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Instruments

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AN AUTOMATIC GAS CHROMATOGRAPH FOR MONITORING OF REACTOR FUEL FAILURES - PART I - DESIGN

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Pile Engineering Division

April 1959

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ABSTRACT

A device was developed for detecting the failure of a fuel element in a reactor by monitoring for the presence of gaseous fission products. Small amounts of gaseous fission products were detected in the presence of radioactive argon by separating the fission product gases from the argon by chromatography. An automatic sequencing device was provided for taking samples at short intervals to ensure rapid detection of failures.

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INTRODUCTION

Fission products are released into the coolant of a reactor when the cladding of a fuel element fails. In order to minimize the spread of radioactivity in the reactor system, it is essential that any fuel element with defective cladding be detected and removed from the reactor as soon as possible. One method of detecting a failure is to monitor the coolant for the presence of gaseous fission products, which are dispersed very rapidly throughout the coolant system after the cladding fails on a fuel element. This report describes a device that was designed to isolate fission product gases and detect their presence by means of radioactivity measurements.

SUMMARY

Initial laboratory tests were successful on a device that was developed to indicate failure of fuel elements in a reactor by detecting the presence of gaseous fission products in the reactor coolant. The basic feature of the device, called a GC Rupture Monitor, is a gas chromatograph which separates trace quantities of the gaseous fission products, xenon and krypton, from radioactive argon. The radioactive background of argon results from the irradiation of air that is dissolved in the coolant. Samples of the gas dissolved in the reactor coolant are stripped from the coolant and fed to a chromatographic column. The argon from samples is bled off as it emerges from the column, and the krypton and xenon, if present, are fed to a beta counter. An automatic timer operates the valves in the system at the proper time to ensure that no argon reaches the counter and that fresh samples are analyzed at desired intervals.

Argon and krypton were successfully separated by the devices at concentrations as low as 10^{-12} mol %, the lower detection limit of the instrument. No mechanical failures occurred during four months of testing in the laboratory, during which time over 15,000 samples were analyzed.

DISCUSSION

PRINCIPLE

Gas chromatography is a separation technique in which a sample, consisting of a mixture of gases, is fed to a suitable sorbent column, and subsequently eluted from the column by a gas carrier. As the sample flows through the column, the various gases are sorbed on and desorbed from the column packing. Differences in sorption coefficients cause the gases to travel at different rates through the column, and to emerge as discrete bands of relatively pure fractions in the carrier. The eluted gases may be collected as purified fractions when they emerge from the column, or may be passed through suitable detectors for analytical purposes.

DESIGN APPLICATION

The GC Rupture Monitor is fed with intermittent samples of gas, which are stripped from the coolant of a reactor. These samples are flushed through a chromatographic column with helium as the elutriant. The samples are separated by the sorbent during their passage through the column, and emerge from the column at fixed time intervals. The nonfission radioisotopes (argon, oxygen, and nitrogen) are the first to emerge from the column, and are vented by a valving system that is automatically timed. The krypton and xenon, which are present in quantities only as fission products, emerge later, and are directed by the valving system to a beta counter. Discrimination between fission product and nonfission product activity is provided by this intermittent change in flow pattern.

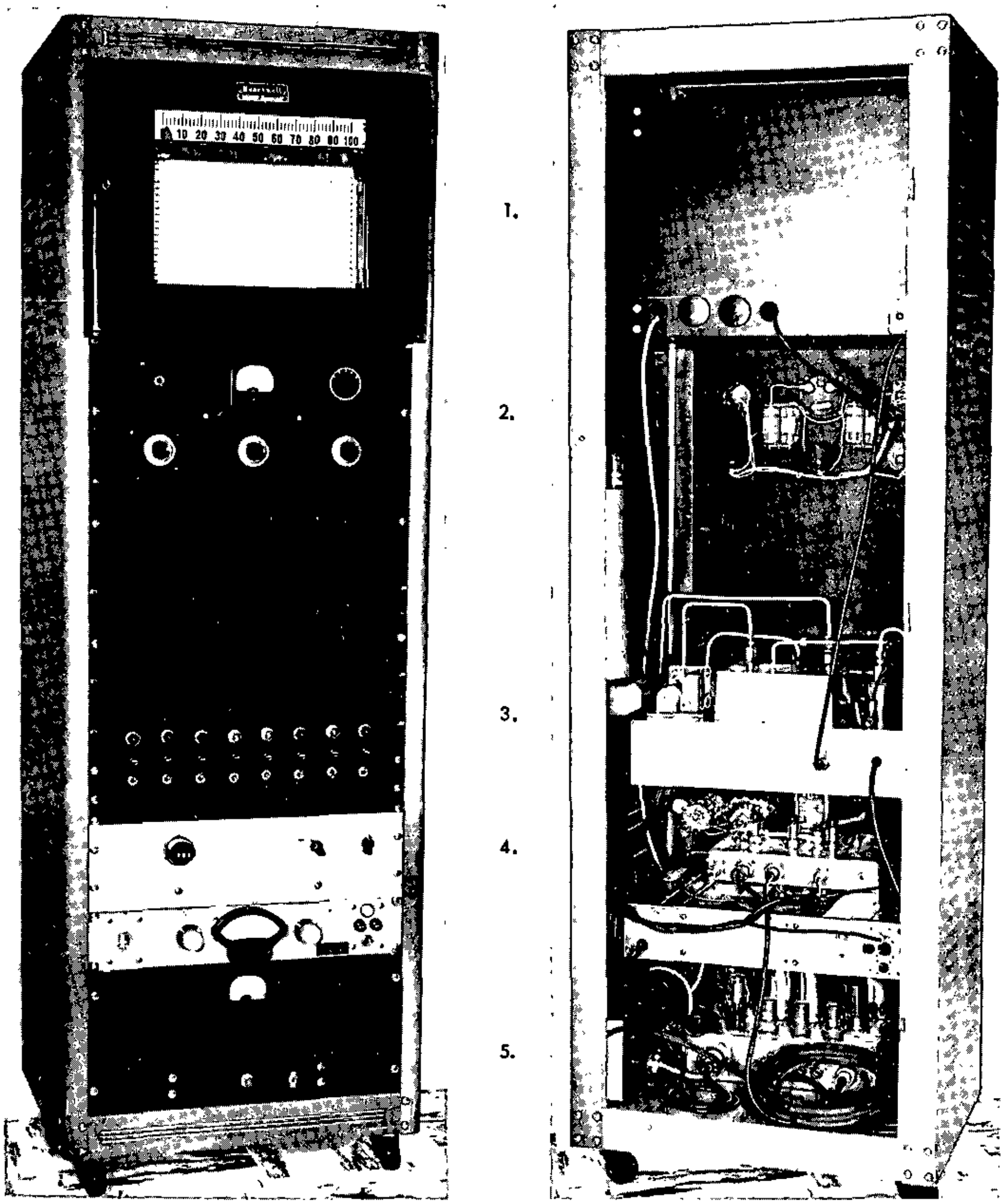
The gas chromatograph and auxiliary components are mounted in a metal cabinet, as shown in Figure 1, page 6. All equipment in this apparatus operates at or slightly above ambient temperatures, and at pressures between atmospheric and 5 psig.

The flow of gas in the GC Rupture Monitor is controlled by sets of three-way solenoid valves (Skinner Type V5D11220). These valves are operated automatically by clock-driven microswitches (Multicam Timer Kit) that operate on a ten-minute cycle. This time cycle was chosen arbitrarily, and can be easily changed by substitution of motor drives or gear assemblies in the timer.

The chromatographic columns in this apparatus are made from sections of 1/4-inch aluminum tubing that are packed with Linde Molecular Sieve Type 5A. These columns are coiled to fit into a constant temperature box, and can be easily replaced.

The main detector in this device is a beta-sensitive scintillation crystal, with associated electronic components to provide a count rate signal output. A bridge circuit for measurements of thermal conductivity is included as a second detector, for use in calibration and analysis of nonradioactive gaseous components. Very small thermistors were used in this detector (Veco Type A-111) for high sensitivity and rapid response, but the minimum concentrations of stable gases that can be detected are about 0.01%.

A schematic diagram of piping and equipment for the GC Rupture Monitor is shown in Figure 2, page 7, as it could be installed in a reactor area. Laboratory tests were made by connecting sample bulbs, with a small circulation pump, to the lines labeled, "Gas Stripped from the Reactor Coolant" and "Stripped Gas Vent."



Front View

Back View

1. Brown recorder, with two-speed, manually selected chart drive (1 in/min or 2 in/hr);
2. Control panel for thermal conductivity detector circuit and switch for selection of detector input to the recorder;
3. Gas chromatograph with associated valves, automatic timer controls and manual control circuits;
4. Beta detector controls; and
5. Beta detector power supply.

FIGURE 1 - PHOTOGRAPHS OF GC RUPTURE MONITOR - MODEL 1

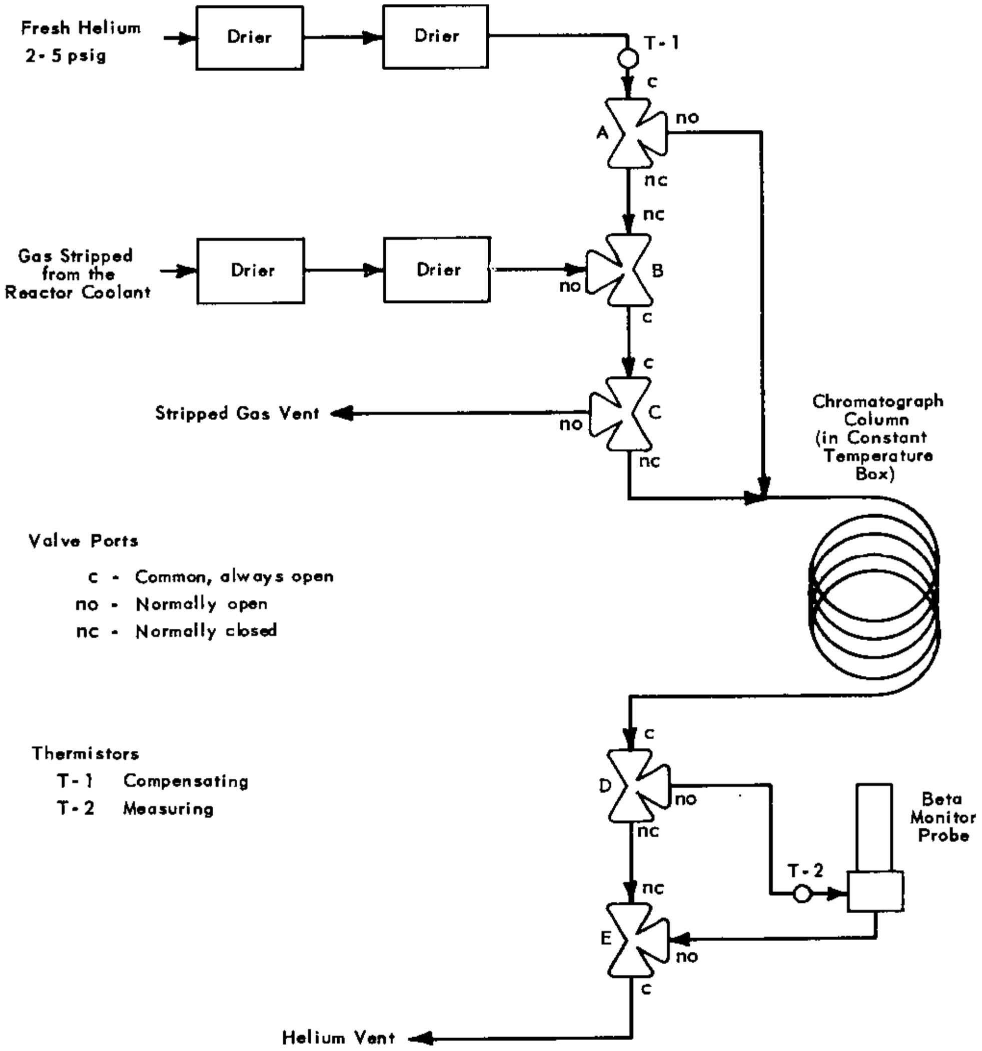


FIGURE 2 - GC RUPTURE MONITOR - SCHEMATIC DIAGRAM

OPERATION

The GC Rupture Monitor (Model 1) is designed for automatic operation, with provision for manual override control. It has required little attention by operating personnel during laboratory tests, and should require almost none in field service.

Figure 2 illustrates the flow patterns in the chromatograph assembly. Fresh helium, at constant pressure, enters valve A through pretreatment traps which remove all moisture and CO_2 from the gas. This stream normally flows directly into the chromatograph column. The gas to be monitored enters the system through pretreatment traps and valve B, then flows through valve C to the "Stripped Gas Vent." At ten-minute intervals, valves A, B, and C are energized by the timer controls, and the flow of sample gas is stopped. Fresh helium then flows through all three sample valves, carrying with it the sample contained between valves B and C. The sample valves remain energized for 15 seconds, after which the flow pattern reverts to normal, to provide a fresh gas sample for the next cycle.

The helium flow in the chromatograph column remains essentially constant during the sample cycle, and development of the chromatogram begins as soon as the sample reaches the column. The first components to emerge from the column are nitrogen and a mixture of oxygen and argon. These components begin to emerge from the column about 80 seconds after sample is introduced, at which time valves D and E are energized to discard the column effluent. The discriminator valves (D and E) remain energized until essentially all of the nonfission product gases have been discarded. The krypton begins to emerge from the column after 250 seconds, at which time the discriminator valves are de-energized, and the remainder of the column effluent passes through the detectors.

Each of the five solenoid valves is provided with a three-way switch and an indicator light. The switch positions are: automatic (timer controlled), off, and manually energized. These valves can be set manually to: 1) sample at any time, 2) pass all components of the sample through the detectors, 3) seal any portion of a sample in the counting chamber for decay rate studies, or 4) pass only selected portions of the samples into the detectors. The timer switches can be adjusted to discriminate against any portion of the sample automatically.

LABORATORY TESTS

The GC Rupture Monitor was first tested with prepared mixtures of inert gases and thermal conductivity detectors, to measure the residence time of each gas in the column. Each of the gases has a characteristic residence time in a chromatographic column under specified operating conditions. The columns chosen for initial field tests are five-foot sections of aluminum tubing of 0.25-inch OD and 0.032-inch wall. The columns are packed with 20-30 mesh particles of Linde Molecular Sieve Type 5A, and are coiled (3-1/2-inch diameter spiral) to fit into a constant temperature box. When these columns were operated with helium flows of 50 cc/min at 25°C, the pressure drop in the system was 2.3 psi. The residence times of the major components, defined as time in seconds from sample introduction to maximum concentration in the detectors, are listed below. The values are not corrected for time required for flow into or out of the columns.

1)	Oxygen and argon	120 sec (not separated under these conditions)
2)	Nitrogen	200 sec
3)	Krypton	300 sec
4)	Xenon	1250 sec

It will be noted that the residence time of xenon is nearly 21 minutes, or more than twice the nominal sampling interval. With automatic sampling every ten minutes, the column contains the xenon fraction of two or three samples at all times, and the more mobile components must overtake and pass the xenon from the previous sample to exhibit the characteristic residence times. Such intermixing of samples is not practical when working with moderate concentrations, in which a large fraction of the available sorption sites are occupied, but is both practical and desirable when working with extreme dilutions. Intermixing permits operation with long residence times, for better separation, and a more rapid sampling sequence for better monitoring service.

Several samples of Kr^{85}, mixed with helium, were used to calibrate the activity counter in this assembly. The samples are diluted in transit through the chromatograph column, and the calibration factors obtained in this way include the dilution effect, as well as such effects as chamber geometry and amplifier gain. Krypton-85 cannot be considered a primary standard for calibration of an instrument that is to be used with mixtures of noble gas radioisotopes, because of differences in disintegration energies. Study of the energy dependency of the scintillation crystal - photomultiplier detector was not considered within the scope of this work, but such information is available elsewhere. The counting efficiency for Kr^{85} was about 0.7%. The lower detection limit for this isotope (10.4-yr half life) was about 10^{-7} mol %, or two counts per second above background. Additional samples, containing Kr^{87} and A^{41} mixed with helium, were used to demonstrate separation of the noble gases with extremely dilute samples. The lower detection limit for these isotopes was about 10^{-12} mol %, and excellent separation was achieved at all measurable concentrations.

A representative trace, for a mixture of fission product gases and activated argon, is shown in Figure 3. This trace shows the argon and krypton activity from one aliquot (No. 22) and the xenon activity from the preceding aliquot (No. 21), which had been introduced ten minutes earlier. Analysis of successive aliquots for a period of several hours permitted verification of the half lives of the active components.

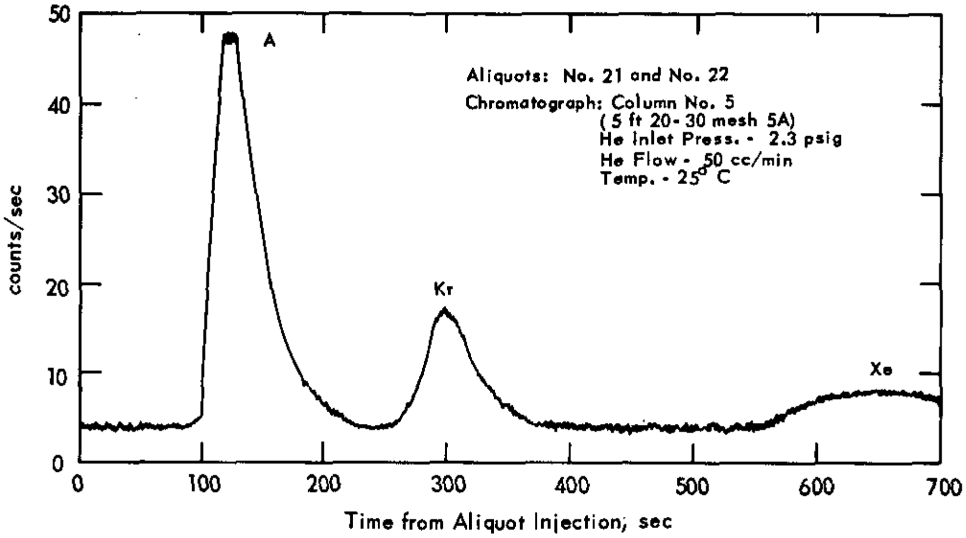


FIGURE 3 - REPRESENTATIVE ACTIVITY TRACE

The Model 1 GC Rupture Monitor has operated almost continually for four months in the laboratory, under simulated field conditions. Over 15,000 sample cycles have been completed without mechanical failure, and with almost no operator attention. One chromatograph column failed as a result of chemical poisoning after three months service. Poisoning was indicated by incomplete separation of argon and krypton, caused by changes in the residence times. This column had been used extensively with laboratory air samples that contained water vapor and CO_2, both of which are poisonous to the molecular sieve packing. These columns are easily replaceable, and can be duplicated with fair precision at negligible cost. Any differences in duplicate columns can be compensated for with minor changes in elutriant flow.

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