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THE GAS ANALYTICAL APPARATUS FOR PROJECT DRIBBLE

Livermore, California

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THE GAS ANALYTICAL APPARATUS FOR PROJECT DRIBBLE

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This paper describes the design and operating characteristics of the gas analytical apparatus constructed for the Salmon event of Project Dribble. The gases resulting from the Salmon event are to be exhausted from the cavity through a chemical processing plant to reduce the radioactivity to acceptable limits. Since high concentrations of hydrogen are expected, the cavity gases will be diluted with air to form a nonexplosive mixture. None of the commercially available hydrogen detectors will operate satisfactorily in the expected gas environment. Therefore, in addition to providing routine gas analyses, one of the prime purposes of this system is the rapid and accurate determination of hydrogen. Such a determination will allow the dilution process to be optimized. Unnecessarily large dilutions are undesirable in that they overload the chemical plant.

The Process and Materials Development Division of the Chemistry Department, which is responsible for the chemical processing plant, made an estimate of the vented gas composition and approximate concentration ranges to be expected (see Table I).

Table I. Gas composition expected from the Salmon event.

Gas	Volume %	Possible instrument range
H ₂	30	0-50
CO	1	0-10
CO ₂	4	0-10
SO ₂	40	0-50
O ₂	20	0-50

Table I (continued)

Gas	Volume %	Possible instrument range
N ₂	1	0-10
CH ₄	1	0-10
C ₂ H ₆	1	0-10
H ₂ O	4	0-4

The instrument described here was designed to provide hydrogen monitoring and to analyze the vented gas for the compounds listed in Table I.

To fulfill the analytical requirements, mass spectrometry and gas chromatographic (GC) methods were reviewed. After careful consideration, the mass spectrometric method was discarded. Although GC is not generally as accurate as mass spectrometry, the equipment is more rugged and easier to repair. To further increase its reliability the apparatus design includes a spare detector and power supply.

Hydrogen can be determined every 7 min, or by overlapping the chromatographic spectra of the two separate units it can be determined every 3.5 min. This satisfies the requirement that hydrogen determinations be done every 10 min. The other determinations are only needed every 30 min, a requirement that is easily met by this apparatus.

APPARATUS

General Description

The apparatus consists of three separate and complete chromatographic systems. The first section is for the determination of hydrogen only (see schematic Fig. 1). Argon is used as a carrier gas. A 5-ft silica gel stripper column is used for the removal of water, carbon dioxide, and sulfur dioxide from the sample. The hydrogen is separated from CH₄, CO, O₂, and N₂ by a 30-ft activated alumina column. There are two parallel sets of columns to implement the 3-1/2-min determination.

Section two (Fig. 2) is for the determination of O₂, N₂, CH₄ and CO. Helium is used as a carrier gas. The analytical separations are obtained

LEGEND FOR FIGURES 1-3

Heavy lines indicate flow from specified system.

Hoke valve

Millaflow micrometering valve

Skinner 3-way solenoid valve

Skinner 2-way solenoid valve

Thermistor detector

Check valve

FIG-1A

FIG-1B

Fig. 1. Section of apparatus for determination of hydrogen.

Fig. 2. Section of apparatus for determination of O_2 , N_2 , CH_4 , CO .

Fig. 3. Section of apparatus for determination of SO_2 , CO_2 , C_2H_6 , and H_2O .

via a 5-ft silica gel stripper column for the removal of H_2O , CO_2 , and SO_2 , followed by an 8-ft 5A molecular sieve column for the resolution of O_2 , N_2 , CH_4 , and CO .

Section three (Fig. 3) determines SO_2 , CO_2 , C_2H_6 , and also H_2O when the latter is needed and meaningful. Again the carrier gas is He. The analytical columns are a 20-ft tricresyl phosphate column in series with a 6-ft silica gel column. The latter column can be bypassed as needed.

All three sections use thermistor detectors.¹ These are immersed in a 35° C water bath that is regulated to $\pm 0.001^\circ\text{C}$ by a proportional temperature controller.² The detectors are operated at 10 mA, with the exception that the detector used for the H_2 determination is operated at 7.5 mA. Chromatograms are recorded at 1 mV full scale. The power supplies are 10-20-volt Con Avionics.³ Figure 4 is the bridge and associated circuitry.

The two 30-ft activated alumina columns of the first section are contained in an insulated air oven. The air is circulated by a fan⁴ and the temperature regulated at $50 \pm 0.03^\circ\text{C}$ by a Thermotrol.² The analytical columns of sections 2 and 3 are contained in a similar oven which is regulated to $90 \pm 0.03^\circ\text{C}$. All three of the silica gel stripper columns are operated at ambient temperature.

Physical Layout and Housing

The gas sample, as received from the wellhead, will be radioactive. Therefore, all sampling valves as well as the analytical sections are contained in glove boxes.

The sampling valves are contained in a glove box (Fig. 5) outside the main analytical laboratory. It houses four remotely operated six-way sampling valves,⁵ each having four interchangeable standard loops⁶ of approxi-

¹Gow-Mac Thermistor Detector No. 9677.

²Hallikainen Thermotrol, Model No. 1109A, Hallikainen Inc., Berkeley, Calif.

³Model R 15-4BF Con Avionics, Westbury, New York.

⁴No. 10B Cooltron 1750-rpm fan, Barber Colman, Lloyd Bowen Assoc., 800 E. 14th St., Oakland 6, Calif.

⁵Loenco six-way switch valves with electropneumatic actuators, LVO 220 HT, Loenco Inc., Altadena, Calif.

⁶The loops were calculated by gas chromatography using pure CO_2 as a calibrating gas. Standard volumes of a similar size were run before and after each unknown. The peak areas were then used to calculate the unknown loop volumes. A typical series of six determinations gave a maximum deviation of $\pm 0.4\%$.

UNIT 2

Fig. 4. (contd)

Fig. 5. Glove box containing sampling valves.

mately 0.3, 1.3, 3.0, and 4.7 cc. Also housed in this box is the main sample manifold and the remote temperature and pressure sensors for the PVT measurements of the sample. The sample manifold is equipped with an in-line particle filter and four solenoid release valves, one for each sampler valve. The glove box is connected to a blower which removes all contaminated gas to the main plant discharge stack and maintains the glove box at a reduced pressure, except when samples are taken and the sample pressure is being measured. To prevent condensation in the valves and lines, this box will be maintained at a temperature about 10° C higher than the sample line running from the wellhead. The relative relationship of this section to the rest of the apparatus is shown in the flow schematic of Fig. 6.

Inside the analytical laboratory (an 8 × 40-ft trailer) is another glove box (Fig. 7) which contains the stripper columns, column ovens, flow control valves, and detectors with associated constant temperature bath. This box is equipped with blowers to constantly circulate air through the box to the exhaust stack, thus minimizing the exposure of the operator to radioactive gas should a leak occur in the system.

The electronics, recorders, electrical control panel, and carrier flow control system are all located outside the glove box as shown in Fig. 8.

Construction Details

All lines are 1/8-in. -o.d. × 1/16-in. -i.d. stainless steel with the exception of the columns. All valves except the flow controllers are stainless steel having 1/8-in. -o.d. Swagelok fittings. These small lines are used to minimize dead volumes, thus allowing the sample to be placed on the column in more nearly plug condition. All connections are made by welding, silver soldering, or by means of Swagelok fittings.

The carrier gases, argon and helium, are regulated at 40 psig as they leave the high-pressure storage bottles. Further regulation of these pressures are obtained by pressure regulators⁷ located on the flow panel manifold (Fig. 9). Both the argon and helium manifolds have outlets to three flowrators.⁸ Each flowrator is followed by a 2-liter "surge volume." These surge volumes

⁷Millaflow Corp., 250 Canal Blvd., Richmond, Calif.

⁸Minirator 10A 4139, Fischer and Porter, Warminster, Pa.

Fig. 6. General flow schematic.

Fig. 7. Glove box containing stripper columns, column ovens, flow control valves, and detectors.

Fig. 8. Electronics, recorders, control panel, and carrier flow control system for Fig. 7 glove box.

Fig. 9. Pressure regulators for the carrier gases.

help to reduce the pressure changes and subsequent flow changes introduced by the pressure regulators. Thermistor detectors are very sensitive to flow and pressure changes, making these surge volumes necessary.

The carrier gas flow rate is regulated by pairs of valves in series located at the inlets of each flowrator. Milliflow micrometering valves⁷ have been found to be the best all-around valve for this purpose.

Schematic layouts of the three chromatographic systems and their relationship to the rest of the system are shown in Figs. 1, 2, 3, and 6. They need no further description other than to stress the importance of constructing a gas-tight system. The thermistor noise level is extremely sensitive to very small leaks.

Since the gas stream being analyzed is radioactive, all carrier gas exits from the chromatograph are vented into the contaminated exhaust stack. Located between the exhaust stack and the chromatographic units is a special 10-way selector valve. This valve allows individual exit lines to be connected to a soap bubble flowrator. The valve has 10 inlets but only 2 outlets, i. e., any line can be connected to the soap bubble flowrator and simultaneously all other lines are connected to the exhaust manifold. Also all lines may be vented when the flowrator is not required.

METHOD OF OPERATION

The three sections of this chromatograph are designed in such a way that the carrier-gas flow path changes during the analysis cycle. In Figs. 1A and 1B the two modes for one half of Section 1 are shown. When a sample is being placed on the alumina column* for a hydrogen determination, the argon carrier gas flows from flowrator 1 through the sampling valve G-1, the valve S1, the alumina column, and the detector. Simultaneously, another argon stream flows through flowrator 3, the reference side of the detector, and out valve S5 to the atmosphere. This sequence is shown in Fig. 1A.

After the hydrogen-containing fraction of the sample has passed through the silica-gel stripper column and onto the alumina column, the flow is switched to that shown in Fig. 1B. To obtain this mode the argon carrier gas passing through the silica gel column is exhausted to atmosphere by actuating valve S1. Simultaneously, valve S5 is operated and the argon

*See Appendix for a description of the column preparations.

carrier gas passes through the reference side of the detector, the alumina column, and back to the detector. It is during this cycle that the H_2 is developed and quantitatively measured.

The reason for this latter mode of operation (Fig. 1B) is to preserve the integrity of the analytical (alumina) column. During this cycle the CO_2 , SO_2 , and H_2O that are eluted from the stripper column are exhausted to the atmosphere.

For rapid analysis, i. e., every 3-1/2 min, the right and left sampling systems of this section are operated alternately. However, it is expected that this second section will serve primarily as an emergency backup unit.

The use of section 2, Figs. 2A and 2B, for the determination of O_2 , N_2 , CH_4 , and CO is similar to that described above for a hydrogen determination in section 1. The major difference being a single sampler valve, 5A molecular sieve column, and a total analysis time of about 15 min.

Since section 3 is used to determine CO_2 , SO_2 , C_2H_6 , and H_2O , no stripper column is used and only one carrier gas supply is needed. The two columns used are a 20-ft tricresyl phosphate (TCP) column followed by a 6-ft silica gel column. The O_2 , N_2 , H_2 , CH_4 , CO , CO_2 , and C_2H_6 come through the TCP column unresolved and are placed onto the front of the silica gel column (Fig. 3A), which is then cut out of the flow stream by actuating valve S4, Fig. 3B. After the SO_2 and H_2O are eluted from the TCP column and measured, valve S4 is again actuated and the CO_2 and C_2H_6 developed and measured (Fig. 3A). From the foregoing description of the operational modes it can be seen that careful balancing of flows and pressures through the various columns is an absolute necessity.

Start-up procedure begins by starting the carrier gas flow through the various columns. This is followed by temperature regulation of the column ovens and detector bath. Pressure and flow of the various carrier gas streams are then balanced grossly by means of the various pressure gages and the soap bubble flowrator. Any given unit is so adjusted that the flow rate and pressure of the carrier gas do not change when the mode of operation is changed. Final flow balancing is accomplished by noting the change in the detector baseline when the unit being tested is switched from one mode to another. With proper care these baseline changes can be kept below $10 \mu V$. During this balancing procedure the surge volumes are bypassed. This is necessary due to the long time constants these volumes introduce into the carrier gas equilibration times.

When the carrier gas flows are balanced, the surge volumes should be introduced into the systems. Also, the flowrators should be bypassed to reduce the noise level.

After the helium and argon flows are balanced, the chromatograph is ready to accept samples. A continuous stream of gas flows from the well-head, the high pressure side of the plant, to the outside glove box and back to the plant at a low pressure point. This stream can be tapped by the gas chromatographer at will. To withdraw a sample, the chromatographer opens valve C (Fig. 6). The gas enters the glove box, passes through filters D and E, which remove particulate matter, and then enters manifold F. Flow can only occur when one or more of the sampler valves (G-1, G-2, G-3, G-4) are in open position. This will allow the sample to sweep through the appropriate calibrated sample loop associated with that particular valve.

After the sample loops have been thoroughly purged of carrier gas, the three-way solenoid valve M is switched to vent the loop to the box atmosphere. At the same time the box blower is turned off, and then the pressure and temperature of the box are recorded. Next the sample is introduced into the carrier gas stream, valve M switched to stack position, and the blower in the box started. From this point on the operations are as described above.

The entire apparatus is operated from a master control panel which shows schematically the entire flow system (see Fig. 9). All the electrical or electropneumatic valves are remotely operated from this panel. The electrical switches are positioned on the panel as the valves appear on the schematic. At all times the gas flow for each system is readily visible to the operator. This is achieved by means of etched overlay panels using edge lighting for illumination.

DISCUSSION

Field Operational Problems

Numerous problems occurred when this unit was reactivated at the test site. The most irritating was the steady vibration of the analytical trailer as a result of its proximity to the drilling rigs. The continuous vibration gradually changed the setting of the metering valves, thus unbalancing the carrier-gas flow rates and pressures. This difficulty was overcome by replacing all the metering valves with Milliflow⁸ valves. These

valves not only have more stem friction, which greatly reduces their sensitivity to vibration, but they also have a finer flow control and less tendency to develop leaks than other valves tested.

Other problems encountered early in the apparatus shakedown were power fluctuations and inadequate electrical grounding. A long copper bar sunk into the ground solved the grounding problem. A voltage regulator alleviated some of the problems caused by power fluctuations; however, they are still a minor annoyance.

Sensitivity and Noise

As a result of carefully controlling the carrier-gas flow rate and pressure, and maintaining the detector temperature constant to $\pm 0.001^\circ\text{C}$, the thermistor signal-to-noise ratio is very high. The noise is approximately $5\ \mu\text{V}$ peak-to-peak as measured on a 1-mV recorder.

Using the columns, detectors, etc., described in this paper, the apparatus under normal operating conditions (3-5-cc sample, STP) has the following sensitivities:

H_2 , 5 ppm

O_2 , 15 ppm

N_2 , 15 ppm

SO_2 , 100 ppm

Accuracy

When the apparatus was in the laboratory at LRL its reproducibility and accuracy were evaluated. Standards of 2.958 cc of hydrogen were run 36 consecutive times. The peak heights had a range of $\pm 0.3\%$ and a standard deviation of 0.12%. This was much better than the disk integrator results, which had a range of $\pm 1.8\%$ and a standard deviation of 0.57%. An automatic base-compensating integrator gave results that ranged $\pm 0.9\%$ and had a standard deviation of 0.18%. Standards of 0.330 cc of hydrogen were run 32 consecutive times and the results were comparable to those listed above.

Reproducibility of identical consecutive hydrogen samples done in the field gave a similar peak height deviation of $\pm 0.3\%$. The other gases were tested and gave peak height deviations ranging from ± 0.3 to 1.0% for similar, though less extensive, series of consecutive determinations.

Probably the largest potential error will be the lack of accurate standards in the range of the cavity gases. For laboratory work requiring a high degree of accuracy, a high and a low standard are made to bracket the sample within 5%. These standards are then run before and after the unknown, thus giving maximum reliability to the determination. In field determinations, this system will be followed as closely as possible; however, lack of facilities, and especially lack of time, will somewhat limit the use of this procedure.

As a partial solution to this dilemma, bottled gas standards⁹ in the expected concentrations will be on hand. In addition, since the plant will initially operate for 1 hour and stop for a limited time before completing cavity bleed-down, time should be available to change the standards to a value closer to the actual gas concentrations.

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APPENDIX

Columns D-1 and D-2 are 30-ft $\times$ 1/4-in. -o.d. aluminum columns of 42-60 mesh activated alumina. Column E-1 is an 8-ft $\times$ 1/4-in. -o.d. copper column of 30-60 mesh 5A molecular sieve. These columns are activated by heating to 350°C under a hard vacuum for 3 hours.

Column E-3 is an 8-ft $\times$ 1/4-in. -o.d. copper column of 42-60 mesh silica gel. Stripper columns A-1, A-2, and A-3 are 5-ft $\times$ 1/4-in. -o.d. copper columns of 42-60 mesh silica gel. These silica gel columns are activated at 250°C under a hard vacuum for three hours.

Column E-2 is a 20-ft $\times$ 1/4-in. -o.d. aluminum column of 5% tricresyl phosphate on Fluoropak. No special activation is required.

⁹Standards were determined by mass spectroscopy analysis, the reliability being approximately $\pm 0.1\%$.

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