyst (BTS) pellets. The body section consists of stainless tube 38 mm diam × 1.3 mm wall with a 70 mm diam stainless steel Varian flange TIG welded on the end. The other end is closed by TIG welding a 1.3 mm wall stainless steel full radius cap to the body. Gas is introduced to the bottom of the reactor through a stainless steel tube 6.3 mm o.d. × 0.9 mm wall, TIG welded

6.3 mm × 0.9 mm wall SS tube
70 mm Varian blank

6.3 mm Cajon SS tube fitting

70 mm Varian flange
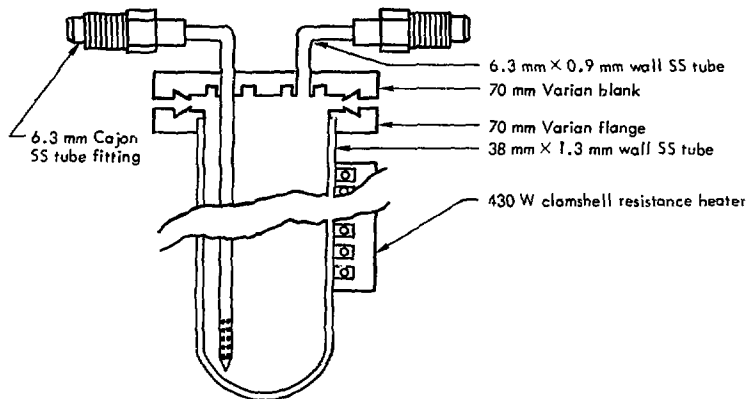38 mm × 1.3 mm wall SS tube

430 W clamshell resistance heater

Fig. 4. Detail of reactor vessel, purifier stages 2 and 3. Stage 2 is charged with Ca metal nuggets, stage 3 with Cu catalyst (BTS) pellets.

into a ported blank Varian flange. Gas collected at the top of the reactor exits through similar construction. Stainless steel "Cajon" tube fittings are TIG welded to the open ends of the inlet and outlet tubes.

Heat is provided to the second and third stage reactors by 430 W clamshell resistance heaters. A Chromel-Alumel thermocouple secured to the reactor in the center of the heated area monitors the temperature. The reactor temperature is set and maintained using a potentiometric temperature controller.

Two interstage coolers (one on each side of third stage reactor) control the temperature of the gas exiting from the heated second and third stages. This is done by forced air circulation over a 3 m coil of 6.3 mm o.d. stainless steel tube (see Fig. 5). A 142 mm diam filter is inserted on the exit side of the fourth stage to trap all particles larger than 0.028 μm (see Fig. 6).

Continuous flow of gas in the closed loop is provided by a welded bellows stainless steel pump (see Fig. 7). This pump is rated at a gauge pressure of 310 kPa. The rate of gas flow is controlled by restricting the inlet flow to the pump using a stainless steel metering valve. The gas flow can be read directly from an argon type flow meter rated at 0-0.33 dm^3/s at 345 kPa gauge pressure (see Fig. 8).

The total gas volume in the system is selectively controlled by using the four stainless steel storage tanks (see Fig. 2). An 8 dm^3 vessel is placed in the primary loop. Three additional 35 dm^3 vessels are available if a large volume of purified gas is required in the experimental gas cell. Table 1 shows several volumes of purified gas available at 300 kPa and 298 K for experimental purposes. To provide high-pressure purified gas, the gas is cryogenically condensed into a stainless steel pressure
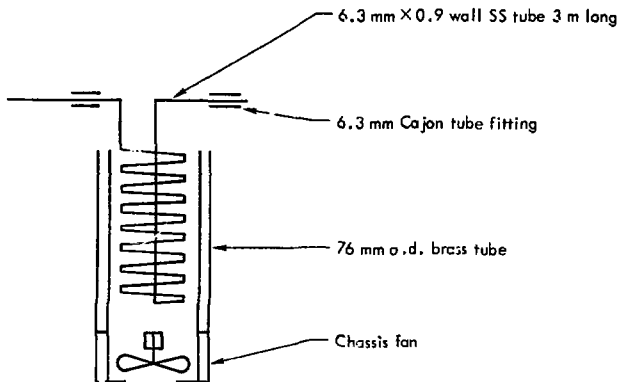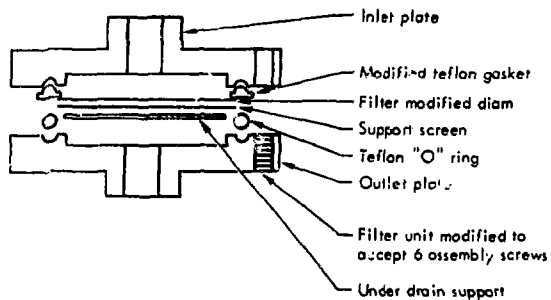

— 6.3 mm × 0.9 wall SS tube 3 m long

— 6.3 mm Cajon tube fitting

— 76 mm o.d. brass tube

— Chassis fan

Fig. 5. Interstage heat exchanger.

Inlet plate
Modified teflon gasket
Filter modified diam
Support screen
Teflon "O" ring
Outlet plate
Filter unit modified to accept 6 assembly screws
Under drain support

Fig. 6.   Millipore 142 mm filter, specially modified.

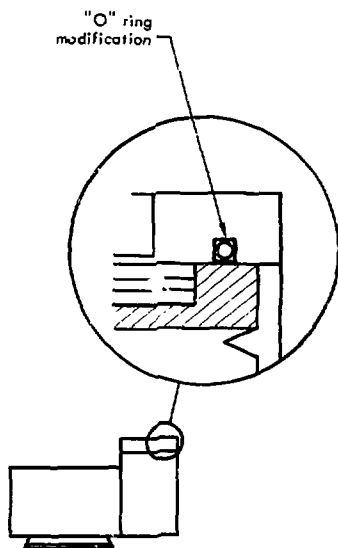"O" ring modification

40
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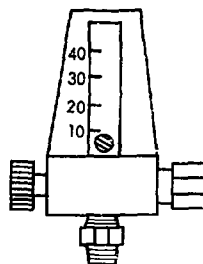10

Fig. 7.   Welded bellows positive displacement pump, modified.

Fig. 8.   National argon flowmeter, 0-0.33 dm^3/s at 345 kPa.

Table 1. Purifier gas capacity
(STP) at 300 kPa.

Segment	Volume, dm^3
System alone	6
System plus volume 1	30.4
System plus volumes 1 and 2	134.4
System plus volumes 1, 2, and 3	238.4
System plus volumes 1, 2, 3, and 4	342.4

vessel and then warmed to ambient temperature (see Fig. 9). A 1 dm^3 bottle will hold 300 dm^3 (STP) of Xe at ~10 MPa.[6]

Supply gas is metered into the system using a stainless steel pressure regulator. Protection against over-pressure in the system is provided by a 350 kPa all welded stainless steel burst disc (see Fig. 10). The pressure drop across the reactors and filter is monitored by two 0-40 kPa stainless steel gauges.

All valves in the system are stainless steel. With the exception of the flow-control valve and the vacuum valves, all valves are welded and bakeable (see Fig. 11). The tubing used in the system is 6.3 mm outside diameter × 0.9 mm wall stainless steel tube which is TIG welded to "Cajon" VCR tube fittings.

Reactor Activation

One of the most important tasks to be performed before operating the purification system is to activate the reactors.

The molecular sieve columns are activated by a 16 h bake at 573 K. A suitable dry gas (He or Ar) flowing (8 cm^3/s) through the hot sieve column for the first 2 h will aid in removing other gases from the sieve material. After 2 h of flowing gas through the hot

TIG weld

SS welded valve
13.8 MPa working pressure

10 mm × 1.7 mm wall SS tube

SS adapter

Dot 3 A 1800 SS 1-2 dm^3 pressure vessel
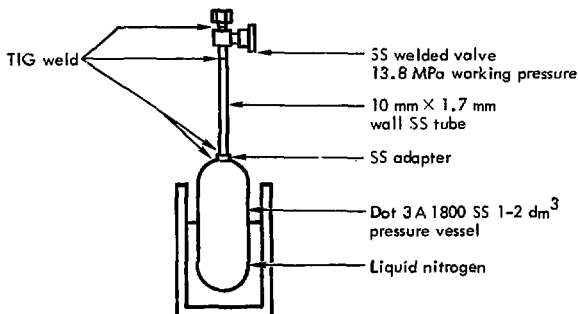
Liquid nitrogen

Fig. 9. Cryogenic pressure intensifier.

column, the column must be evacuated. A continuous vacuum should be maintained for the remainder of the bakeout cycle.

The calcium metal reactor is activated by heating the calcium to 773 K under vacuum for 3-4 h. Copper catalyst activation is more complicated. Copper in its oxidized state must be reduced.

Reduction is accomplished using heat and hydrogen gas (see Fig. 12). The reaction is started at ~373 K by flowing a gas mixture (10% H_2 and 90% He or Ar) through the reactor. The total flow rate is approximately 5 cm^3/s.

The exothermic chemical reaction will heat the copper catalyst to destruction if not controlled. Control of the reaction rate, i.e., the heat, is achieved by limiting the available hydrogen. With the reactor at 375 K and an initial 10/90 H_2/He mixture, the H_2 flow rate should be slowly increased, keeping the reactor temperature below 393 K until a 50/50 H_2/He mixture is obtained. Maintaining the temperature at 390 K, the He flow rate is reduced until a 100% H_2 flow is obtained. The temperature of the reactor is then slowly increased to 423 K. The final phase of the activation process (100% H_2) continues for ~3 h at 423 K.

Operation

Prior to operation, the purifier must be leak tested to ensure vacuum integrity. The initial gas charged into the system flows through the molecular sieve columns but may bypass the Ca and Cu reactor. The final gauge pressure of the system (139-310 kPa) determines the total volume required. The restriction valve on the inlet side of the pump should be set to allow a flow rate of ~28 cm^3/s. At this point, the gas should be allowed to flow through the reactors. The Ca and Cu
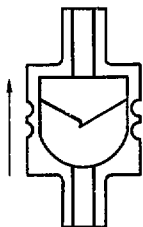

Fig. 10. Stainless steel welded burst disc, 340 kPa, Pike #A3897-4.

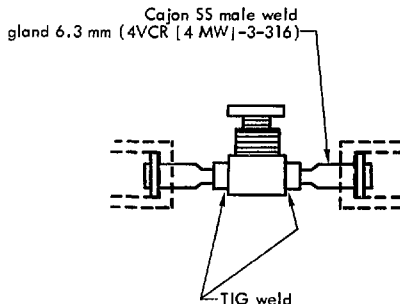Cajon SS male weld gland 6.3 mm (4VCR [4 MW]-3-316)

TIG weld

Fig. 11. Nupro stainless steel bakeable vacuum valve, SS-4H-SW.

reactor temperatures are then raised to 870 K and 450 K, respectively. It is important to monitor the temperatures and flow rate frequently. At appropriate intervals, the impurity concentration of

the gas is checked with the gas chromatograph and hygrometer. Finally, the purified gas is drawn into the cryogenic pressure intensifier by cooling the bottle with liquid N_2.

Discussion

The described purifier was a key element in the sucessful operation of gamma-ray and electron beam pumped, high-pressure noble gas lasers. To produce lasing in the purest commercially available noble gas would require

extremely high beam currents to overcome the intrinsic losses due to impurity absorption. For example, absorption measurements in Xe have shown that a few ppm of H_2O produce significant absorption at the peak vacuum uv
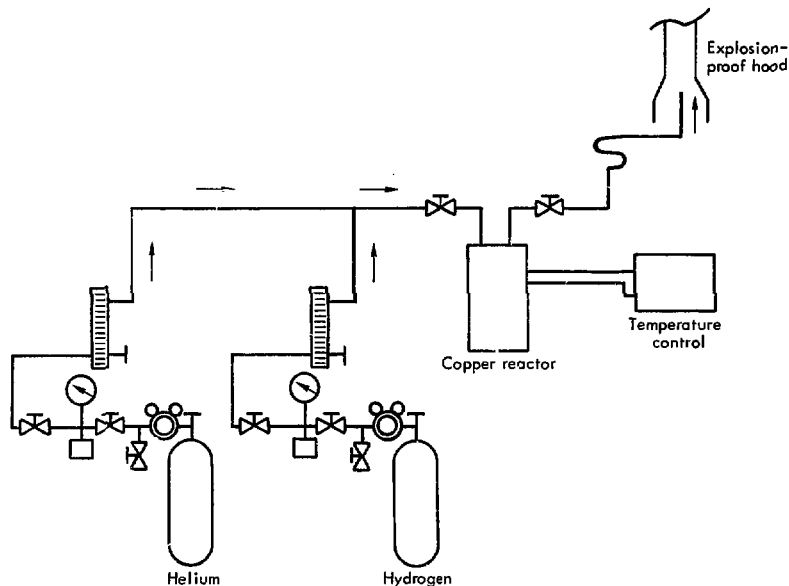

Fig. 12. Copper reactor activation system.

emission wavelength and O_2 has a similar effect at shorter wavelengths. Furthermore, to examine the vuv spectroscopic properties of the noble gas molecules, the impurities affecting the measurable quantities must be removed. Also, continuous irradiation of flowing noble gases requires a purifier as an integral part of the experimental gas cell.

Detailed analyses of the impurity concentrations at different times during the purification process are indicated in Tables 2 through 4. The total impurity concentration as a function of purification time is shown in Fig. 13. A significant reduction in the impurity level was obtained a few hours after startup with a subsequent nearly constant level. This
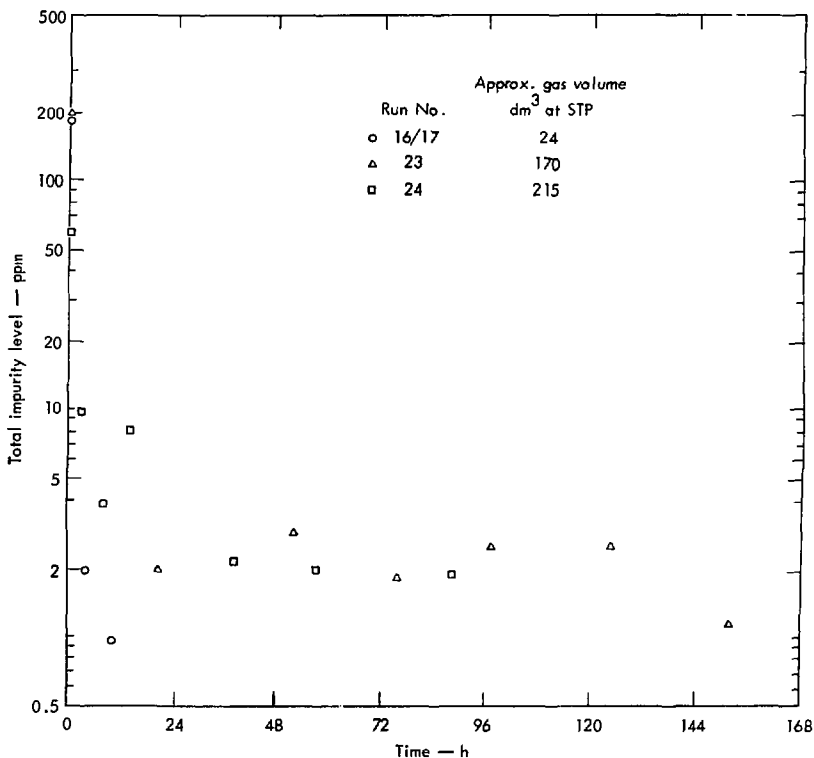

Fig. 13. Total impurity levels (ppm) of combined H_2, O_2, N_2, and CH_4), runs 16/17, 23. and 24.

clearly indicates that larger reactor volumes are desirable for more efficient operation.

Table 2. Levels of representative impurities (ppm) during run 16/17— purification of 24 dm³ (STP) of xenon.

	Supply	1 h	4 h	11 h
H_2	16	0.3	0.06	—
O_2	54	1.2	1.2	0.8
N_2	112	0.8	0.8	0.15
CH_4	0.04	0.09	0.08	0.05
Total	182.04	2.39	2.14	1.00

Although the purification system was continuously operated successfully for over two years, several unavoidable problems occurred in the design and operation. For instance, the purchased Millipore filter leaked, ; the gasket (see Fig. 6) had to be redesigned and the compression on the sealing cover increased. The "welded bellows" vacuum/ pressure pump arrived with a leak in the checkvalve assembly. The manufacturer would not guarantee He mass spectrometer tightness on this model (MB-151). This leak problem was solved (with the manufacturer's concurrence) by installing an "O" ring in the checkvalve assembly.

Table 3. Levels of representative impurities (ppm) during run 23 — purification of 170 dm³ (STP) of xenon.

	Supply	$3\frac{1}{2}$ h	9 h	39 h	58 h	88 h
H_2	18	2.2	1.4	0.46	0.43	0.35
O_2	9	4.5	1.8	0.7	0.65	0.63
N_2	31	—	—	0.77	0.82	0.79
CH_4	2	1.0	0.24	0.09	0.08	0.06
Total	60	>7.7	>3.4	2.02	1.96	1.83

Table 4. Levels of representative impurities (ppm) during run 24 — purification of 215 dm³ (STP) of xenon.

	Supply	22 h	50 h	74 h	98 h	125 h	152 h
H_2	6.6	0.2	0.23	0.19	0.10	0.07	0.08
O_2	51.7	0.7	0.8	0.63	0.64	0.60	0.58
N_2	102.5	0.8	1.7	0.94	1.7	1.9	0.60
CH_4	1.8	—	0.04	0.03	0.04	0.11	0.03
Total	162.6	1.7	2.77	1.79	2.48	2.69	1.29

The calcium metal was melted on initial attempts to run this reactor at 933 K. The thermocouple junction was relocated and the operating temperature lowered to 870 K.

The flow control with a low-pressure regulator on the inlet side of the pump presented three problems: questionable gas contamination, air leakage under vacuum, and erratic flow control. The function of the low-pressure regulator is to control the inlet pressure to the pump and thus control the flow rate in the system. Visual inspection through the inlet port revealed a large quantity of a grease-like sealing material. The regulators were disassembled, cleaned, and re-assembled with a limited amount of vacuum grease. Regulators cleaned and assembled as above still leaked under vacuum. The installation of a clean, stainless steel vacuum leaktight shutoff/metering valve solved the problems associated with the low-pressure regulator.

Some improvements that were thought to be valuable but were not incorporated in the present purifier or its operation are:

1. A way of determining the completion of the copper catalyst activation reaction by monitoring the H_2O emission content.

2. Replacement of the calibrated flow meter with one made of stainless steel and glass.

3. Enlarging the reactors to hold 5 kg reactive material. This would significantly shorten the purification time of large quantities i.e., 200-400 dm^3 (STP) of gas.

On occasion the H_2, O_2, N_2 and CH_4 gas chromatograph peaks disappeared completely. At the completion of purification runs, water was not detectable on a model 719 Beckman Electrolytic Hygrometer. Any improvement in the purifier parallels an equal improvement in the sensitivity of the gas analyzer as we use it. To detect the moisture level of the purified gas requires a more sensitive instrument.

Acknowledgments

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