PROCESS GAS CHROMATOGRAPHY FOR
MONITORING A RARE-GAS SEPARATION SYSTEM

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MASTER

JUNE 1978

**UNION
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OAK RIDGE GASEOUS DIFFUSION PLANT
OAK RIDGE, TENNESSEE

*prepared for the U.S. DEPARTMENT OF ENERGY under
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Special Services Department
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Oak Ridge Gaseous Diffusion Plant
Union Carbide Corporation
Oak Ridge, Tennessee

Prepared for the U.S. Department of Energy
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ABSTRACT

An automatic process gas chromatograph analytical system has been designed for monitoring a pilot plant absorption process used for the separation and concentration of the rare gases krypton and xenon. Chromatographic columns have been developed which allow analysis of a wide variety of gases from simple mixtures of nitrogen, krypton, and refrigerant, to more complex mixtures containing oxygen, nitrogen, refrigerant, carbon dioxide, nitrous oxide, methane, krypton, and xenon.

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PROCESS GAS CHROMATOGRAPHY FOR MONITORING
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INTRODUCTION

Analytical support of an engineering development program at the Oak Ridge Gaseous Diffusion Plant (ORGDP) required an on-stream analyzer for the determination of rare gases and other constituents in a process to be applied to the separation and concentration of radioactive krypton and xenon.

The radioactive gases, krypton and xenon, are produced as fission products in the normal use of nuclear fuel and are, at some point, released. This can occur during normal operation of the nuclear reactor if it uses vented fuel elements, or from the rupture of sealed fuel elements during reprocessing. With the increasing need for nuclear fuels in the power industry, and concern about subsequent discharge of radioactive nuclides to the atmosphere, a program has been undertaken at ORGDP to define and develop a process to remove small amounts of krypton and xenon from a matrix gas.¹⁻³ This program is being conducted by the Materials and Systems Development Department of the Gaseous Diffusion Development Division at the request of the Division of Reactor Development, U.S. Department of Energy (DOE).

The separation process is based on the preferential absorption of krypton and xenon in liquid Refrigerant-12 (R-12) (dichlorodifluoromethane) at a relatively low temperature and high pressure, followed by fractionation at higher temperature and lower pressure to reclaim the krypton-xenon gas product.⁴ A diagram of the adsorption process pilot plant is shown in Figure 1.

Automatic, on-stream analysis is useful in monitoring many processes. In a development program involving many variables, it is especially advantageous because of the speed and ease with which data can be obtained. Gas chromatographs have received extensive development and now find wide application as process analyzers. In a gas processing system requiring the determination of several components, gas chromatography is often the analytical technique of first choice.

SUMMARY

A commercial gas chromatograph was adapted for the determination of a variety of constituents. Automatic continuous program cycling, multiple column valving, and a thermal conductivity detector permitted the convenient measurement of krypton and xenon over a range of from 10 to 20 ppm up to several percent. Methane and nitrous oxide from 0.01 to about 5%; carbon dioxide and Refrigerants-11 and -12 (R-11 and R-12) from a few tenths of a percent to about 7%; and oxygen from a few percent to about 20% were also determined by this technique. A wide variety of columns was examined

Figure 1
KRYPTON- XENON ABSORPTION PILOT PLANT

to provide a capability for determining all of these constituents in a single sample. Simple mixtures such as nitrogen, R-12, and krypton may be analyzed in 15 min; more complex mixtures require up to 30 min. Multiple-column switching techniques were used. Only nonradioactive gases were examined during these studies.

PREVIOUS WORK BY OTHERS

Gas chromatography columns suitable for the determination of krypton and xenon in air have been critically examined by Aubeau, Champeix, and Reiss.⁵ Silica gel, activated carbon, and 13X molecular sieves were all found to be suitable; however, the authors indicated a preference for activated carbon or molecular sieves.

Whilhite and Hollis⁶ have shown that columns packed with porous polymer beads give excellent separations of air, carbon dioxide, nitrous oxide, and methane. The authors also stated that the polymers have essentially no vapor pressure and thus no significant bleeding.

EXPERIMENTAL WORK

Nonradioactive krypton in air was used as the feed gas in initial studies (Phase I). More recent work has expanded those studies to include xenon, with carbon dioxide, nitrous oxide, and methane as representative contaminant gases (Phase II).

INSTRUMENTATION

Any of a number of commercial process gas chromatographs may be used. A block diagram of a typical system is shown in Figure 2.

PHASE I

Initial pilot plant operations were concerned with a mixture of oxygen, nitrogen (air with carbon dioxide and water removed), R-12, and ppm levels of krypton. The best overall analytical separation, in terms of peak shapes and sensitivities for this mixture, was achieved using a series of solid absorbent columns operating above 100°C.

The conditions for analysis of a mixture of oxygen, nitrogen, R-12, and trace levels of krypton were:

*Halocarbon Products Corporation, 52 Burlews Court, Hackensack, New Jersey.

Figure 2
PROCESS GAS CHROMATOGRAPH

Temperature: 121°C

Carrier Gas: Helium, 44 cc/min

Column I: Silica gel, 1/4-in. OD x 20 cm

Column II: Section 1 - Activated carbon, 1/4-in. OD x 3 m

Section 2 - Molecular sieves 5A, 1/4-in. OD x 1-1/2 m

Order of Elution: R-12, oxygen, argon, nitrogen, and krypton

Total analytical cycle time: 15 min

A pilot chromatogram, produced from a qualitative mixture of gases made in the laboratory, is shown in Figure 3. This chromatogram was used to establish the sequence of operations and the elution order.

In operation, the R-12 component was diverted directly to the thermal conductivity detector from Column I by automatic valving, while air and krypton were stored in Column II. After the R-12 was measured, Column II was automatically returned to the carrier gas stream for the separation of oxygen, nitrogen, and krypton. The activated carbon section of Column II began the isolation of the trace quantities of krypton from the major constituent (air), while the molecular sieve section separated the air into oxygen (plus argon) and nitrogen, and further isolated the krypton. The use of a compound column allowed adequate separation of the ppm levels of krypton from the major constituents, without prolonging the analysis through excessive separation of oxygen-argon and nitrogen, as would have been the case with a simple molecular sieve column.

Calibration for the krypton measurement was provided for an operating range from 20 ppm to 0.74% by volume. A limit of detection of 5- to 10-ppm was established for 10-cc samples at 4-psig pressure and 121°C. At 77-ppm krypton, the standard deviation was ± 2 ppm and the limit of error for one determination (95% confidence level) was $\pm 6\%$ (relative). Calibration for the R-12 component was made over a range of 0.5 to 4%; at 1.84% the standard deviation was $\pm 0.06\%$ (absolute) and the limit of error for one determination (95% confidence level) was $\pm 8\%$ (relative). The precision for the oxygen determination was not ascertained. Suitable attenuation levels for each desired constituent are programmed for automatic operation. These attenuation levels are precisely reproducible and are easily changed for the widely varying concentrations encountered in normal operation.

A planned change in the rare-gas pilot plant separating medium, from R-12 to R-11, required that the silica gel column be changed from 1/4-in. OD x 20 cm to 1/8-in. OD x 40 cm to maintain proper elution time. No other changes were made in the analytical operating conditions. The chromatogram of the mixtures containing R-11 followed the same elution sequence shown in Figure 3.

Figure 3
CHROMATOGRAM OF LABORATORY MIXTURE OF O_2 , N_2 , R-12, Kr

PHASE II

The pilot plant study was expanded to cover the behavior of carbon dioxide, nitrous oxide, methane, and xenon in the rare-gas separation system, as well as the gases previously studied. The separating medium used was R-12; the matrix gas was either dry air or nitrogen.

Several column packing materials were investigated for the separation of these additional gases. Among these were porous polymer beads and deactivated silica gel.

Of the porous polymer beads investigated, the best results were obtained with Porapak S* and Chromosorb 102.** These two materials are essentially equivalent for the separation of carbon dioxide, nitrous oxide, and xenon. More recent work indicates that Chromosorb 105 would also be suitable. Sufficiently long columns (1/4-in. OD x 35 ft) of any of the porous polymer beads will separate methane and krypton. The polymers were not suitable for the separation of R-12 at the relatively low temperatures (40 to 50°C) necessary for separating the other gases.

These polymer materials are reported to have little or no bleed of organic vapor; however, the vendor recommended conditioning of new material at an elevated temperature with a helium purge for 2 hr to remove volatile material remaining from the manufacturing process. At the high detector sensitivities employed in this procedure, conditioning for a minimum of 48 hr is required; even so, some changes in base line levels are evident on column-switching which suggest some slight bleeding of volatiles.

In the multiple column procedure, separation of R-12 on a normal silica gel column was no longer feasible at the low temperatures required for the porous polymer column. Satisfactory R-12 elution time and peak shape were obtained by partially deactivating silical gel with a 2% (by weight) coating of polyethylene glycol 4000.

Revised operating conditions for the gas chromatograph were:

Temperature: 49°C,

Carrier: Helium, 90 cc/min,

Column I: 1/8-in. OD x 6 ft, silica gel inactivated with 2% polyethylene glycol 4000,

*Waters Associates, Inc., 61 Fountain Street, Framingham, Massachusetts 01701.

**Applied Science Laboratories, Inc., P. O. Box 440, State College, Pennsylvania 16801.

Column II: 1/4-in. OD x 19 ft, Chromosorb 102,

Column III: Section 1 - 1/4-in. OD x 2 ft, activated carbon,

Section 2 - 1/4-in. OD x 11-1/2 ft, molecular sieve 5A, and

Total Analytical Cycle: 30 min.

The elution and sequence of operation are shown in Figure 4. Column lengths and valving times were chosen to allow separation of the resolved constituent gases, and to ensure that the gases were eluted from the proper column without cross-over into columns inapplicable to their separation (e.g., R-12 into Chromosorb 102, or carbon dioxide into molecular sieves). A determination of nitrogen was not required for this process.

A typical process chromatogram is shown in Figure 5. Nitrogen was the matrix gas. This chromatogram shows some base line problems, due to a slight bleed from the Porapak column and a long tail from the large nitrogen peak. This requires base line corrections as shown; while not an ideal situation, this has nonetheless proved to be a practical approach which provides acceptable levels of accuracy.

DISCUSSION

The column systems which were examined allow analysis of a wide variety of gases, from simple mixtures to more complex mixtures containing several species. Table 1 lists relative retention times of a variety of columns for the gases discussed. This table includes relative retention times for some additional column materials which were more recently examined. Such empirical data may be useful both in selecting column materials and in column-switching programs.

The analytical techniques described in this report have been applied to stable, nonradioactive krypton and xenon only. The use of radioactive gases in the rare-gas separation system development program, or application of the analytical system to a real process situation, requires consideration of the effects of radioactivity on the chromatograph. Glueckauf⁷ has shown that the separation of krypton from xenon is affected by the radioactivity of the gas. During the passage of a band of radioactive gas through a chromatographic column, the absorption of β -radiation raises the temperature of the column packing; the trailing end of the gas band then tends to move faster, resulting in a contraction of band width; the retention time of the gas is also reduced. Glueckauf stated that with moderately radioactive gases, separation is slightly more efficient due to band contraction; however, when the energy approaches a value of 14 J/ml of gas, a separation is no longer possible except under specified conditions. It seems probable that a krypton-xenon separation can be achieved under the operation conditions expected in this rare-gas separation system.

Figure 4
CHROMATOGRAM OF LABORATORY MIXTURE
OF N₂, O₂, CO₂, N₂O, CH₄, Kr, Xe, R-12

Figure 5
PROCESS GAS CHROMATOGRAM

Table 1

RELATIVE RETENTION TIMES

	<u>Deactigel</u>	Davidson 08 <u>Silica gel</u>	Davidson 12 <u>Silica gel</u>	<u>Activated Carbon</u>	<u>Alumina F-1</u>	Molecular Sieve 5A	<u>Chromosorb</u>	
							102	105
Kr	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Xe	5.75	2.80	2.38	12.5	3.60	5.64	5.90	5.50
CH ₄	0.75	0.53	0.40	1.12	1.20	1.43	0.90	1.40
CO ₂	14.1	20.0	10.1	3.16	-	-	2.50	2.90
N ₂ O	14.2	6.20	5.53	4.64	6.93	-	3.70	3.70
R-12	80.4	17.3	43.3	-	47.0	-	37.5	44.1
O ₂	-	-	-	-	-	0.29	-	-
N ₂	-	-	-	-	-	0.83	-	-

While the possibility of radiolytic decomposition of column packing remains, the small samples normally encountered in gas chromatography should minimize this.

CONCLUSIONS

Process gas chromatography greatly reduces the need for manual sampling and laboratory determination of gas constituents; control of the pilot plant process is improved by providing direct and prompt on-site analysis. Process gas chromatographs are also readily integrated into computer systems for rapid acquisition and treatment of data. The value of improved process efficiency is greater than savings in analytical costs.

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