# The Process Gas Chromatography of Fatty Acid Distillation Streams. I. Analytical Chemistry

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## Abstract

It was decided to build a process gas chromatograph to monitor the fatty acid stills. The initial work led to the development of phosphoric acid treated polyester columns for the GLC of unesterified fatty acids. The design and construction of a process analyzer for the fatty acid stills was then begun. When this gas chromatograph was completed, it was used to monitor the still. Chromatograms of the fatty acid streams are shown and discussed. Quantitative results are compared to those obtained by conventional methyl ester analysis. Work with inert support column packings is also described.

## Introduction

ONE OF THE MOST important processes in making commercial fatty acids is their distillation. Fatty acid mixtures of known composition and even acids of high purity can be made in this way. The distillation streams are usually controlled by a titer and a simple titration. Such control procedures do not always reflect the true composition of the fatty acids in the stream. This is particularly true when closely controlled cuts are desired and their is a narrow specification range on the trace acids. Gas chromatography of the fatty acid methyl esters in the control laboratory will give the required information. However, this information is often only historical and of limited value in the operation of the still.

A process gas chromatograph to monitor the fatty acid stills would provide the necessary composition information. At the time it was first considered, no such instrument had ever been built. One difficulty was the high temp at which the chromatograph would have to operate automatically for long periods. Furthermore, at that time no practical column for separating the higher unesterified fatty acids had been developed. The initial work on this project was the development of a gas chromatographic column that would separate the unesterified fatty acids. The separation of unesterified fatty acids has interested workers from the earliest days of gas chromatography (7). Fatty acids are difficult to gas chromatograph because of their extreme polarity. This polarity and tendency toward dimerization cause extreme tailing and often complete adsorption on the column.

There are three general approaches to overcome these polar effects: 1) the modification of the liquid phase; 2) the modification of the carrier gas; and 3) the use of inert solid support materials. The modification of the inert liquid phase has been reported by a number of workers (5,6,8,11,12,15,17).

More recent approaches have been to modify the carrier gas with a volatile acid such as formic acid (1,2). Some workers have had success with using inert solid support materials (3,10). Other approaches have been combinations of the modified liquid phase with glass bead supports (9,14), and capillary columns (10).

In the search for a column that would separate fatty acids, certain specific requirements were laid out. The column had to be capable of separating a wide range of fatty acids, at least $C_6$–$C_{20}$, at reasonable temp. It would have to separate saturated and unsaturated fatty acids and be capable of continuous operation for many months without loss of efficiency. Compatability with a thermal conductivity detection system was necessary. Good recoveries of acids would be necessary in order to quantitate the results.

A column consisting of a phosphoric acid treated polyester on Celite was developed that met these requirements (11,12). This particular column packing has since been widely used for the separation of fatty acids and many other materials. With the advent of this column, the design and construction of a completely automatic process stream gas chromatograph for the fatty acid stills was begun. Experiments using the phosphoric acid column in the automatic plant chromatograph that was eventually developed are described in this report. These experiments were concerned with the quantitative analysis of fatty acids sampled from the still streams. Samples of the fatty acids chromatographed on the process instrument were obtained. These samples were gas chromatographed as methyl esters in the laboratory to obtain data that could be compared to the results obtained as free acids.

A column of Carbowax 20M terminated with terphthalic acid on a Teflon support was recently reported (3). Excellent results were obtained with this column. It was decided to report the results of the experiments with this column packing in this paper. A column using this packing material was also used in the plant instrument with good results and is reported here.

A complete process gas chromatography system for the fatty acid stills has been developed. The entire project involved devising columns that would separate the unesterified acids, the design and construction of an automatic gas chromatograph, and finally its operation. The total project was one of great technical difficulty that has never been tried before. Nevertheless, a great stride has been made toward its final solution.

## Experimental

*Apparatus.* Process and conventional laboratory gas chromatographs were used in this work. The design and construction of the process instrument will be fully described in Paper II of this series (16).

*Column Packings.* The phosphoric acid modified polyester column packing was made by dissolving the 20% by wt (based on the column packing wt) of diethylene glycol adipate polyester in chloroform. To this solution was added 3% w/w phosphoric acid (85% $H_3PO_4$). The liquid was mixed thoroughly. Hexa-

methyl disilazane (HMDS) treated, acid washed, Chromosorb W, 60–80 mesh, (Johns-Manville) was stirred into the liquid mixture. The chloroform was then evaporated on a steam bath. The packing was then heated in an oven at 106C to remove the balance of the solvent. The Carbowax 20M Terphthalic acid terminated, 10% on Teflon T-6, 60–80 mesh, was obtained from the Wilkens Instrument & Research Co., Walnut Creek, Calif.

The packings were vibrated into 0.25-in. copper tubing that had been treated with a chloroform solution of HMDS and the ends of the column were also plugged with HMDS treated glass wool.

The HMDS treatment consisted of filling the copper tube with a 10% (v/v) solution of hexamethyl disilazane and letting it stand for one hr. The glass wool was also allowed to stand in the HMDS solution for one hr. The solution was then removed and the tube and wool allowed to air dry. The columns used in this work varied from 30–60 in. in length.

*Fatty Acids.* Fatty acid mixtures used for determining quantitative factors were made by weighing pure distilled fatty acids into the mixture. The fatty acids used in the plant instrument were sampled directly from the still streams. Samples from the three still stream acids were also taken and converted to methyl esters with $BF_3$-methanol (13) for further quantitative studies using the laboratory instrument.

*Gas Chromatographic Technique.* The gas chromatography data of the acids in the stills was obtained using the automatic features of sample injection and tape programming, built into the process instrument. Provision had also been made for manual injection of samples with syringes and this technique also was used in the experimental work. The general chromatograph conditions are as follows:

The injection temp was 280C, the column temp 225C and the helium flow rate was 75 ml/ min when the DEGA-$H_3PO_4$ columns were used. With the 30-in. column of Carbowax 20M-Terphthalic acid on Teflon 6, the column temp used was 240C and the helium flow was 100 ml/min.

When the laboratory instruments were used, the columns and conditions were similar to those used in the process chromatograph. The samples were introduced into these instruments with Hamilton microsyringes.

## Results and Discussion

*Application of the Process Instrument.* Before a column is used on the plant instrument, it is conditioned and tested thoroughly on the laboratory gas chromatographs. Quantitative results are obtained with known mixtures and optimum temp and flow rates are determined. This information is placed on the column identification tag so that when the column is first used the plant operator will know exactly what to expect from the column. A sample laboratory chromatogram is also attached to the column. All this information is useful in initially setting up the automatic program for the process chromatograph.

Figure 1 shows the chromatograms obtained from a sample automatically injected and also a manual syringe injection of fatty acid from the No. 1 Overhead still tower during a "Coco" fatty acid distil-

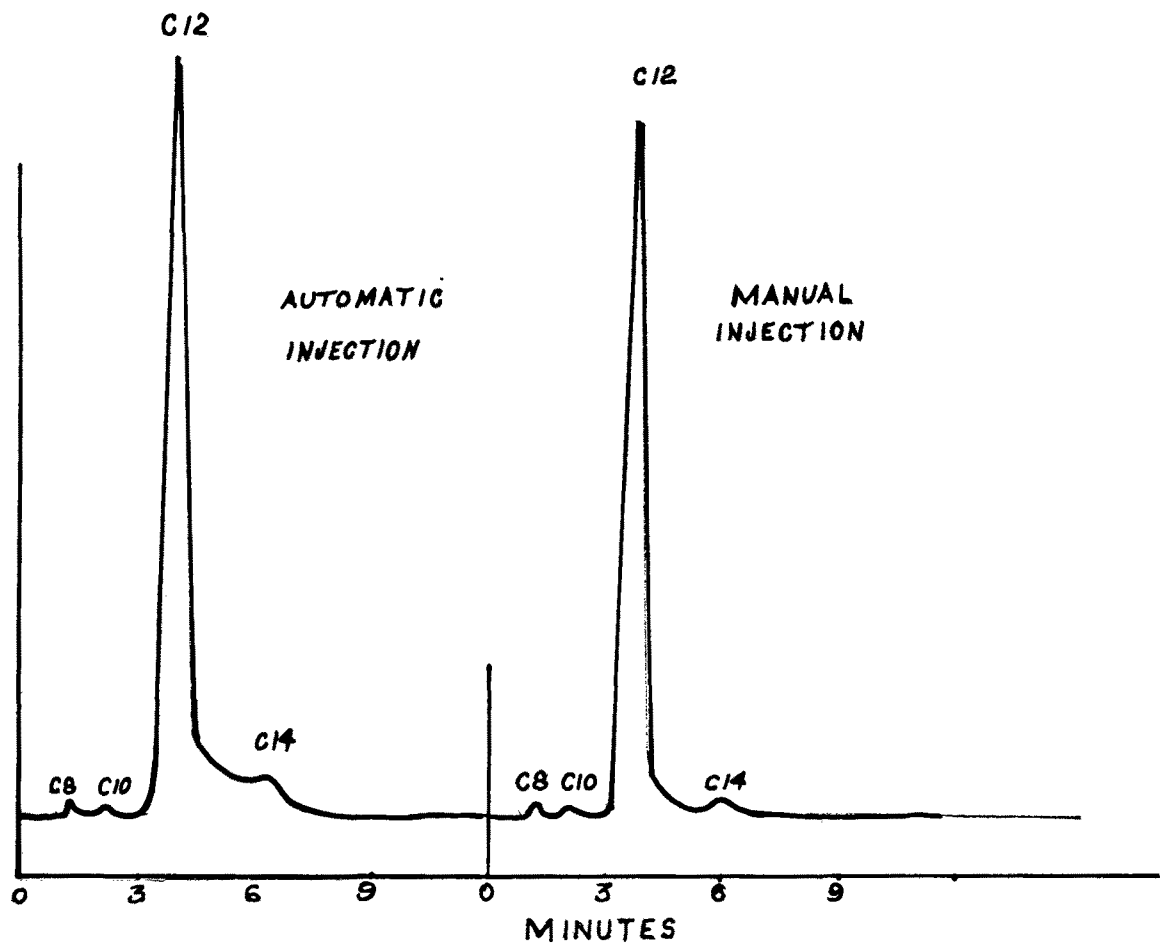


FIG. 1. Automatic and manual injections of the No. 1 overhead still stream during a Coco fatty acid distillation using the process gas chromatograph. Column: 5-ft, 20% DEGA, 3% $H_3PO_4$, 60–80 mesh, Chromosorb W.

lation. It will be noted that the automatic injection tails more than the hand injection (this tailing effect was an artifact due to the automatic sample injection system and was subsequently corrected by a design change). In spite of the tailing, these peaks were easily measured by the automatic integrator. The integration can be programmed so that the results obtained compare favorably with the analytical results obtained by a laboratory analysis of the methyl esters.

Table I shows a comparison of the quantitative results of the fatty acids displayed in Figure 1. One result is the most recent control laboratory analysis; another result is that of the process instrument. The third result is that obtained from a sample taken at the same time the process instrument sampled the fatty acid stream. This sample was converted to methyl esters and run on a DEGA column in the conventional manner. Each result varies slightly from the others. The process instrument analysis is lower for lauric acid and higher for myristic than the two laboratory analyses. This was caused by the fact that the integrator did not take into account the tailing effect. This can be partly corrected by adjusting the integration base line to a higher base. Nevertheless, for all practical purposes, the results are acceptable. The process instrument was intended as a rapid guide for the still operators. It was not our intention to replace the control laboratory analysis as the final authority of fatty acid composition. All samples must still meet control laboratory analytical specifications before being shipped.

TABLE I
Analysis of Fatty Acids in the Still Streams

| Acid | Process analysis | Laboratory analysis[a] | Most recent[a] control laboratory analysis |
|---|---|---|---|
| No. 1 Stream | | | |
| Caprylic | 0.6 | 0.4 | 0.4 |
| Capric | 0.6 | 0.4 | 0.6 |
| Lauric | 95.7 | 97.3 | 96.6 |
| Myristic | 3.1 | 1.9 | 2.4 |
| No. 3 Stream | | | |
| Myristic | nil | nil | 3.5 |
| Palmitic | 44.0 | 44.3 | 50.2 |
| Stearic | 56.1 | 55.6 | 46.3 |

[a] Analyzed as methyl esters.

The quantitative results of the No. 3 stream are also shown in Table I along with the comparable laboratory methyl ester analysis. Also shown is the most recent control analysis. In this case, the difference between these analyses is striking. The myristic acid has disappeared, and the quantitative composition of the $C_{16}$ and $C_{18}$ acids has reversed. In this case the process chromatograph gave a more correct picture of the stream composition than the most recent control analysis which was many hours old. This experiment demonstrates the purpose of the process instrument, i.e., to give the still operators a running picture of the fatty acid stream composition.

Figure 2 shows a complete analytical profile of the three overhead still streams during a Coco fatty acid distillation. The time scale on the chart was varied so that all three chromatographs could be shown in one figure. The total time involved for the three analyses

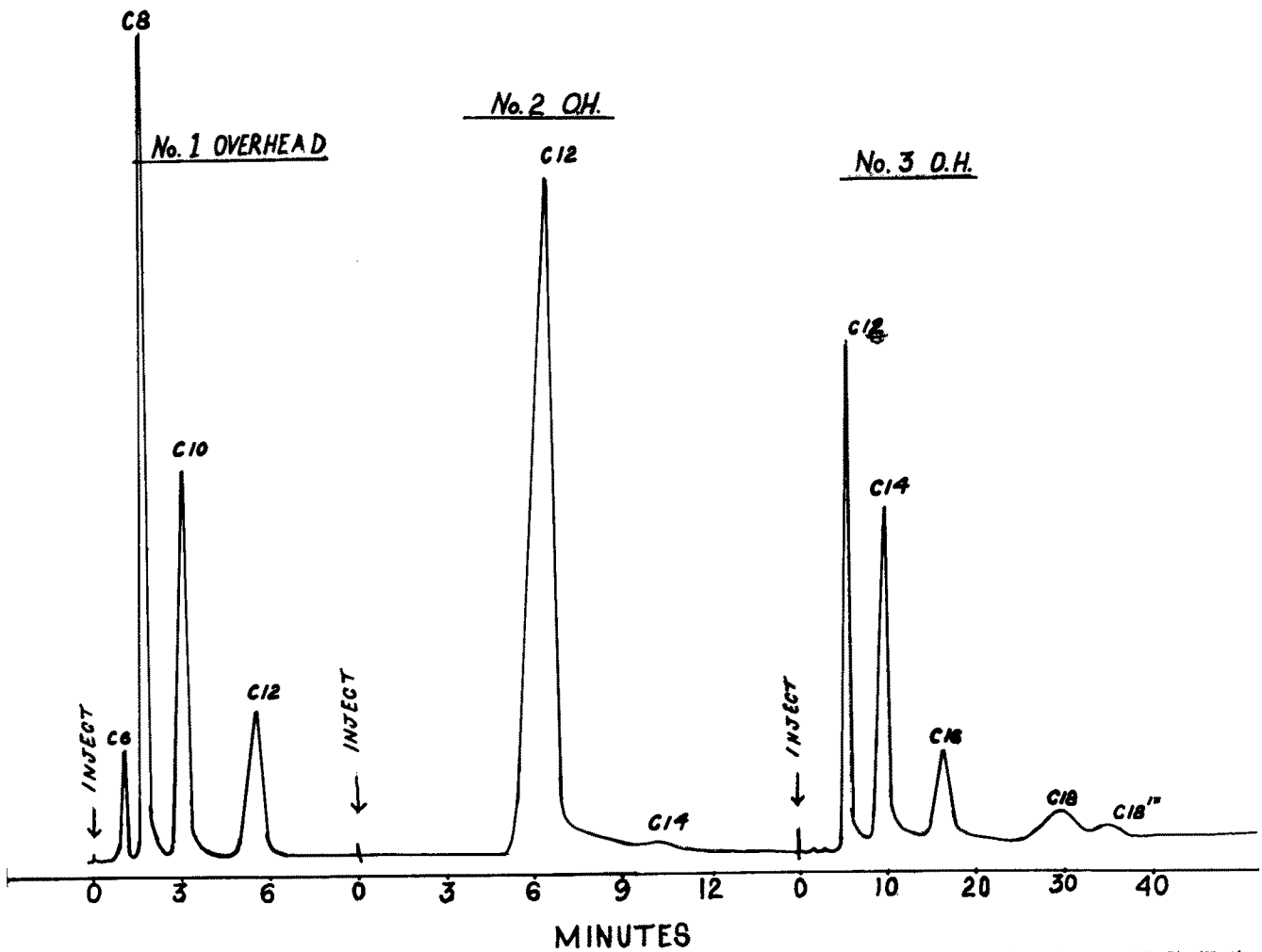


FIG. 2. Process gas chromatographic analysis profile of the three overhead still streams during a Coco fatty acid distillation run. Column: 5-ft, 20% DEGA, 3% $H_3PO_4$, 60–80 mesh, Chromosorb W. No. 1—20X. No. 2—20X. No. 3—5X.

TABLE II

Relative Retention Time (Palmitic Acid = 1.00) for Normal Fatty Acids Using Two Different Columns

| Acid | 20-M TPA column [a] | DEGA column [b] |
|---|---|---|
| Caproic | 0.07 | ..... |
| Caprylic | 0.12 | ..... |
| Capric | 0.18 | 0.20 |
| Lauric | 0.31 | 0.34 |
| Myristic | 0.56 | 0.56 |
| Palmitic | 1.00 | 1.00 |
| Stearic | 1.76 | 1.73 |
| Oleic | 1.69 | .... |
| Arachidic | 2.65 | |

[a] Five-ft column, 10% Carbowax 20-M terminated with Terphthalic Acid on 80–100 mesh Teflon-6 at 240C.
[b] Four-ft column, 20% diethylene glycol adipate, 3% $H_3PO_4$ on 60–80 mesh Chromosorb W at 225C.

was approx one hr. The number one stream was monitored for the $C_6$–$C_{12}$ acids in 10 min. The analysis of the No. 2 stream through myristic acid took 15 min to complete. A little more than 30 min was the time required for the $C_{18}$ acids to emerge during the No. 3 stream analysis.

The analytical time can be speeded up for less complicated acid mixtures than Coco acid in any number of ways. This can be done by changing operating conditions or modifying the column. However, using an isothermal system, the separation must be balanced with the time of analysis so that all the $C_6$–$C_{18}$ peaks can be resolved and their areas integrated. From the above examples, one can easily see how the automatic GLC program can be set up to follow the distillation run from start to finish. During this time the operators have almost continuous knowledge of composition of the three streams. It is also possible to set the program to monitor any individual stream more often than the others if necessary. As many as six complete analyses/hr of the No. 1 stream could be programmed if so desired.

TABLE III

GC Analysis of a Known Fatty Acid Mixture Using a Five-Ft Column of Carbowax 20M-Terphthalic Acid on Teflon

| Acid | Calculated | | By area | Difference | |
|---|---|---|---|---|---|
| | Mass % | Mole % | | Mass | Mole |
| Capric (C-10) | 9.8 | 13.4 | 11.1 ± 0.5 | +1.3 | −2.3 |
| Lauric (C-12) | 14.7 | 17.3 | 16.2 ± 0.4 | +1.5 | −1.1 |
| Myristic (C-14) | 19.8 | 20.4 | 21.3 ± 0.4 | +1.4 | +0.9 |
| Palmitic (C-16) | 26.2 | 24.4 | 23.3 ± 0.3 | −2.9 | −1.1 |
| Stearic (C-18) | 29.6 | 24.6 | 28.1 ± 0.7 | −1.5 | +3.8 |

*Use of Inert Support Column.* A five-ft column of 10% Carbowax 20M terminated with terphthalic acid on Teflon 6 was constructed. The use of this packing for free fatty acids had been recently reported (3). This packing was tested using fatty acid samples for its separating ability, relative retention time, and also for quantitative results. The peaks showed very good symmetry with excellent separation of the chain lengths. Table II gives the relative retention time (Palmitic Acid = 1.00) for a series of fatty acids, $C_6$–$C_{20}$. Table III shows the quantitative analysis of the $C_{10}$–$C_{18}$ fatty acid mixture using peak areas and calculated as both mass and mole percentage. The composition by area using this column is slightly closer to mole percentage than mass percentage. In earlier work (12) using phosphoric acid DEGA columns, we reported that the uncorrected quantitative results with fatty acids were also closer to mole percentage. Normally response correction factors are used when analyzing fatty acids and their methyl esters by GLC. The correction factors are most important when the sample has equal amt of acids of widely varying chain lengths. The factors are least important when there is one major acid with small amt of adjacent chain length acids. Since the latter case represents the most important samples encountered, correction factors

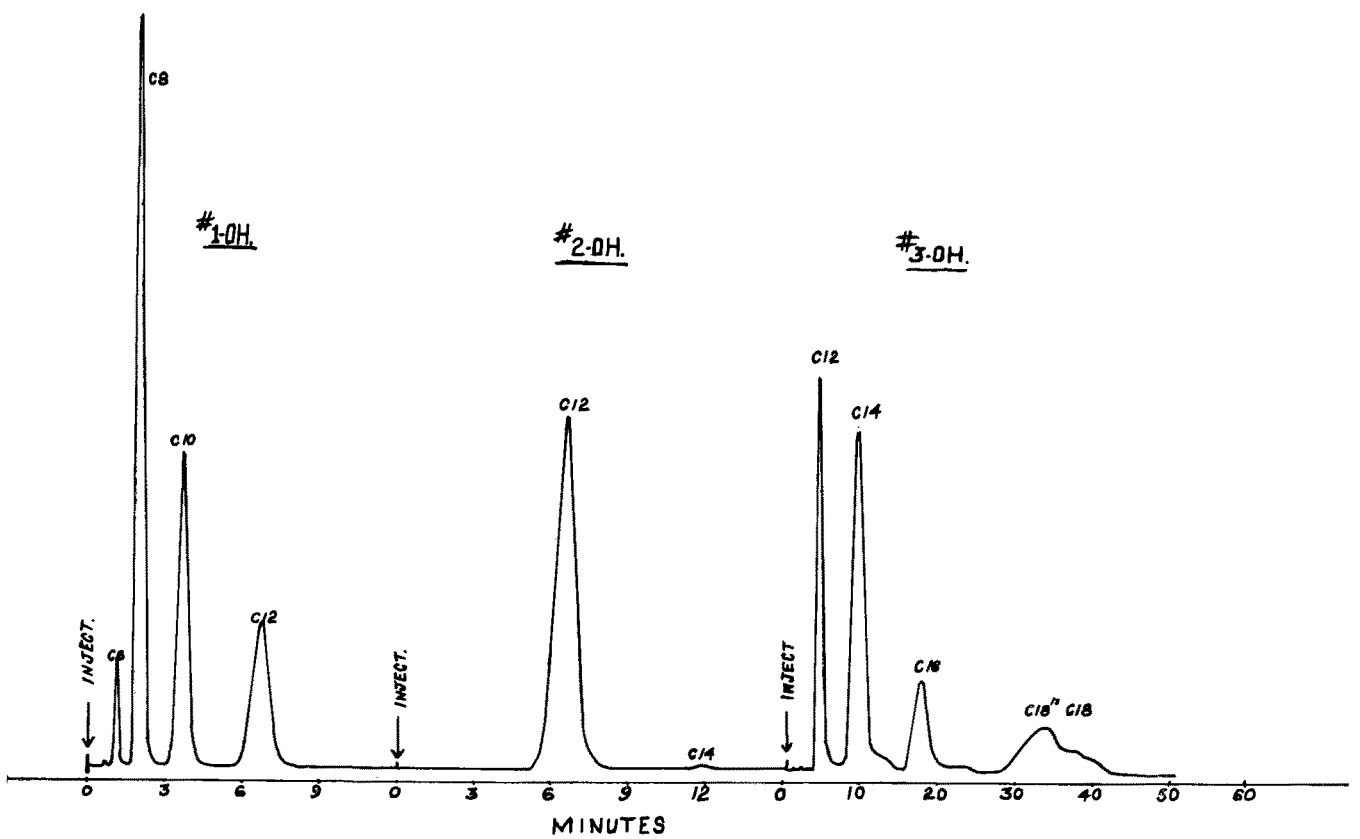


FIG. 3. Process gas chromatographic analysis, using an inert support column, three overhead still streams during a Coco fatty acid distillation run. Column: 30-in., 10% Carbowax, 20M Terphthalic acid on Teflon 6. No. 1—20X. No. 2—20X. No. 3—5X.

were not built into the instrument. With such good results obtained on the laboratory instrument, a 30-in. column was prepared and used on the process instrument. Figure 3 shows the still stream profile obtained with the column on the plant instrument during a Coco fatty acid distillation. The quantitative results compared favorably with those obtained by the chromatography of the same acids as esters.

This particular column packing shows great promise for the gas chromatography of unesterified fatty acids. The drawbacks of this column are that it requires higher temp than the polyester columns; the fatty acid emergence time is longer for a given column length; the unsaturated and saturated acids are not completely resolved. However, these disadvantages are more than offset by the fine symmetrical peaks and the excellent quantitative results obtained using peak areas alone. How long these columns will maintain their efficiency is not known at this time. The DEGA-$H_3PO_4$ columns have operated as long as six months before replacement was necessary.

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# Process Gas Chromatography of Fatty Acid Distillation Streams.[1] II. Design and Construction of the Process Chromatograph

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## Abstract

When applied to fatty acid process chromatography, conventional instrumentation is inadequate because of the temp required for effective vaporization of the sample. The instrument described uses a special injector operating at 300C for analysis of distillate streams containing fatty acids $C_6$ through $C_{18}$. Tape programmed operation presents analytical data as a chromatogram or as digital printout of electronically integrated peak areas. Details of construction are discussed together with some design problems.

## Introduction

A TROUBLESOME, IF NOT a serious, problem hindering process chromatography of the fatty acids has been the necessity for converting these acids to their methyl esters before injection into the chromatograph instrument. By eliminating this step, the phosphoric acid column opened the way for designing a practical process analyzer which can accept samples of these acids directly from the process stream (1,2).

This analyzer was designed specifically to monitor continuously the composition of distillate streams in a fractionating process where the acids range from 6–18 atoms in carbon chain length. Because of the elevated temp needed in handling the higher boiling acids, special techniques and departures from conventional design were required, making the instrument somewhat unique. A description of its construction and operation are given here, and some problems encountered in its design are also treated. The chemistry and column technology related to this project are covered in another paper (3).

## Sample Handling

Since the materials in the processing stream require a temp of ca. 80C to keep them fluid, all pumps and sample lines leading into the chromatograph are steam traced. The hairpin column and its heater, together with the thermal conductivity detector, are housed in an insulated cabinet held at an environmental temp of 80C by a 750-w fin heater. The temp is regulated by a mercury bulb thermostat through its electronic control circuit.

Separate sample loops of ⅝ in. stainless steel tubing constantly circulate fresh materials from the three still overhead lines to a common point about 40 in. from the chromatograph cabinet. Rated pump capacity (Eastern Industries, Hamden, Conn., Model DH-11, Type 100/C99) is 1 gal/min. Upon programmed command, the proper stream is diverted through its solenoid valve into the instrument. While the previous sample is being analyzed, the new stream flushes out the lines in preparation for its own analysis.

To insure fresh sample at the time of injection flow rates of 10 cc/min are used. Correspondingly, dead space and sample volume are kept to less than 15 cc by using miniature inline filters, ⅛ in. OD sample lines of minimum length and a sample chamber of only 0.2 cc capacity in the injectors. Waste sample flows through a channel common to all three streams and, after passing through a flow meter, is discarded. The sample handling system is pictured in Figure 1.

Each of the three injectors delivers a $3.5 \times 10^{-3}$ cc sample metered by a calibrated undercut in a sample

[1] AOCS Bond Award, Fall 1964.