SINGLE DETECTOR AND FORECOLUMN TRAP FOR SERIES GAS-CHROMATOGRAPHY ANALYSIS

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INTRODUCTION

The purpose of this investigation was to establish a reproducible chromatographic technique for the analysis of fixed gases related to a pilot plant operation at Iowa State University in which gaseous sulfur dioxide is produced by the reductive decomposition of gypsum. The gases of relative interest to the process are oxygen, nitrogen, hydrogen, carbon monoxide, methane, hydrogen sulfide, carbon dioxide, and sulfur dioxide. The mixture is usually saturated with water vapor.

PREVIOUS INVESTIGATIONS

Several references[1-4] can be cited for the separation of oxygen, nitrogen, methane, and carbon monoxide on columns of Types 5A or 13X molecular sieves (The Linde Co., Tonawanda, New York). The separation of carbon dioxide from the same mixture was usually obtained by use of a silica gel column. It has been reported[5] that carbon dioxide could be separated on a molecular sieve column by linear temperature programming.

MURAKAMI[3] developed a method for the analysis of these gases by using an arrangement of two columns in series. He obtained a continuous chromatogram by passing the gases through a silica gel column first, then through the reference side of a thermal conductivity detector, then through a molecular sieve column and finally through the sample side of the detector. The peaks from the silica gel column were detected by reversing the polarity of the recorder input and the peaks from the molecular sieve column were detected with normal polarity. The chromatogram contained a peak for the mixture of oxygen, nitrogen, methane, and carbon monoxide, followed by a carbon dioxide peak from the silica gel column. Then the individual peaks of oxygen, nitrogen, methane, and carbon monoxide appeared from the molecular sieve column. One objectionable feature of the method was that carbon dioxide contaminated the molecular sieve column by permanent adsorption on the active sites.

OTTENSTEIN[6] made the same separations with similar arrangements of dual columns in series except that he used two separate detectors. His separation, depending on the columns used, also included hydrocarbons, sulfur dioxide, and hydrogen sulfide. The column used to separate carbon dioxide, hydrogen sulfide, and sulfur dioxide was a 9 ft. by $^1/_4$ in. column of 10 % di-2-ethylhexylsebacate (commercially available as Octoil-S Vacuum Pump Fluid, Consolidated Vacuum Corp., Rochester, N.Y.) on 40–60 mesh Teflon-6. It gave a peak for the mixture of oxygen, nitrogen, methane, and

carbon monoxide followed by individual peaks of carbon dioxide, hydrogen sulfide, and sulfur dioxide. The other column in the arrangement had two parts. It was composed of 5 ft. by $^1/_4$ in. of uncoated Chromosorb-P (60–80 mesh) followed by 7 ft. by $^1/_4$ in. of Type 13X molecular sieve (40–60 mesh). The uncoated Chromosorb-P "forecolumn" which preceded the molecular sieve column made no separation; it delayed the composite mixture from the first column so that the oxygen, nitrogen, methane and carbon monoxide peaks from the second column would appear at the proper time. The disadvantages of the system were that (1) two detectors were required, and (2) the molecular sieve column became contaminated with the three compounds (carbon dioxide, hydrogen sulfide, and sulfur dioxide) that were separated on the first column.

Other columns[7,8] have been reported for the separation of sulfur dioxide and various sulfur compounds in the absence of many of the fixed gases.

PRESENT CHROMATOGRAPHIC ARRANGEMENT

For the pilot plant gases a multiple-column gas chromatographic analysis system is used so that all the desired separations can be obtained from a single gas sample. Although only two columns perform the actual separation, a series of three columns is used. The extra column, in the middle position, traps the gases that are separated on the first column and provides the proper time delay for peaks appearing from the third column. The time delay permits the use of one thermal conductivity cell to obtain a continuous chromatogram without having any peak overlap.

Column 1 is a 20 ft. long section of $^1/_4$ in. O.D., 20 gauge, Type 304, stainless steel tubing filled with 10 wt. % dibutyl sebacate on the —20 + 80 U.S. standard screen fraction of Fluoropak (Wilkins Instrument and Research Corp., Walnut Creek, California). This column gives a peak of the mixture of hydrogen, oxygen, nitrogen, methane, and carbon monoxide followed by individual peaks of carbon dioxide, hydrogen sulfide, and sulfur dioxide in that order.

Column 2, a "forecolumn trap", is a 11 ft. long section of $^1/_4$ in. O.D. copper tubing filled with 25 wt. % potassium hydroxide on the —30 + 60 U.S. standard screen fraction of Chromosorb W (Johns Manville Corp., Manville, New Jersey). The packing is prepared by adding a solution of 5 g of potassium hydroxide in 100 ml of methanol to 20 g of Chromosorb W and then evaporating the methanol while stirring the entire mixture continuously. The potassium hydroxide in the column permanently absorbs carbon dioxide, hydrogen sulfide, sulfur dioxide, and water vapor. The length of the column creates the proper time lag for the remaining gas mixture to enter Column 3.

Column 3 is a 7 ft. long section of $^1/_4$ in. O.D., 20 gauge, Type 304, stainless steel tubing filled with the —14 + 30 U.S. standard screen fraction of Type 13X molecular sieves (The Linde Co., Tonawanda, New York). After the column was activated at 300° for 12 h, it separated hydrogen, oxygen, nitrogen, methane, and carbon monoxide in that order.

The detector used was a Model TR-II-B Gow-Mac (Gow-Mac Instrument Co., Madison, N. J.) thermal conductivity cell, geometry 9193, with a Model 9293-B Gow-Mac power supply control unit.

The column arrangement, Fig. 1, uses the reference side of the thermal conductivity cell to detect gases from Column 1 and the sample side to detect gases from Column 3. Peaks from either side of the thermal conductivity cell can be recorded in a

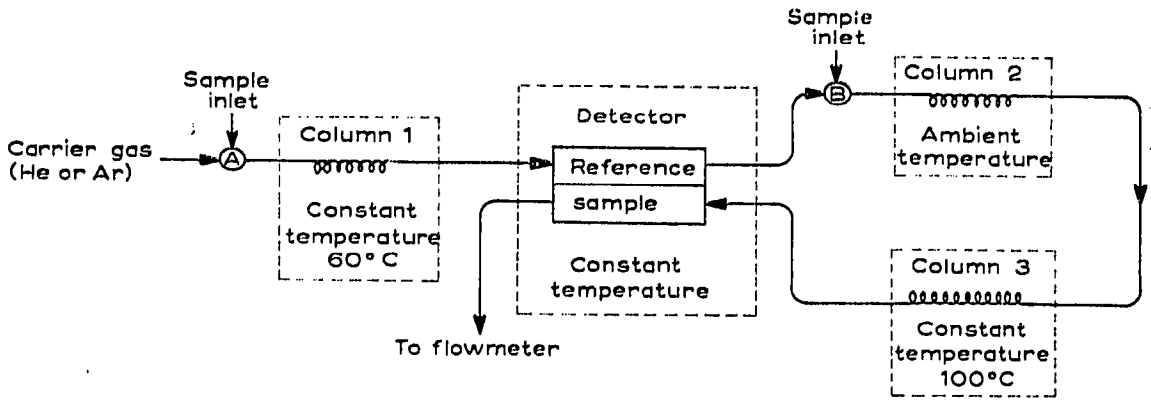

Fig. 1. Column arrangement.

continuous chromatogram by reversing the polarity of the signal from the detector cell with a double-pole, double-throw switch on the recorder input leads. The recorder input signal must be adjusted to zero potential at the beginning of a chromatogram so reversal of polarity does not affect the base line.

Separation of all components requires a helium flow rate of 40 ml/min. Column 1 is operated at 60°, Column 2 at ambient temperature, and Column 3 at 100°. With the polarity of the signal reversed, Column 1 gives a peak of the mixture of hydrogen, oxygen, nitrogen, methane, and carbon monoxide followed by individual peaks of carbon dioxide and hydrogen sulfide. The polarity is then switched to normal to obtain peaks of hydrogen, oxygen, nitrogen, methane, and carbon monoxide from Column 3. Finally the polarity is reversed again for the sulfur dioxide peak from Column 1. Water vapor appears from Column 1 about 5 min. after the final peak, but appears only as a very low hump with a seven minute base width. It consequently does not interfere

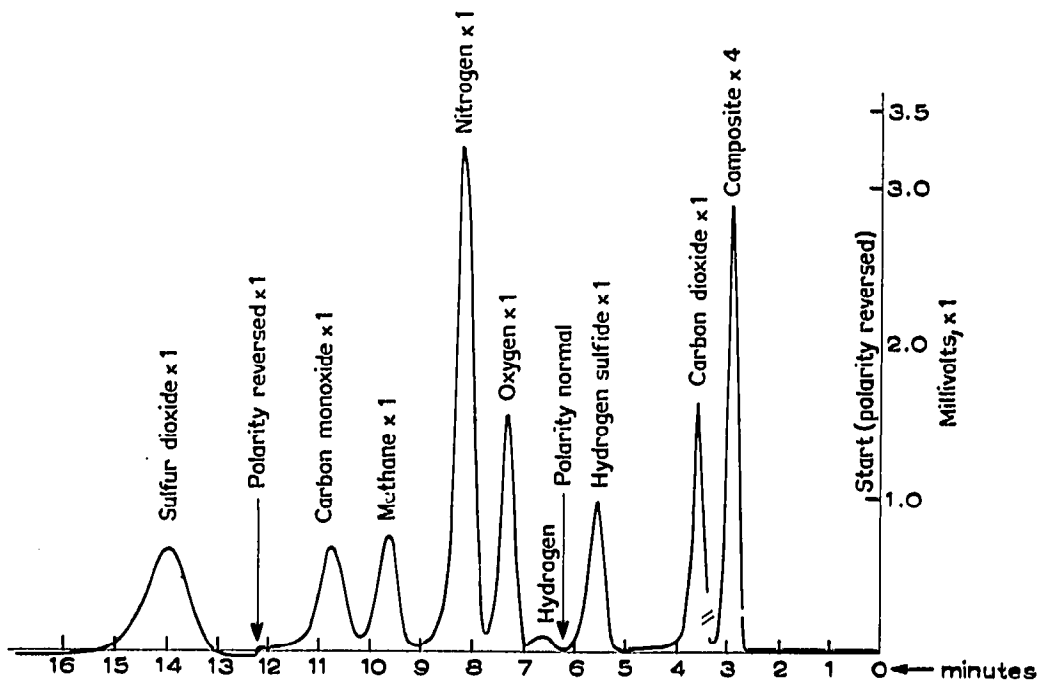

Fig. 2. Sample chromatogram for all components.

with the chromatogram and is trapped on Column 2 along with carbon dioxide, hydrogen sulfide, and sulfur dioxide.

Fig. 2 shows a chromatogram for the separation of all components in 15 min. The sample contained 50 μl of all components except for 250 μl of hydrogen. Usually the pilot plant gases do not contain all of the components. In this case the flow rate is increased to 80 ml of helium/min and an analysis is completed in 8 min. Fig. 3 is a

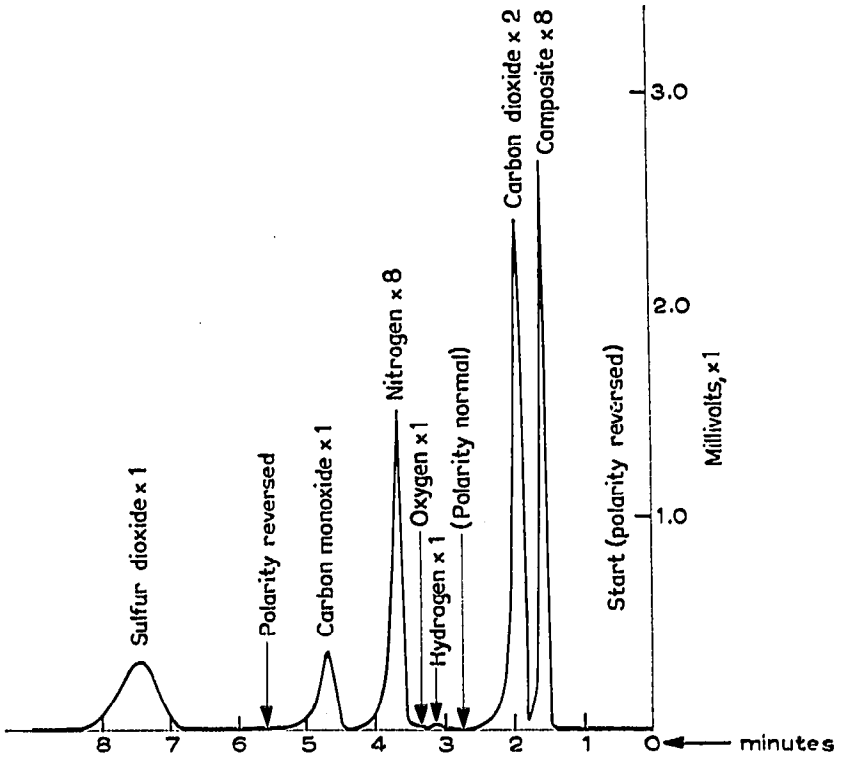

Fig. 3. Sample chromatogram for limited number of components

typical chromatogram of a 1-ml sample. The sensitivity of hydrogen is poor when helium is used as the carrier gas; so argon is used as the carrier gas for the determination of small concentrations of hydrogen. The separation of hydrogen takes place on the molecular sieve column; so the sample is injected just preceding Column 2 (inlet B) when hydrogen is analyzed alone.

ACKNOWLEDGEMENT

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SUMMARY

A gas chromatography system is described for analysis of carbon dioxide, hydrogen sulfide, hydrogen, oxygen, nitrogen, methane, carbon monoxide, and sulfur dioxide from a single gas sample. The system consists of three columns in series. Column 1 separates the polar gases which are then irreversibly absorbed on Column 2. Column 2 delays but does not absorb the other gases which are subsequently separated on Column 3. Eluted peaks from Column 1 are detected in the reference side of the thermal conductivity cell and peaks from Column 3 in the sample side of the cell.

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