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MASS SPECTROMETRIC ANALYSIS OF KRYPTON
AND XENON IN LOW CONCENTRATIONS

J. C. Horton

OAK RIDGE GASEOUS DIFFUSION PLANT
OAK RIDGE, TENNESSEE

*prepared for the U.S. ATOMIC ENERGY COMMISSION
under U.S. GOVERNMENT Contract W-7405 eng 26*

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Oak Ridge Gaseous Diffusion Plant
Union Carbide Corporation
Oak Ridge, Tennessee

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ABSTRACT

Krypton and xenon were analyzed by mass spectrometry in concentrations as low as 0.1 ppm in the presence of air components and halocarbons. Nitrogen, oxygen, and halocarbons were removed by exposing the samples to hot titanium sponge, enabling the remaining inert gases to be measured with a 100-fold increase in sensitivity.

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MASS SPECTROMETRIC ANALYSIS OF KRYPTON AND XENON IN LOW CONCENTRATIONS

INTRODUCTION

Radioactive krypton and xenon are among the products of nuclear fission and are largely contained in the fuel during reactor operation but released to the off-gas system during nuclear fuel processing. As a consequence of cladding failure or leakage, part of these gases is, however, released through the coolant system to the gaseous vent streams from nuclear reactors. The removal of these gases by selective absorption with a halo-carbon solvent was studied in a pilot plant designed and built at the Oak Ridge Gaseous Diffusion Plant (ORGDP).¹ Analytical methods were needed to monitor krypton and xenon in the presence of air and halocarbons, and in concentrations as low as 1 ppm.

The typical gas-analysis mass spectrometer can detect 10 to 100 ppm of a component in a gas mixture. One way to lower this detection limit is to selectively remove most of the gas in a sample, leaving only the components of interest. Roboz² analyzed ultrapure oxygen by quantitatively removing the oxygen with a sodium-potassium alloy while retaining all of the inert impurities for mass spectrometer analysis. No reaction was observed between nitrogen and the sodium-potassium alloy. Kyle and co-workers³ used titanium sponge to remove nitrogen from oxygen-free argon. Oxygen partially inhibits the titanium-nitrogen reaction, and as much as 3% nitrogen may remain unreacted after passing through a bed of titanium at 1000°C when oxygen is present.⁴ In both cases cited above, a dynamic system was used, so that a continuous stream of gas passed through the bed of hot titanium.

Complete removal of nitrogen was achieved in the ORGDP system by allowing the gas to remain in contact with the hot titanium for several minutes.

SUMMARY

A method was developed for the analysis of krypton and xenon in concentrations as low as 0.1 ppm, in a mixture of air components and halocarbons. Complete removal of nitrogen, oxygen, and halocarbons was effected by exposure to hot titanium sponge for a few minutes. The remaining argon, krypton, and xenon could then be measured by mass spectrometry with a 100-fold increase in sensitivity. A preliminary analysis of the original sample established the argon content, and in the final analysis argon served as an internal standard for krypton and xenon.

APPARATUS

A diagram of the system is shown in figure 1. The reactor was designed to fit in a standard combustion tube furnace, and consisted of a stainless steel (type 310) tube 1 in. in diameter, with 3/8-in. elbows welded to each end to withstand the high temperature. All other joints were silver soldered. This tube was completely filled with titanium sponge of various particle sizes, the majority of which ranged from 1 to 3 mm in diameter. A thermocouple of chromel-alumel was used in the measurement of furnace

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Figure 1
TITANIUM REACTOR

temperature, and a rheostat was used to manually control the temperature at a constant level. Two separate lines connected the reactor to the spectrometer manifold, so that sample could be admitted either before or after reaction with titanium.

A second reactor of identical construction was used as back-up to ensure continuous operation.

PROCEDURE

A two-part analysis was made of each sample; first of a portion of the unreacted gas for all components except krypton and xenon, and then of the remaining gas after exposure to titanium. In addition to nitrogen and oxygen, the halocarbon solvent was completely removed in the hot furnace, so that only inert gases remained. Since argon was quantitatively analyzed in the first portion of gas, it served as an internal standard for the determination of krypton and xenon in the second half of the analysis. (The argon content of normal air was altered by exposure to the process solvent.)

The sample tube, containing 100 ml of gas at atmospheric pressure, was attached to the reactor manifold at point A (figure 1). After pumping away the trapped air through the mass spectrometer manifold, a small portion of the sample was admitted to the spectrometer through line BE for the first part of the analysis. During the few minutes required to mass scan this portion of the sample, the entire remaining content of the sample tube was opened to the reactor through valve C and allowed to react with the hot sponge. The temperature of the reactor was maintained between 900 and 920°C for all analyses, since stainless steel could not withstand much higher temperatures in contact with titanium.³

The remaining inert gas was admitted to the spectrometer manifold through valve D for analysis. Sample flow to the ion source was increased to a point just short of a nonlinear relation between pressure and peak height. Since argon-40 would be far off-scale on the recorded spectrum, argon-36 was measured against krypton-84 and xenon-129.

SENSITIVITY CHECK

Atmospheric air contains approximately 1 ppm krypton and 0.1 ppm xenon, and it was convenient for testing the sensitivity of the method. The same procedure was followed as described above, except that the first half of the analysis was omitted, since normal air composition is well known.

At maximum sample flow to the ion source, a peak height of 20 chart divisions at mass 84 was recorded on the 10-mv scale, corresponding to a krypton sensitivity of 0.05 ppm per chart division. Repetitive measurements with successive portions of air showed a mass 84 peak height variation of only 1 chart division, or 5%. Xenon-129 yielded a peak height of 7 chart divisions on the 1-mv scale. Background noise was approximately one-half of these 7 chart divisions on the 1-mv scale, so xenon was barely detectable in air.

REACTOR RECLAMATION

After 423 analyses were made as described in the procedure, a small amount of nitrogen (0.1%) remained in the sample after the reaction with titanium. One atmosphere of hydrogen was added to the hot reactor and allowed to remain for a few minutes before pumping it away. Following this treatment, more than 150 analyses were made without any further breakthrough of nitrogen. Presumably, hydrogen reduced the titanium oxide so that the poisoning effect of oxygen was eliminated.

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