NASA CR-
144636

# STUDY OF VOLATILE CONTAMINANTS IN RECLAIMED WATER

*Final Report*

*Contract NAS 9-12843*
*SwRI Project 01-3391-001*

(NASA-CR-144636) STUDY OF VOLATILE CONTAMINANTS IN RECLAIMED WATER Final Report (Southwest Research Inst., Houston, Tex.) 40 p HC $4.00 CSCL 06K
N76-14805
Unclas
G3/54 05648

Prepared for

Health Services Division
Johnson Space Center
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*October, 1975*

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# I. INTRODUCTION

This report presents the results obtained in evaluating different methods which might be used to reduce the volatile contaminants found in water recovered from urine by distillation. Two previous reports[1,2] described earlier work done on this subject by Southwest Research Institute to define the nature of the problem and to identify some of the pertinent distillation factors involved in its occurrence.

The work reported here utilized the same distillation apparatus and experimental techniques used in the previous studies. In a preliminary study, the use of activated carbon and catalytic oxidation were investigated to see what techniques might be useful in absorbing or preventing the occurrence of volatile contaminants. In a subsequent study, more detailed experimental data were obtained using several different types of activated charcoal and using an oxidation catalyst of the type used in catalytic converters for automobile emission control.

Charcoals tested were recommended and supplied by Westvaco of Covington, Virginia (Nuchar WV-G 12 x 40 mesh, WV-L 8 x 30 mesh, and WV-W 12 x 40 mesh) and Barnebey Cheney of Columbus, Ohio (PE).

The catalyst evaluated was Girdler G-43 produced by the Chemetron Corporation. Its typical chemical composition is 0.1% platinum, 3.0% nickel, and the balance $Al_2O_3$.

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1. Herbert C. McKee and Rudy Marek, Jr., "A Study of Volatile Contaminants in Recovered Water." NASA Contract NAS 9-11580. Southwest Research Institute. May, 1972.

2. Herbert C. McKee, Rudy Marek, Jr., and John D. Millar, "A Study of Volatile Contaminants in Reclaimed Water." NASA Contract NAS 9-12843. Southwest Research Institute. April, 1974. This report is repeated as an addendum after the discussion of additional work reported here.

## II. PRELIMINARY EXPERIMENTAL TESTS

As a guide in planning more detailed experiments, preliminary tests were conducted to evaluate different methods of removing or preventing the carryover of volatile contaminants. These results are described here as background information for the more detailed tests reported in the next section of this report.

### A. Use of Activated Carbon

Activated carbon is frequently used to adsorb organic vapors and other organic materials, and thus activated carbon was an obvious choice to attempt to remove organic constituents from urine distillate. According to the "Encyclopedia of Chemical Technology" (Kirk-Othmer), there is little difference between highly activated carbon for use with liquids and that for use with gases. The latter is usually granular rather than powdered and may have more surface area per unit of weight. The product used in this work was prepared for use with gases and was judged the easier to handle in this application.

Distillate from urine was prepared as previously done in this program. A volume of activated carbon equal to about 1/3 of the volume of distillate was added to the distillate and contact was maintained for three hours, during which period the mixture was agitated periodically by shaking. Headspace analyses on 10-ml portions of the treated and untreated distillate indicated a substantial reduction in peaks on the chromatogram obtained with the treated distillate.

The same procedure was carried out again, but the contact time was increased to six hours. An even greater reduction in volatiles was indicated. Comparison of peak heights on the chromatograms of before and after treatment samples shows a reduction of the major components (acetone and dioxane) in excess of 95% and a reduction in the minor components to levels below the sensitivity of detection in several instances and no less than 50% in the worst instance.

The contact period was then increased to 44 hours. Contrary to what was anticipated, the analytical results showed that the volatiles had not been reduced below the levels produced by the three hours and six hours of contact in any instance, and in the case of acetone, the peak was appreciably higher than that obtained at the shorter contact times. The 3-hour contact experiment was repeated at this point with results being very close to the first experience. The reason for the increase in acetone with longer contact time is not known.

The distillation apparatus was modified to the extent that an activated carbon bed was installed between the Vigreaux column and the distilling head, and urine was distilled as per usual, with the carbon unheated and heated to 200° C. The temperature of the carbon bed did not influence the results. In both cases, the dioxane peak was reduced a substantial amount but the other peaks were scarcely reduced, if at all. The overall effects were much less than the ones noted with the slurrying of the carbon and distillate in the liquid phase.

### B. Other Adsorbents

Substitution of Molecular Sieves 5A for the activated carbon in the slurrying experiments mentioned above resulted in no decrease in the volatiles present in the distillate. This type of treatment was abandoned in view of the negative results obtained.

### C. Addition of Potassium Permanganate

Potassium permanganate was added to distillate in the amount of 1-2% of the weight of distillate recharged into the still pot, and redistillation was carried out. The usual distillation pressure could not be attained, presumably because of the oxygen released from the decomposing potassium permanganate. Pressures ran as high as 60-70 mm during part of the redistillation. Also, $KMnO_4$ was entrained to the extent that a slight purplish color appeared in the redistilled material. Analysis of the redistilled material showed some reduction in most peaks except the dioxane peak. The partial reductions achieved were less than when activated carbon was used to treat ordinary distillate. The permanganate did not sublime when heated to 100° C, and it was concluded that the carryover likely was due either to chemical decomposition in the presence of water or more probably to simple mechanical carryover or entrainment. At any rate, addition of potassium permanganate did not appear to be as effective as the use of activated carbon for reducing volatile constituents in urine, and no further tests were conducted.

## D. Reuse of Activated Carbon

An experiment was conducted to determine whether or not activated carbon used to adsorb volatiles could be reused after a simple recovery treatment.

Carbon was kept in contact with distillate for 20 hours and then the distillate was poured off. After a short drain period, the carbon was placed under vacuum with a conventional laboratory vacuum system (approximately 50-75 torr) at room temperature for 48 hours. At the end of this period, the carbon was free-flowing and had the appearance of unused carbon. The recovered carbon was placed in contact with fresh distillate for six hours, a time period previously established as adequate for near maximum adsorption. Volatiles in the distillate were then measured by the standard head space analysis technique. The recycled carbon reduced the volatiles to some extent but not nearly as much as fresh carbon except with respect to dioxane which was reduced 50-75%. It was concluded that vacuum desorption at room temperature was not satisfactory to allow reuse of activated carbon.

## E. Low Temperature Adsorption

To provide an indication of the possible effects of temperature, fresh carbon was put into each of two portions of distillate, and one was placed in a refrigerator and the other left at room temperature. At the end of six hours, the volatiles in the room temperature sample had been reduced to the usual level but the refrigerated sample had volatiles at the same level as the untreated sample. After 20 hours of contact, the refrigerated sample showed some reduction in volatiles, especially the dioxane, but the level was still higher than that found in the room temperature vessel after only six hours. Therefore, it is concluded that low temperature treatment is not an effective way of increasing the efficiency of removal.

## F. Use of Oxidation Catalysts

The heated carbon bed was replaced with a bed of silver metal strips, and the nitrogen sweep gas was replaced with oxygen. Distillation of urine was carried out at temperatures of 200° C and 360° C in the silver bed. Analyses of the distillates obtained showed no reductions in volatiles.

Next, reagent grade copper oxide and silver oxide were evaluated as catalysts. Catalyst bed temperature was maintained at 260° C. Distillate which had passed through the copper oxide bed showed no reduction in volatiles. The distillate from the silver oxide bed showed a substantial reduction in acetone level, but the dioxane level was unaffected. This indicated some possibility for the use of catalysts, but it appeared that specially prepared catalysts will be required rather than using conventional laboratory grade metals or metal oxides. Therefore, catalyst manufacturers were contacted to see if any of the new materials developed for use in vehicle exhaust emission control might be used for this purpose.

In summary, these preliminary experiments showed that activated carbon could be used to reduce volatile constituents and that the use of oxidation catalysts showed some promise. None of the other methods tested showed sufficient promise to warrant additional laboratory experiments.

Therefore, the final phase of study consisted of laboratory experiments to evaluate several different grades of activated carbon to learn more about this method of removing volatile constituents, and tests with a commercial catalyst used for automotive emission control. These experiments are described in the next section of this report.

# III. DETAILED LABORATORY TESTS

## A. Experimental Conditions and Apparatus

The laboratory distillation apparatus was similar to that employed in previous work as described in the previous reports. The Vigreaux column was replaced with a 22-mm x 300-mm column, the lower 150 mm being packed with Heli-pak 2918, a nichrome column packing supplied by Podbielniak, Inc., and the upper 150 mm packed with Girdler G-43 1/4" x 1/4" pellets. The lower section served as a preheater during evaluation of the oxidation catalyst.

The entire column was wound with nichrome resistance tape and was insulated with Pyrex glasswool. Temperatures were monitored by thermocouples placed in thermowells located at the center and top of the column.

Distillations were carried out at 36 mm Hg, the vacuum source being a water aspirator and the pressure being regulated by an air bleed through a fine-metering valve. Air was bubbled through the material in the distillation flask during all distillation runs.

The urine was a composite sample obtained from one subject and was stored in a refrigerator maintained at 2-3° C. To each 250 ml of urine placed in the still was added 1.45 g of the Biopal VRO-20 premix, as previously described.

Gas chromatographic analyses were performed using the "head-space" technique on a Varian A-700 modified to accept a flame ionization detector. The column employed was a 1/4" x 10' section of copper tubing packed with 8% Carbowax 600 + 7% Carbowax 1540 + 1 ml 2N NaOH on GasChrom Q 60-80 mesh. Oven temperature was 65°, injection temperature 125°, detector temperature 170°, and nitrogen carrier gas flow was 50 ml/min. Sample size was 1.0 ml of the head space vapor.

A standard aqueous solution containing 7.9 ppm acetone and 10.3 ppm 1,4-dioxane was prepared and analyzed by the above technique. Peaks 8 and 17 of the chromatograms of the urine distillate (see Table I) were identified as acetone and 1,4-dioxane, respectively, by comparison of retention times, and calibration factors of $9.5 \times 10^{-4}$ ppm · $mm^{-2}$ and $7.1 \times 10^{-3}$ ppm · $mm^{-2}$ were calculated. These factors were used to estimate concentrations in the experimental samples from the chromatographic chart records.

## B. Experimental Data and Discussion

There were no appreciable differences between the activated charcoals tested. Each had the effect of substantially reducing the amounts of most of the volatile components of the urine distillate (see Tables I and II). This was not unexpected at the concentrations used (1/3 by volume, consistent with previous work). It may be that some differences would appear as the ratios of charcoal to distillate were decreased.

Table I presents data for distillation runs in which the catalyst temperature was controlled at 35° and at 435°. The four overhead fractions were analyzed both with and without charcoal treatment. It is noted that three peaks appeared in the overhead fractions which did not appear in the urine charge stock (chromatographic retention times of 1.7, 5.9, and 10.5 minutes), possibly as the result of conversion by catalytic and/or thermal reaction. The charcoals used to treat the various overhead fractions were as follows:

Fraction 1 without heat - Barnebey Cheney PE
Fraction 1 with heat - Westvaco Nuchar WV-L
Fraction 2 without heat - Westvaco Nuchar WV-W
Fraction 2 with heat - Westvaco Nuchar WV-G
Fraction 3 without heat - Westvaco Nuchar WV-G
Fraction 3 with heat - Barnebey Cheney PE

### TABLE I. RESULTS OF DISTILLATION TESTS

(Numbers shown are arbitrary values relative to urine charge which was set at 1.0. Analysis by headspace technique.)

| Peak No. | $^{t}R$ min. | Urine Charge 250 ml | Catalyst Bed Temp. °C | Charcoal Treatment(1) | Fraction 1(2) | Fraction 2(2) | Fraction 3(2) | Fraction 4(2) |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.4 | 1.0 | 35 | U | 0.11 | 0.00 | 0.19 | 19.58 |
| | | | 435 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 35 | T | 0.01 | 0.10 | 0.18 | 0.20 |
| | | | 435 | T | 0.16 | 0.46 | 0.46 | 0.40 |
| 2 | 1.7(3) | none | 35 | U | 1.00 | 0.99 | 0.68 | 0.00 |
| | | | 435 | U | 0.21 | 0.13 | 0.34 | 0.08 |
| | | | 35 | T | 0.06 | 0.00 | 0.11 | 0.00 |
| | | | 435 | T | 0.04 | 0.39 | 0.45 | 0.51 |
| 3 | 1.9 | 1.0 | 35 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 4 | 2.2 | 1.0 | 35 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 5 | 2.6 | 1.0 | 35 | U | 0.00 | 0.06 | 0.00 | 0.00 |
| | | | 435 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 6 | 2.9 | 1.0 | 35 | U | 0.24 | 0.16 | 0.53 | 2.17 |
| | | | 435 | U | 36.38 | 5.30 | 0.87 | 2.29 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.66 | 0.08 | 0.00 | 0.00 |
| 7 | 3.6 | 1.0 | 35 | U | 0.01 | 0.01 | 0.00 | 0.00 |
| | | | 435 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 4.6 | 1.0 | 35 | U | 1.47 | 0.24 | 0.21 | 0.45 |
| | | | 435 | U | 0.59 | 0.04 | 0.02 | 0.12 |
| | | | 35 | T | 0.04 | 0.02 | 0.00 | 0.00 |
| | | | 435 | T | 0.02 | 0.01 | 0.01 | 0.01 |
| 9 | 5.9(3) | none | 35 | U | 1.00 | 1.17 | 2.29 | 6.15 |
| | | | 435 | U | 0.15 | 0.85 | 0.19 | 0.27 |
| | | | 35 | T | 0.05 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.05 | 0.00 |
| 10 | 6.5 | 1.0 | 35 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 11 | 7.5 | 1.0 | 35 | U | 0.51 | 0.00 | 0.00 | 0.62 |
| | | | 435 | U | 0.54 | 0.00 | 0.00 | 0.53 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 12 | 9.0 | 1.0 | 35 | U | 0.96 | 0.43 | 0.00 | 0.32 |
| | | | 435 | U | 0.00 | 0.38 | 0.00 | 0.00 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 13 | 10.[illegible](4) | none | 35 | U | 0.00 | 0.00 | 0.00 | 0.00 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 11 | 7.5 | 1.0 | 35 | U | 0.51 | 0.00 | 0.00 | 0.62 |
| | | | 435 | U | 0.54 | 0.00 | 0.00 | 0.53 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 12 | 9.0 | 1.0 | 35 | U | 0.96 | 0.43 | 0.00 | 0.32 |
| | | | 435 | U | 0.00 | 0.38 | 0.00 | 0.00 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 13 | 10.5[4] | none | 35 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 35 | T | 1.00 | 0.00 | 0.00 | 0.35 |
| | | | 435 | T | 0.23 | 0.00 | 0.45 | 0.00 |
| 14 | 12.2 | 1.0 | 35 | U | 0.79 | 0.15 | 0.10 | 0.42 |
| | | | 435 | U | 0.17 | 0.00 | 0.00 | 0.00 |
| | | | 35 | T | 1.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 15 | 14.5 | 1.0 | 35 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | U | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 35 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.00 | 0.00 | 0.00 | 0.00 |
| 16 | 16.8 | 1.0 | 35 | U | 0.17 | 0.29 | 0.00 | 0.18 |
| | | | 435 | U | 0.00 | 0.12 | 0.00 | 0.00 |
| | | | 35 | T | 0.10 | 0.14 | 0.15 | 0.22 |
| | | | 435 | T | 0.22 | 0.10 | 0.09 | 0.15 |
| 17 | 21.9 | 1.0 | 35 | U | 6.03 | 0.58 | 0.25 | 0.20 |
| | | | 435 | U | 1.50 | 0.08 | 0.00 | 0.00 |
| | | | 35 | T | 0.04 | 0.00 | 0.00 | 0.00 |
| | | | 435 | T | 0.01 | 0.00 | 0.00 | 0.00 |
| 18 | 30.5 | 1.0 | 35 | U | 1.58 | 0.94 | 0.97 | 0.99 |
| | | | 435 | U | 0.42 | 0.00 | 0.10 | 0.42 |
| | | | 35 | T | 0.39 | 0.68 | 3.78 | 0.98 |
| | | | 435 | T | 0.36 | 0.36 | 1.16 | 1.00 |

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(1) U = Distillate untreated with charcoal.
T = Distillate treated with charcoal.

(2) 250 ml urine plus Biopal VRO-20 Premix #2 charged. Four 50-ml fractions collected.

(3) No peak found in urine charge. Amount in 1st fraction, untreated and 35°, was set at unity.

(4) No peak found in urine charge or in untreated fractions. Amount in 1st treated fraction, 35°, was set at unity; presumably charcoal contaminant.

## TABLE II. COMPARISON OF CARBON EFFICIENCIES

| | Untreated Distillate | (1) PE | | (2) WV-G | | (3) WV-L | | (4) WV-W | |
|---|---|---|---|---|---|---|---|---|---|
| Peak No. | Peak Area | Peak Area | % Reduction | Peak Area | % Reduction | Peak Area | % Reduction | Peak Area | % Reduction |
| 1 | 162.0 | 135.0 | 16.7 | 162.0 | 0.0 | 158.4 | 2.2 | 104.4 | 35.6 |
| 2 | 108.8 | 15.3 | 85.9 | 11.9 | 89.1 | 8.5 | 92.2 | 3.4 | 96.9 |
| 3 | 4.4 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 |
| 4 | 176.0 | 16.5 | 90.6 | 11.0 | 93.8 | 13.8 | 92.2 | 11.0 | 93.8 |
| 5 | 14.2 | 10.7 | 24.6 | 10.7 | 24.6 | 14.2 | 0.0 | 14.2 | 0.0 |
| 6 | 22.8 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 |
| 7 | 55.0 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 |
| 8 | 15.0 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 |
| 9 | 37.6 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 | 0.0 | 100.0 |

Variable: x = % Reduction

Transformation: y = arcsine

Analysis of Variance Table

| Source | df | SS | MS | F |
|---|---|---|---|---|
| Charcoals | 3 | 102.95 | 34.32 | <1* |
| Peaks | 8 | 31370.94 | 3921.37 | - |
| Error | 24 | 1664.01 | 69.33 | |
| Total | 35 | 33137.90 | | |

*Not significant. F does not exceed $F_{.05}(3,24) = 3.01$. No detectable difference among charcoals.

Null Hypothesis: All charcoals equivalent

$\alpha = 0.05$

(1) Barnabey Cheney charcoal PE

(2) Westvaco charcoal Nuchar WV-G, 12 x 40 mesh

(3) Westvaco charcoal Nuchar WV-L, 8 x 30 mesh

(4) Westvaco charcoal Nuchar WV-W, 12 x 40 mesh

Fraction 4 without heat - Westvaco Nuchar WV-L
Fraction 4 with heat - Westvaco Nuchar WV-W

In contrast to earlier attempts to catalytically decompose the volatile organics, the Girdler G-43 under the experimental conditions described had the effect of reducing the amounts of most of the various components. This comparison was made by carrying out two separate distillations in which the only variation was that in one case heat was applied to the column to obtain an average temperature of 435°. The assumption was made that no substantial oxidation would take place at the column temperature obtained (35°) without external heat being applied. Comparing the first 50-ml fractions exhibiting peaks at 35°, ten of the twelve components measured were reduced (at 435°) from ca. 60 to 100% and two increased, one by a factor of ca. 150. No attempt was made to identify this compound (or compounds).

## C. Statistical Treatment of Data

In order to ascertain the effect of the oxidation catalyst, a statistical test was applied. The test chosen was the non-parametric Sign Test for equality of mean between paired groups. The sign of the difference between each pair is recorded, and the number of pluses and minuses recorded. If there has been no change, there should be an approximately equal number of each. To determine significance, the difference between the pluses and minuses is compared to a standard table, and a significant difference is noted if the difference is greater than would be expected on the basis of chance alone.

The Sign Test was used to test the hypothesis that no change in the relative areas resulted from the use of the oxidation catalyst. The percentage area of peaks of the chromatogram of each fraction for the untreated with catalyst was subtracted from that of the untreated without catalyst and the sign of the difference recorded. The total number of pluses and minuses for each sample is shown in Table III, with zeros ignored. Taken individually, the effect on Fractions 1 and 2 was shown significant at the 10% and 5% levels, respectively. The effect on Fractions 3 and 4, though strongly positive, was not significant, due largely to the number of peaks that did not appear either with catalyst or without catalyst. For the four fractions considered together, the result was 33 pluses and 7 minuses, which was a significant result at the 1% level. Thus, we can say that the components were reduced by the oxidation catalyst.

A similar analysis was done to evaluate the effect of the charcoals, and the summary is contained in Table IV. The comparison was again component by component, with the difference taken between the treated and untreated fractions, both with and without catalyst. This gave the eight individual results shown. The first, second, and third fractions, without catalyst, showed significant differences taken by themselves, with the fourth strongly positive but not significant. These intermediate values were grouped in two ways. First, the fractions were combined as either with or without catalyst, and second, these two were combined for an overall estimate.

The composite for those without catalyst showed an extremely significant decrease in the components, with a significance level of less than 0.01. The composite for the fractions with catalyst was not significant at all. However, the catalyst has been shown above to cause a significant reduction in the components, and there were numerous zeros in these comparative results. For all results taken together, the decrease in the components was significant at the 1% level, and the indication is confirmed that the charcoal was effective in reducing the level of the organics.

The charcoals were assigned to fractions randomly, and the effectiveness of the different charcoals was investigated. There was

## TABLE III. SUMMARY OF SIGN TEST FOR EFFECT OF CATALYST

| Fraction | No. + | No. - | Significance Level |
|---|---|---|---|
| 1 | 9 | 2 | 0.10 |
| 2 | 9 | 1 | 0.05 |
| 3 | 7 | 1 | >0.10 |
| 4 | 8 | 3 | >0.10 |
| Composite | 33 | 7 | >0.01 |

## TABLE IV. SUMMARY OF SIGN TEST FOR EFFECT OF CARBON

| Fraction | Catalyst Bed Temp. °C | Charcoal | No. + | No. - | Significance Level |
|---|---|---|---|---|---|
| 1 | 35 | PE | 10 | 1 | 0.05 |
|  | 435 | L | 8 | 2 | >0.10 |
| 2 | 35 | W | 10 | 1 | 0.05 |
|  | 435 | G | 5 | 3 | >0.10 |
| 3 | 35 | G | 7 | 1 | 0.10 |
|  | 435 | PE | 3 | 4 | >0.10 |
| 4 | 35 | L | 8 | 2 | >0.10 |
|  | 435 | W | 4 | 4 | >0.10 |
| 1-4 | 35 | - | 35 | 5 | >0.01 |
| 1-4 | 435 | - | 20 | 13 | >0.10 |
| Composite | - | - | 55 | 18 | >0.01 |

no clear tendency for one charcoal to be more effective. Charcoals PE, WV-W, and WV-G each achieved a significant decrease once, with WV-L showing a large positive trend once. The effect of the catalyst was strong enough to mask out any charcoal differences that may have been present.

The data in Table II were analyzed using an analysis of variance (ANOVA) model to determine if there were significant differences among the charcoals in their effectiveness. This procedure is used to simultaneously test for the equality of the means of several groups. The total sum of the square deviations from the overall mean is partitioned into sums of squares (SS) due to each factor in the experiment. If the means for each group are not significantly different, then the ratio of the treatment mean square (MS) to its appropriate denominator should be close to one. This F-ratio is compared to a table of F-distribution with appropriate degrees of freedom to determine if there is a significant effect due to the differing treatments.

The ANOVA procedure requires that the variability within each group be constant, independent of the mean level. When this assumption is not valid, a transformation of the data may be used and the ANOVA done in the transformed scale.

In this case, the variable chosen was the percent reduction in peak area from the blank. To normalize these percentages in order to make them suitable for the ANOVA, the percentages were transformed using the arcsine transformation, and the analysis was done in the transformed scale. The ANOVA table appears at the bottom of Table II.

The test statistic was the F-ratio for charcoals shown in the ANOVA table. Since the ratio was less than the appropriate table value, the conclusion is that for all components taken together, there was no significant difference among the charcoals in the percent reduction of the volatile organics.

## IV. SUMMARY AND EVALUATION

The statistical treatment provides additional evidence to confirm the conclusions that can also be observed by inspection of the data. Catalytic oxidation was effective in reducing the volatile constituents by a substantial amount under the conditions of the experiments conducted. This is not surprising in view of the fact that platinum catalysts have been used to promote many oxidation reactions, and within the past few years a tremendous amount of development work has been conducted to develop suitable catalysts to reduce hydrocarbon and carbon monoxide emissions from automobiles. The catalyst used was typical of those now in commercial production, consisting of a small amount of platinum on an alumina support. Most automotive catalysts are of this type, with some variations in type of support and geometrical configuration.

To determine whether or not catalytic oxidation might be feasible to decompose organic contaminants in water, tests were conducted at 435° C, a temperature deliberately chosen because it is near the anticipated operating temperature of this particular catalyst in automotive applications. If catalytic oxidation appears to be a reasonable option, further design studies would be needed to develop specifications for actual spaceflight hardware, and such studies should include detailed investigations of temperature. Reasonable reaction rates at lower temperatures might be possible, depending on the space velocity and other operating conditions of an actual unit. This would be expected from reaction kinetics, since the function of a catalyst is to increase the speed of reaction to the point that oxidation rates will be fast enough to be practical at lower temperatures.

Operating temperature would be an important variable to investigate in further design studies since the operation of the catalyst at temperatures much in excess of cabin temperature would require an undesirable input of energy in the form of heat, with a corresponding weight penalty. If a source of waste heat were available elsewhere in the spacecraft to maintain a satisfactory operating temperature, the use of an oxidation catalyst might be an attractive option. If not, providing additional heat to maintain proper operating temperature might impose such a weight penalty that catalytic oxidation would not be the method of choice.

The limited scope of these experiments did not make it possible to identify any reaction products produced by the catalytic decomposition. However, since the reaction was conducted with an excess of air present, it is presumed that the organic constituents were oxidized to carbon dioxide and water. This would be the reaction mechanism in an automotive emission control system and indeed with any platinum catalyst which promotes the reaction of organic compounds with oxygen. Since the amounts of organic matter involved would be small, the carbon dioxide and water produced would be small in comparison to the larger amounts normally present in the spacecraft atmosphere, and thus little or no additional requirement would be created for the atmospheric control system.

As a result of these experiments, catalytic decomposition appears to be a feasible alternative worth further investigation for possible development of spaceflight hardware. The possible energy penalty involved in maintaining the catalyst at an effective operating temperature would be an important variable for further study.

These experiments indicate that very little difference can be obtained by changing from one variety to another of activated charcoal. Treatment of distillate with charcoal is a feasible method of reducing the volatile constituents present and is recommended as the most readily available interim solution for further spaceflight use where water recycling is required. However, regeneration and reuse of the charcoal has not been demonstrated by the work done to date, although experiments on vacuum desorption were attempted. For extensive water recycling, one-time use of activated charcoal would result in the accumulation of large quantities of used charcoal, and desorption and reuse would be required for flights of long duration if an excessive weight penalty were to be avoided. This also would appear to be a suitable subject for further investigation to develop detailed design criteria and to develop suitable means for regeneration and reuse of the carbon. In the meantime, the use of activated carbon could be developed readily for space flights of short or intermediate duration where the lack of regeneration and reuse would not impose an excessive weight penalty.

# ADDENDUM

A Summary Report describing the first phases conducted under this contract was submitted in April, 1974. This report is presented here, together with the preceding report, to document all work performed under the contract.

# A STUDY OF VOLATILE CONTAMINANTS IN RECLAIMED WATER

*Summary Report*

*Contract NAS 9-12843*
*SwRI Project 01-3391-001*

Prepared for

**Health Services Division**
**Johnson Space Center**
**National Aeronautics and Space Administration**
**Houston, Texas 77058**

By

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*April, 1974*

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# SUMMARY AND CONCLUSIONS

Previous work had demonstrated that volatile impurities present in urine samples were carried over during distillation to occur in the distillate, thus presenting possible problems in water recovery during space flights of long duration. This investigation was undertaken to obtain more information on these potential problems.

Laboratory distillation apparatus was used for experiments to study the effects of changing distillation variables. Operating characteristics were similar to the anticipated operation of future space flight hardware. Carryover of volatile impurities into the distillate was determined by analyzing samples of the original still charge, fractions recovered by distillation, and the remaining residue. The results are summarized as follows:

1. Distillation pressure was varied from atmospheric to 36 mm Hg, causing some changes in the amounts of volatile impurities in distillate but not resulting in any major changes in the carryover and occurrence of volatile impurities.

2. Distillation rate is not a major variable. Slower rates cause a slight increase in volatile contaminants, presumed to be due to thermal decomposition during heating. However, effects are relatively small and are only quantitative, not qualitative.

3. Solids content of the still residue was increased to 69% by successive additions of feed without any marked operating problems or large changes in the handling of materials in the distillation apparatus. Bacterial action between successive additions of feed did not appear to increase volatile contaminants, despite the loss of iodine (bactericide) during distillation.

From these results, it is concluded that the occurrence of volatile constituents cannot be eliminated by any reasonable changes in distillation methods or procedures. Distillation conditions can be manipulated over a wide range with only relatively minor effects on the amounts of volatile impurities occurring.

To identify some of the volatile impurities present, special gas chromatographic techniques were used, in addition to combination gas chromatograph - mass spectrometer methods. The following compounds were identified in distillate from urine containing an iodophor germicide, BioPal VRO-20: dioxane, acetone, acetaldehyde, methyl alcohol, ethyl alcohol, and methyl ethyl ketone. Other volatile compounds were indicated

as probably present. The dioxane originates from the addition of the BioPal VRO-20 to the urine before distillation.

Future effort will be devoted to studying methods of removing volatile impurities from distillate or preventing their carryover during distillation.

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# I. INTRODUCTION

In a report of a previous investigation by Southwest Research Institute,(1) the occurrence of volatile organic impurities in water recovered from urine by distillation was documented. This is of concern for space flights of long duration, where water reclamation and reuse is contemplated as an integral part of the environmental control systems. This work demonstrated the possibility of problems of water purity from volatile organic contaminants, in addition to the problems of microbial and nonvolatile (salt) impurities which had long been understood.

In that work, a laboratory distillation apparatus was used to duplicate many of the operating characteristics of prototype equipment now being considered for space use. Laboratory data obtained with this unit indicated that trace organic constituents present in urine were removed readily by distillation and were concentrated in the first portions of distillate recovered. Distillation at reduced pressure reduced the amount of volatile impurities in the distillate, due apparently to the decreased rate of thermal decomposition at the lower temperatures. However, measurable quantities of volatile impurities were still recovered at 36 mm pressure, the anticipated operating pressure for space flight hardware. It was also found that iodine from the bactericidal premix used in water recovery was also collected in the distillate.

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(1) Herbert C. McKee and Rudy Marek, Jr., "A Study of Volatile Contaminants in Recovered Water." NASA Contract NAS 9-11580, Southwest Research Institute. May, 1972.

This study was undertaken in order to obtain more detailed information on the problem of volatile contaminants and to investigate possible methods that might be used to alleviate the problem. In particular, it was desired to examine the effect of changing distillation variables and to identify some of the trace constituents that had been observed. This report outlines the results obtained in these two areas.

The remainder of the present project will be devoted to evaluating various methods of treatment that might be appropriate for alleviating the problem.

## II. STUDY OF DISTILLATION VARIABLES

To obtain additional data on the effect of changing operating variables during distillation, the same laboratory apparatus was used which had been used in the first investigation. Laboratory runs were conducted in this apparatus using urine samples which had been subjected to various premix treatments simulating the anticipated operating procedures for spacecraft use. Distillation variables were changed as desired in order to conduct the various experiments outlined below. Samples of the original charge to the still, the distillate fractions recovered, and the still residue were analyzed by the same method developed in the previous investigation to provide a convenient screening technique to determine the presence of volatile impurities without necessarily identifying the various individual compounds present. Details of still operation and sample analysis were covered in the previous report and will not be repeated here. The sections which follow describe the individual experiments and discuss the results that were obtained.

### A. Distillation Pressure

Since the previous work had indicated that temperature variations accompanying pressure changes affected the formation of volatile constituents by thermal decomposition, a series of tests was conducted to obtain quantitative data on the effect of changes in distillation pressure. For this purpose, 500-ml portions of urine treated with 0.6% of a BioPal premix were distilled. Three distillation pressures were used:

1. 36 mm (anticipated pressure for possible space use; corresponding distillation temp. approximately 34° C).
2. 380 mm (0.5 atm; corresponding temp. approximately 82° C).
3. 760 mm (atmospheric pressure; corresponding temp. 100° C).

Table I summarizes the analytical data obtained, showing the relative levels of various volatile constituents as a fraction of the concentration of the same constituent in the original charge to the distillation apparatus. Because of random variations which occur from one distillation run to another, a rigorous mathematical treatment of the data was not warranted. However, a visual inspection of the data obtained serves to illustrate the basic principles involved in the relationship of pressure to distillate contamination. In most cases, the highest concentrations of the various volatile constituents were found in the atmospheric pressure experiment, confirming the previous results. Much lower levels were found at a pressure of 36 mm, and as before this was attributed to the decrease in thermal decomposition at the lower temperature. This supposition was confirmed by the results at 0.5 atm, in which most of the volatile constituents occurred at levels intermediate between the atmospheric and 36-mm runs. From these results, it appeared that volatile constituents could be expected to occur at any reasonable operating pressure and that the problem could not be avoided by any manipulation of pressure and temperature during distillation. Distillation at reduced pressure, however, as contemplated in space flight hardware, would serve to minimize the problem compared to the

## Table I. Effect of Distillation Pressure Changes

| **Atmospheric Pressure** | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) |
|---|---|---|---|---|---|---|---|---|---|
| Original Charge | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0 | 1.0 | 1.0 | P |
| 1st Fraction | 8.0 | 8.3 | 8.4 | 2.0 | 21.3 | + | 8.3 | 8.0 | + |
| 2nd Fraction | 1.3 | 0.5 | 0.78 | 1.3 | 8.1 | + | 0.94 | 2.3 | + |
| 3rd Fraction | 0.75 | P | 0.7 | 0.87 | 5.3 | 0 | 0.13 | 2.0 | P |
| 4th Fraction | 0.37 | P | 0.48 | 0.75 | 3.8 | 0 | 0.02 | 1.0 | P |
| Cold Trap | 1.3 | 0 | 0.43 | 0 | 0 | 0 | 0 | 0 | 0 |
| Residue | 2.8 | 0 | 0.07 | 0.13 | 0.28 | 0 | 0 | 0 | P |
| **Vacuum (36 mm)** | | | | | | | | | |
| Original Charge | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0 | 1.0 | 1.0 | P |
| 1st Fraction | 3.0 | 1.0 | 3.2 | 1.9 | 1.6 | 0 | 8.0 | 0.5 | 0 |
| 2nd Fraction | 1.5 | 0 | 0.03 | 1.0 | 0.77 | 0 | 3.0 | 0 | P |
| 3rd Fraction | 0.63 | 0 | 0 | 0.62 | 0.35 | 0 | 1.4 | 0 | 0 |
| 4th Fraction | 0.38 | 0 | 0.03 | 1.2 | 0.18 | 0 | 0.71 | 0 | 0 |
| Cold Trap | 0.94 | 0 | 6.3 | 1.2 | 0.06 | 0 | 0.08 | 0 | 0 |
| Residue | 2.1 | P | 0.11 | 0.12 | 1.1 | 0 | 0 | 0.5 | + |
| **Vacuum (380 mm)**<br>0.5 Atmosphere | | | | | | | | | |
| Original Charge | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0 |
| 1st Fraction | 6.7 | .57 | 5.3 | 1.3 | 5.9 | 1.9 | 7.2 | 9.8 | 0 |
| 2nd Fraction | .50 | P | .63 | 1.3 | 4.3 | .83 | 4.2 | .88 | 0 |
| 3rd Fraction | 1.3 | .18 | .29 | 2.1 | 1.2 | .25 | 1.9 | .63 | 0 |
| 4th Fraction | .44 | P | .25 | 1.0 | 1.4 | .19 | 1.8 | .50 | 0 |
| Cold Trap | .89 | P | .06 | .83 | .06 | 0 | 0 | 0 | 0 |
| Residue | .11 | .07 | .08 | .43 | .23 | 0 | 0 | 0 | 0 |

(1) Concentration of each constituent in original charge was arbitrarily assigned a value of 1.0. Other concentrations are expressed as a ratio relative to the original charge (to two significant figures).

(2) P - present, but concentration too low to obtain quantitative results.
\+ - present in sample, but ratio could not be calculated because concentration in original charge was zero.

(3) Tentative identifications (based only on elution time):
(1) Methanol, (2) Ethanol, (3) Acetone
The remaining peaks were not identified.

(4) Each distillate fraction was approximately 50 ml, leaving approximately 300 ml residue for each run.

use of a higher pressure which would result in a corresponding higher temperature.

## B. Volatile Accumulation During Extended Runs

Previous experiments had been conducted as single "batch" distillations in order to study the effects of distillation variables. In actual space flight hardware, however, it is contemplated that additional charge will be added periodically to the same still residue so that distillation can be continued for extended periods of time. This suggested the possibility that organic contaminants might accumulate over an extended period of time and thus result in a more severe problem than that which would result with successive batch distillations. In order to check on this possibility, a series of runs was made in which additional feed was added to the residue from the preceding run and additional distillate was recovered. Fresh feed in each case consisted of urine plus iodophor premix. The entire series of runs was conducted at a pressure of 36 mm to simulate the anticipated operation of space flight hardware.

This operating cycle simulated the operation of a unit in which the residue would be allowed to accumulate until a high concentration of dissolved solids was reached. For this purpose, a 5-liter sample was distilled in successive runs until the solids concentration in the residue exceeded 50% in order to check on the operating characteristics of the laboratory still at high residue levels. The urine sample was treated with premix in the usual manner (2.25 g premix to 390 ml urine) and distilled at a moderately rapid rate. Separate 500-ml portions were added as the level was reduced until the entire 5 liters had been distilled. Distillate was collected at approximately 300 ml per hour for the first portion of the run, but the rate decreased near the end of the run as the liquid level in the still became lower. Except for this decrease in distillation rate, however, no difficulties in still operation were encountered. When the distillation rate became quite slow and liquid level in the still was low, the run was discontinued. The total solids content of the residue was then determined and found to be 69%. At this level, the residue was still liquid at room temperature but solidified when refrigerated overnight. This residue appeared to contain primarily heavy dark oily material from the iodophor complex plus some crystallized inorganic material.

Table II tabulates the analytical results obtained from this series of runs. As in the previous runs, results are shown for eight different peaks representing eight volatile constituents that were measured with the experimental technique used. In addition, ratios from the individual peaks were added together to obtain an arbitrary "total" value for each run. The "total" values cannot be related to the absolute quantity of volatile constituents in each run since they are obtained from arbitrary ratios relative to the amount of each constituent in the original charge. However, the "total" values for each fraction provide a relative com-

## Table II. Volatile Constituents
### Successive Distillation Runs (Residue Accumulation)

| | | Peak Numbers | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Total |
| Original Sample | | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | |
| 1st Fraction | M | 4.4 | 0.5 | 2.1 | 1.0 | 3.5 | 3.3 | 5.8 | 2.4 | 23.0 |
| | N | 3.9 | 0.9 | 3.5 | 0.6 | 3.5 | 3.0 | 4.5 | 5.0 | 24.9 |
| | O | 4.2 | 1.0 | 6.8 | 0.6 | 10.8 | 7.1 | 4.5 | 10.0 | 45.0 |
| | P | 0.4 | 1.1 | 0.2 | 1.0 | 5.3 | tr | 0.1 | 1.6 | 9.7 |
| | Q | 2.5 | 0.6 | 5.5 | 0.6 | 3.0 | 4.2 | 4.2 | 8.0 | 28.6 |
| | R | 0.1 | 0.6 | 0.1 | 1.0 | 1.5 | 0.4 | 0.01 | 0.6 | 4.3 |
| 2nd Fraction | M | 1.3 | 0.2 | 0.05 | 1.2 | 2.0 | 0 | 3.9 | 0 | 8.7 |
| | N | 0.7 | 0.1 | 0.1 | 1.0 | 2.0 | 0 | 3.1 | tr | 7.0 |
| | O | 3.8 | 0.7 | 0.4 | 0.5 | 3.7 | tr | 3.4 | 0.1 | 12.6 |
| | P | 0.1 | 0.2 | 0 | 1.2 | 2.5 | 0 | 0.03 | 0 | 4.0 |
| | Q | 1.5 | 0.2 | 0.2 | 0.6 | 1.5 | 0 | 1.8 | 0 | 5.8 |
| | R | 0.1 | 0.4 | 0.03 | 0.8 | 2.1 | 0 | 0 | 0 | 3.4 |
| 3rd Fraction | M | 0.4 | 0 | 0 | 1.8 | 1.5 | 0 | 0.2 | 0 | 3.9 |
| | N | 0.5 | tr | 0.03 | 0.3 | 1.5 | 0 | 0.6 | tr | 2.9 |
| | O | 1.2 | 0.3 | 0.1 | 1.3 | 2.5 | tr | 1.8 | 0.1 | 7.3 |
| | P | 0.06 | tr | 0 | 0.7 | 1.3 | 0 | 0 | 0 | 2.0 |
| | Q | 0.6 | 0.3 | 0.04 | 0.6 | 0.8 | 0 | 0.7 | 0 | 3.0 |
| | R | 0.06 | 0.07 | 0.03 | 0.8 | 1.5 | 0 | 0 | 0 | 2.5 |
| 4th Fraction | M | 0.1 | 0 | 0 | 2.0 | 1.0 | 0 | 0.1 | 0 | 3.2 |
| | N | 0.2 | 0 | 0 | 0.5 | 1.5 | 0 | 0.3 | tr | 2.5 |
| | O | 0.3 | 0.3 | 0.03 | 0.6 | 1.5 | 0 | 0.8 | tr | 3.5 |
| | P | 0.06 | tr | 0 | 0.5 | 1.4 | 0 | 0 | 0 | 2.0 |
| | Q | 0.1 | tr | 0.04 | 0.6 | 1.5 | 0 | 0.2 | tr | 2.4 |
| | R | 0.06 | 0.06 | 0 | 0.6 | 0.7 | 0 | 0 | 0 | 1.4 |

## Table II. Volatile Constituents
## Successive Distillation Runs (Residue Accumulation)
## (Continued)

| | | Peak Numbers | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Total |
| Residue | M | 0.2 | 0.5 | 0.05 | 0.8 | 1.7 | 0 | 0 | 0 | 3.2 |
| | N | 0.1 | 0.2 | 0.04 | 0.7 | 0.7 | 0.4 | 0 | 0.2 | 2.3 |
| | O | 0.7 | 2.6 | 0.1 | 1.7 | 3.3 | tr | 0 | 0.4 | 8.8 |
| | P | 1.6 | 4.0 | 0.2 | 1.0 | 5.0 | tr | tr | 0.8 | 12.6 |
| | Q | 0.1 | 0.6 | 0.04 | 0.8 | 0.08 | 0 | 0 | 0.2 | 1.7 |
| | R | 0.03 | 0.4 | 0.02 | 0.6 | 0.03 | 0 | 0 | 0 | 1.1 |

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Numbers shown are arbitrary values relative to original sample which was set at 1.0. Analysis by headspace gas technique.

Successive distillations were made as follows:

M - Original charge to still was run on Monday. Total charge = 500 ml. Four 60-ml distillate fractions were collected, plus 60-ml residue sample, leaving 200 ml residue in still.
N - Additional 500-ml charge added to still and run on Tuesday. Four distillate samples and residue sample withdrawn as before, leaving 400 ml residue in still.
O - Additional 500-ml charge added to still and run on Wednesday. Four distillate samples and residue sample withdrawn as before, leaving 600 ml residue.
P - No new charge of urine added to still. Distilled residue Thursday to reduce volume. Four distillate samples and residue sample taken before leaving 300 ml residue in still.
Q - Additional 500-ml charge added to still and run on Friday. Distillate samples and residue sample taken as before, leaving 500 ml residue.
R - No new charge added. Residue distilled on Monday and distillate samples and residue sample taken as before.
tr - Trace, too small to be measured quantitatively.

parison between the successive runs to show the decrease that occurred in the total of all of the measured volatile constituents.

As in previous work, the highest concentration of volatile constituents occurred in the first distillate fraction that was recovered. Successive fractions contained lower concentrations, showing a depletion of volatiles in the charge in the still as distillation progressed. The "total" value showed this same trend as well as the ratios for the individual constituents.

These results show that volatile constituents did not accumulate to a significant degree during successive distillations with fresh charge added to the still residue. As an approximation, it appeared that the volatile constituents from each fresh charge were formed when the charges heated or were distilled off and collected in the distillate in much the same manner that occurred when single runs are made with fresh charge. From this, it was concluded that the exact manner of altering the distillation procedure with respect to adding fresh charge and removing still residue was not of major importance in determining the extent of possible contamination from volatile constituents recovered in the distillate.

Since these successive runs were made over a period of a week, the data also provide an additional insight into the possibility of bacterial action over a period of time. Since there was no increase in volatile carryover as the run progressed, it is concluded that little or no bacterial action occurred in the residue between runs to promote the formation of volatile constituents. Thus, despite the loss of iodine during volatilization as had been shown previously, the manner of using iodophor preparations appears to be effective in preventing excessive buildup of volatile contaminants by bacterial action in the intervals between successive runs.

### C. Rate of Distillation

Since pressure and temperature had been shown to exert some influence on volatile contaminants, it was reasonable to question the possibility that distillation rate might also be important. To examine this possibility, several runs were completed in the laboratory distillation apparatus with all experimental conditions held constant except distillation rate. Table III shows the results obtained in two runs that illustrate the trends that were evident. In the first run, the distillation rate was 100 ml per hour, which is a relatively slow rate for the apparatus used. In the second run, the heat input to the still was increased to obtain a distillation rate of 300 ml per hour, which represented fairly active boiling and a reasonably high rate for the apparatus used. Pressure was controlled at 36 mm in both runs, giving a distillation temperature of approximately 34° C.

As in previous experiments, samples of the original charge, four distillate fractions, and still residue were analyzed by gas chromatography. Results are expressed in this table as a ratio relative to the amount of each component in the original charge. From these results, it is obvious that a change in distillation rate does exert some influence

### Table III. Effects of Distillation Rates on Volatile Constituents

| | Sample Designation | Peak Number | | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Original Sample | T | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | |
| | U | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | |
| 1st Fraction | T | 6.1 | 0.7 | 10.4 | 1.0 | 9.1 | 2.5 | 6.1 | 5.8 | 41.7 |
| | U | 4.1 | 0.5 | 9.7 | 1.1 | 4.1 | 1.3 | 4.3 | 4.6 | 29.7 |
| 2nd Fraction | T | 2.3 | 0.4 | 0.3 | 0.7 | 3.3 | 0 | 2.0 | 0.1 | 9.1 |
| | U | 1.3 | - | 0.1 | 1.0 | 1.8 | 0 | 1.1 | 0 | 5.3 |
| 3rd Fraction | T | 1.5 | - | 0.1 | 1.1 | 1.8 | 0 | 0.8 | 0.1 | 5.4 |
| | U | 0.7 | 0 | - | 0.7 | 1.3 | 0 | 0.5 | 0 | 3.2 |
| 4th Fraction | T | 0.4 | - | 0.1 | 0.7 | 1.2 | 0 | 0.2 | 0 | 2.6 |
| | U | 0.1 | 0 | - | 1.1 | 0.7 | 0 | 0.1 | 0 | 2.0 |
| Residue | T | 0.2 | - | - | 0.9 | 0.3 | 0 | 0 | 0 | 1.4 |
| | U | 0.1 | 0 | - | 0.9 | 0.3 | 0 | 0 | 0 | 1.3 |

Numbers shown are arbitrary values relative to original sample which was set at 1.0. Analysis by headspace gas technique.

Original samples T and U taken from same composite urine sample.
Sample T distillation rate = 100 ml/hr - slow
Sample U distillation rate = 300 ml/hr - fast

on volatile contaminants, but the differences are not great enough to change the basic nature of the problem. In both runs, the greatest amounts of volatile constituents were recovered in the first fraction, with decreasing amounts in succeeding fractions; this confirms the trend established in previous experiments in which distillation rate was not varied. In addition, the same constituents were found in samples from each run. From this it was concluded that changing the distillation rate did not eliminate any organic constituents from the distillate or cause the appearance of any new constituents.

The only significant differences appear to be quantitative changes in the amounts recovered. With only a few minor exceptions, greater amounts were found in the distillate samples from the run which was conducted at the slower distillation rate. This likely was due to thermal decomposition of higher molecular weight organic constituents during the distillation. Such decomposition occurs in urine samples heated to boiling at both atmospheric pressure (100° C) and at reduced pressure (36 mm and 34° C), and these results indicate that the time of heating also exerts some effect.

The column marked "Total" was obtained by adding the ratios for the individual constituents to obtain a relative estimate of the total amounts of volatile organic constituents found, as was also done in Table II. These figures reflect the same general trend indicated by the individual constituents, and give an indication of some increase in volatile organics with a slower distillation rate.

From the standpoint of water recovery during space flight, these results indicate that distillation rate is not a major factor. Maintaining the distillation rate as high as practical for the apparatus used will result in some decrease in the occurrence of volatile organic constituents in the distillate, but will not eliminate the problem. Otherwise, no significant effect on the design or operating characteristics of space flight hardware was revealed by this series of experiments.

## III. IDENTIFICATION OF VOLATILE CONTAMINANTS

In order to provide additional data to understand the problem of volatile contaminants and plan any necessary corrective measures, it was desirable to identify at least some of the contaminants found. This was accomplished using the same laboratory distillation apparatus used in other experiments to obtain samples, analyzing samples to measure and isolate volatile constituents, and then conducting supplementary tests to confirm identifications. The "headspace technique" used in other experiments was used for analysis, but additional sample processing methods were required to obtain enough sample for confirmatory tests. Details of these experiments and the results obtained are presented and discussed in the sections which follow.

### A. Preparation of Distillates

Distillation of urine was performed at the reduced pressure of 36 mm Hg, as in previous experiments. Urine specimens for distillation were obtained from the same subject throughout this series of experiments in order to reduce variation in the profile of volatiles to a minimum. Zlatkis, *et al*, (2) has previously reported that the profile of urinary volatiles remained remarkably constant in an individual, despite dietary changes, during an observation period of two months' duration. Specimens were collected in glass containers and kept

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(2) Zlatkis, A., *et al*, *Anal. Chem.*, *45*, 763-767 (1973).

refrigerated until charged into the still pot. Specimens were never more than 40 hours old at the time of distillation. The initial charge to the still pot was always 500 ml plus additives.

The additives used, per 500 ml of urine, were as follows:

1. Premix containing the iodophor — 2.9 g (BioPal VRO-20, 1.4 g; sulfuric acid, reagent grade, 0.2 g; Dow Corning Antifoam AF or C, 0.06 g; water 1.24 g)

or,

2. Antifoam + acid — 0.26 g (Dow Corning Antifoam AF or C, 0.06 g; sulfuric acid, reagent grade, 0.2 g)

or,

3. Sulfuric acid, reagent grade — 0.2 g.

The first 50-ml fraction of distillate was known to be considerably richer in volatiles than subsequent fractions. Distillation was terminated once the first 50 ml had been collected in the receiver, since even the richest fraction did not have a concentration of volatiles sufficient for analysis without further concentration.

## B. Analysis of Samples

The gas chromatographic analyses, except where coupled with a mass spectrometer, were made with an instrument equipped with a flame ionization detector. Direct analysis by injecting the liquid distillate provided no information, even at the most sensitive electrometer settings, owing to the low concentration of volatiles in the distillate.

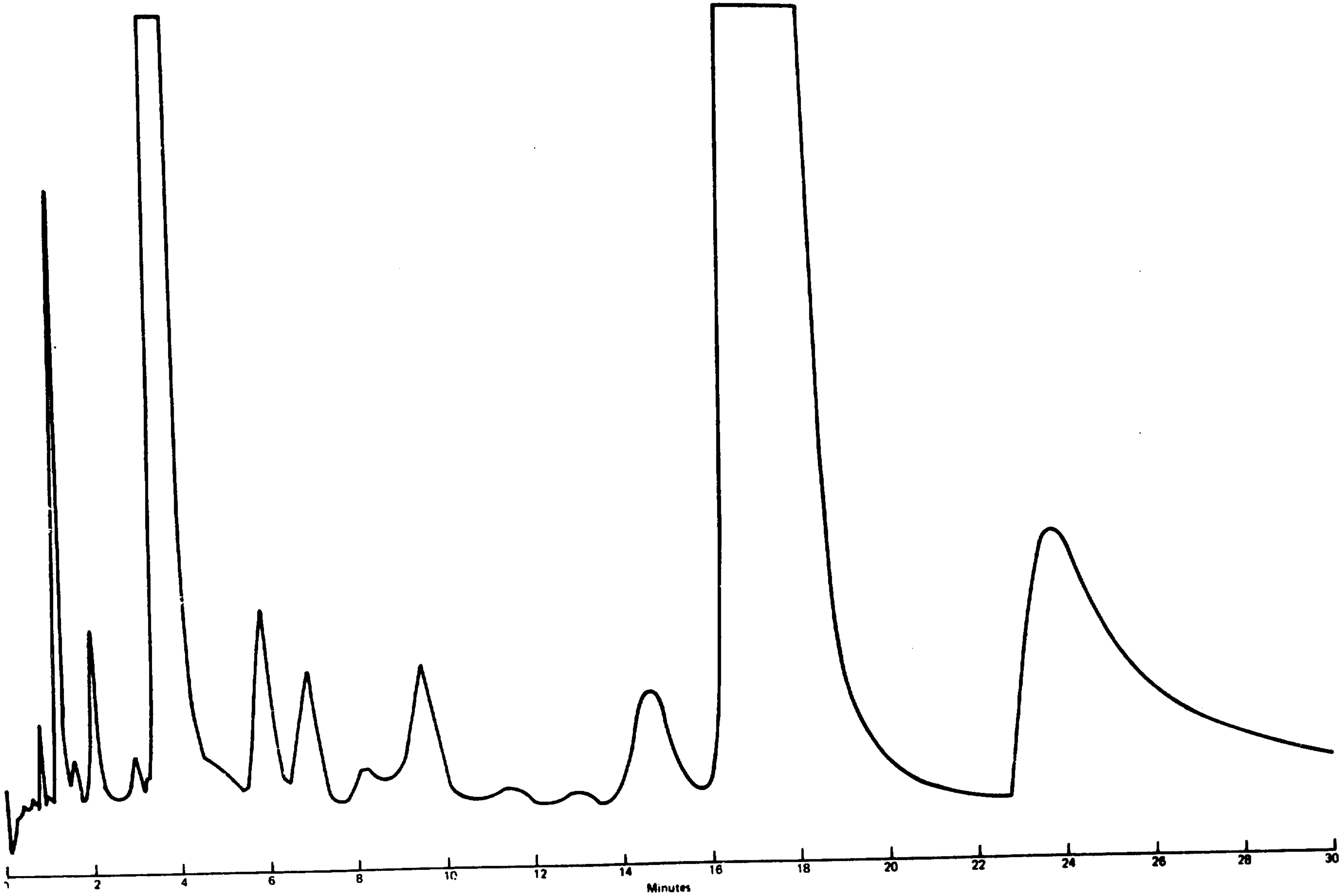
Therefore, it was necessary to employ the headspace analysis procedure described previously.

The following columns were evaluated:

1. Chromosorb 105
2. Chromosorb 101
3. Porapak Q
4. 7% Hallcomid M-18 on Gas Chrom P (80-100 m)
5. 10% Carbowax 1540 + 0.08 g NaOH per 2 g of Carbowax on Gas Chrom Q (60-80 m)
6. 8% Carbowax 600 and 7% Carbowax 1540 on Gas Chrom Q (60-80 m)
7. 8% Carbowax 600 and 7% Carbowax 1540 + 0.08 g NaOH per 3 g of mixed Carbowaxes on Gas Chrom Q (60-80 m).

The addition of the small amount of sodium hydroxide to Columns 5 and 7 was for the purpose of reducing column bleed. The column affording the best separation of peaks was Column 6 (see Figure 1) which had an unacceptably high bleed rate in some applications. With the exception of Column 1, all columns were useful to some extent in this work. However, no column gave complete separation of all the volatiles encountered, which is hardly surprising in view of the wide variation in boiling point and polarity of the compounds previously reported in urine.(1) In order to prevent carryover of volatiles from one injection to another, the syringe had to be purged for a 10-15-minute period between injections.

Figure 1. Headspace Volatiles from Distillate from Urine Which Contained BioPal VRO-20, Antifoam, and Acid GC Column No. 6



This was accomplished most easily by drawing ambient air through the syringe barrel by attaching it to the laboratory vacuum line.

Through comparison of chromatograms of headspace vapors from distillates obtained in one instance from urine containing the complete premix and in the other instance only antifoam and acid (see Figures 2 a and 2b), it was established that the BioPal VRO-20 was the likely source of the large peak eluting between 18 and 26 minutes. Injection of headspace vapor from a bottle of BioPal VRO-20 gave an identical peak. Also, by similar procedures, it was demonstrated that the antifoam and acid were not sources of the peak. Headspace vapor from the bottle of BioPal VRO-20 was swept with dry nitrogen through a trap containing, first $CS_2$, then $CCl_4$, submerged in an ice bath. The solutions were subjected to infrared scans and the spectra were found to match those of dioxane. For brevity's sake, only the scans of the $CS_2$ solutions are shown as Figures 3a and 3b. Injections of the unknown and of authentic dioxane into the gas chromatograph resulted in peaks with matching elution times.

By this time, it had become apparent that trapping peaks eluting from the chromatograph and subjecting them to infrared analysis was not a workable approach, due to the impractically long time that would be required to collect a sufficient quantity of the volatiles and the observed incomplete separation of the constituents by gas chromatography. However, tentative identification of several peaks was reinforced by trapping

Figure 2a. Headspace from Distillate from Urine
Which Contained BioPal VRO-20, Antifoam, and Acid
GC Column No. 2

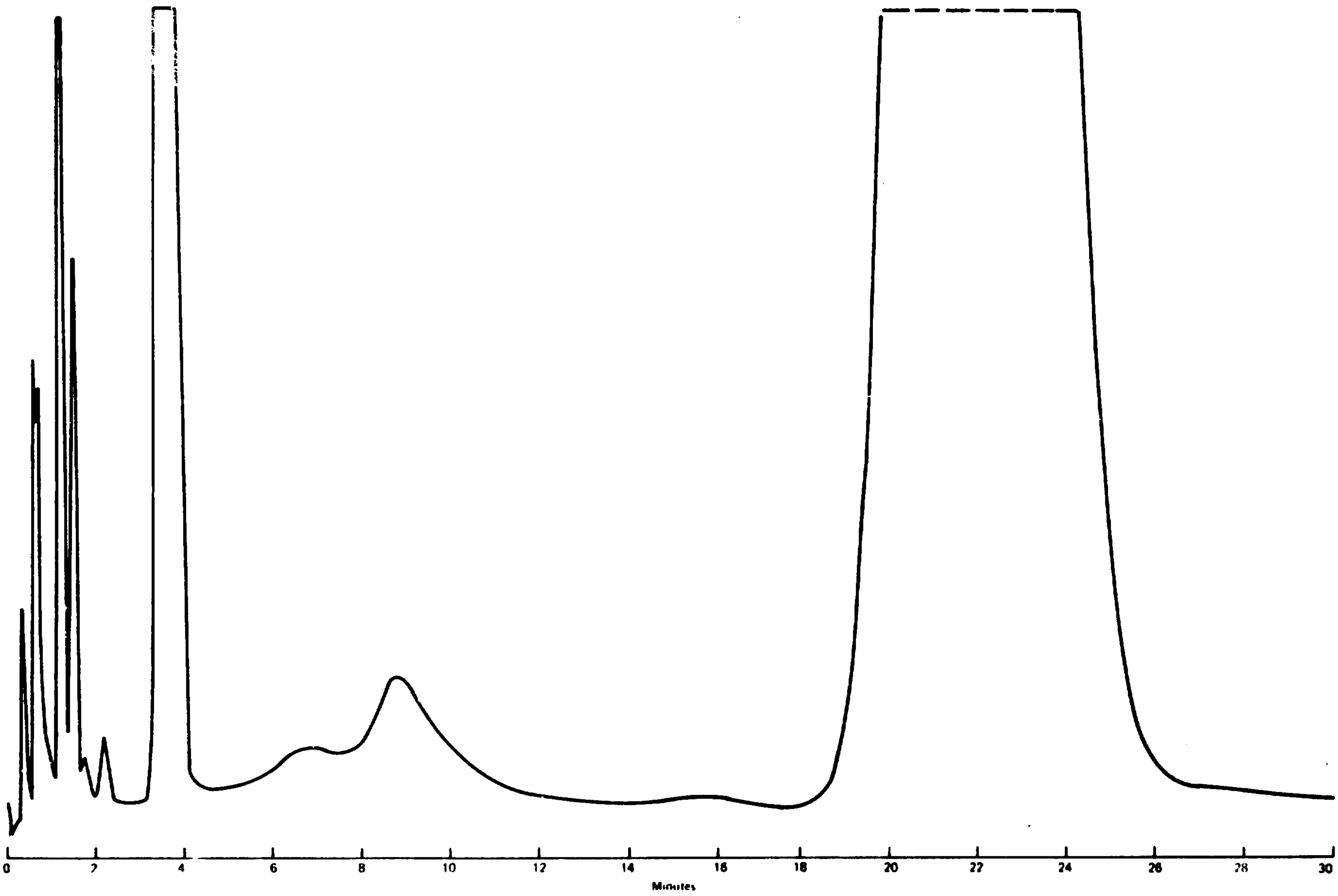


Figure 2b. Headspace from Distillate from Urine Which Contained Only Antifoam and Acid GC Column No. 2

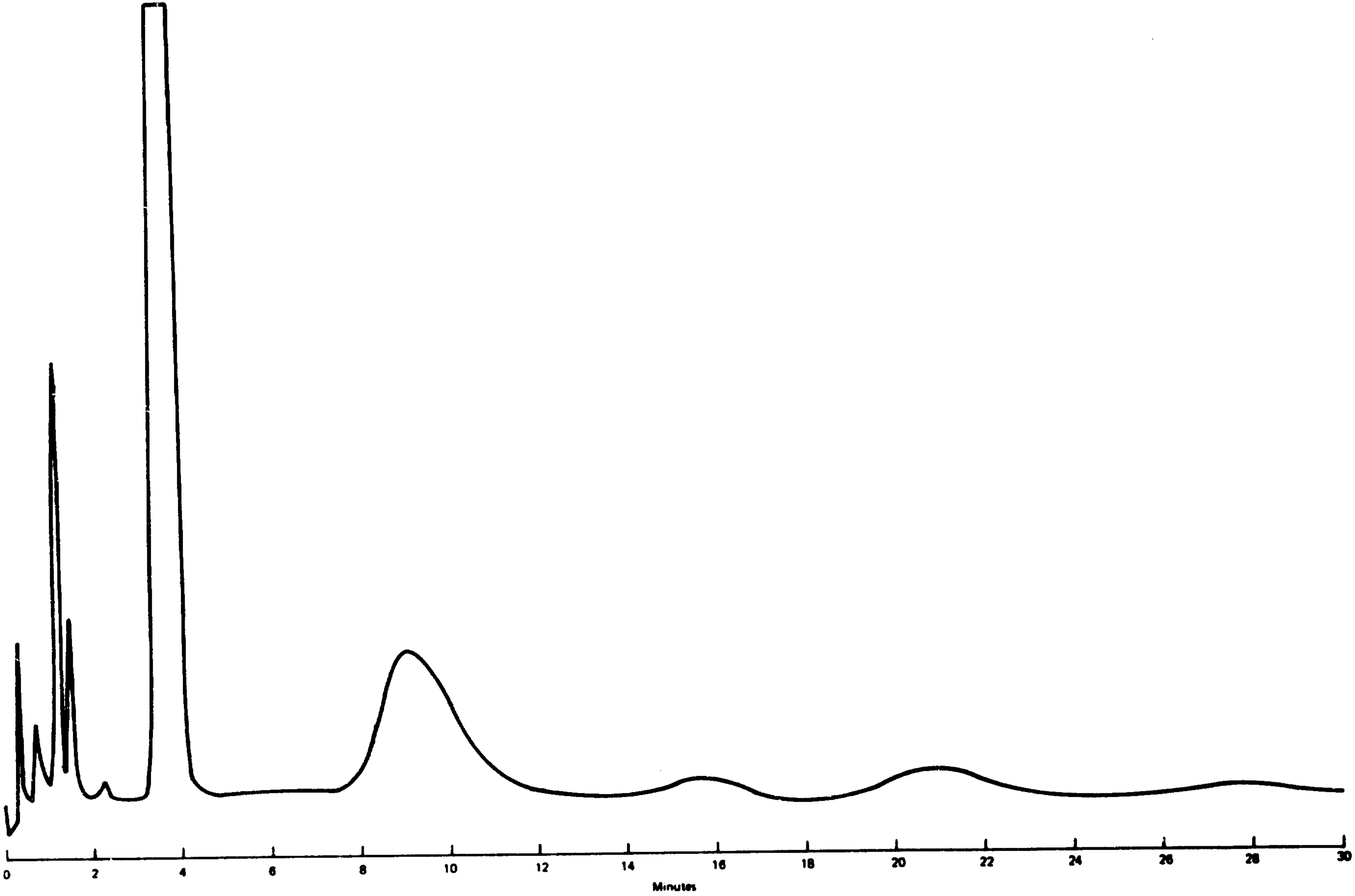
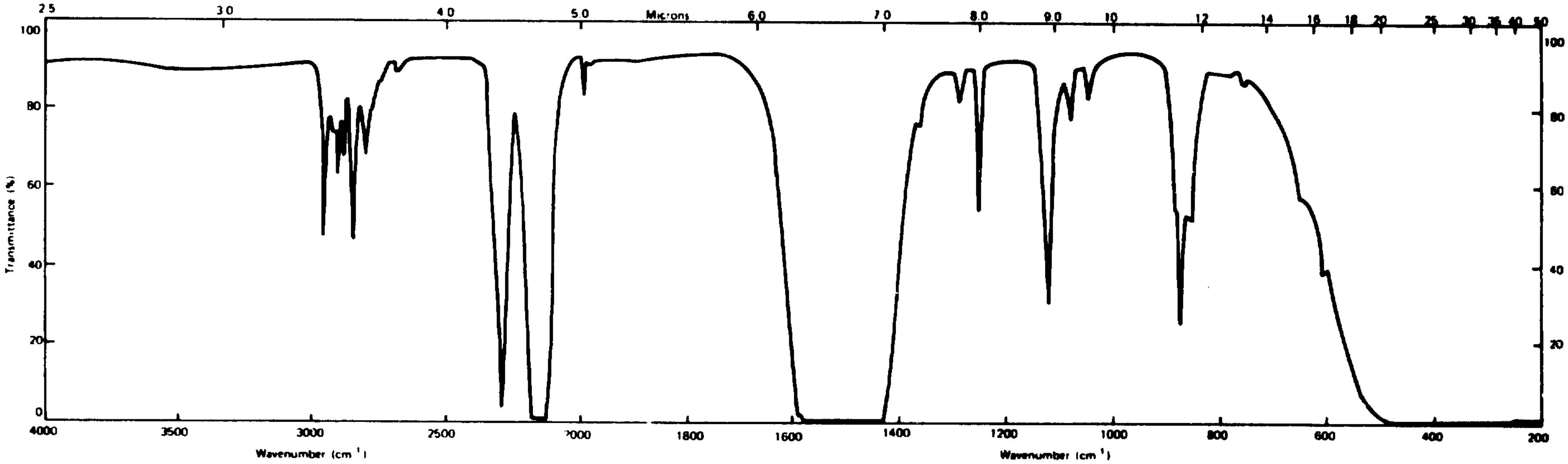
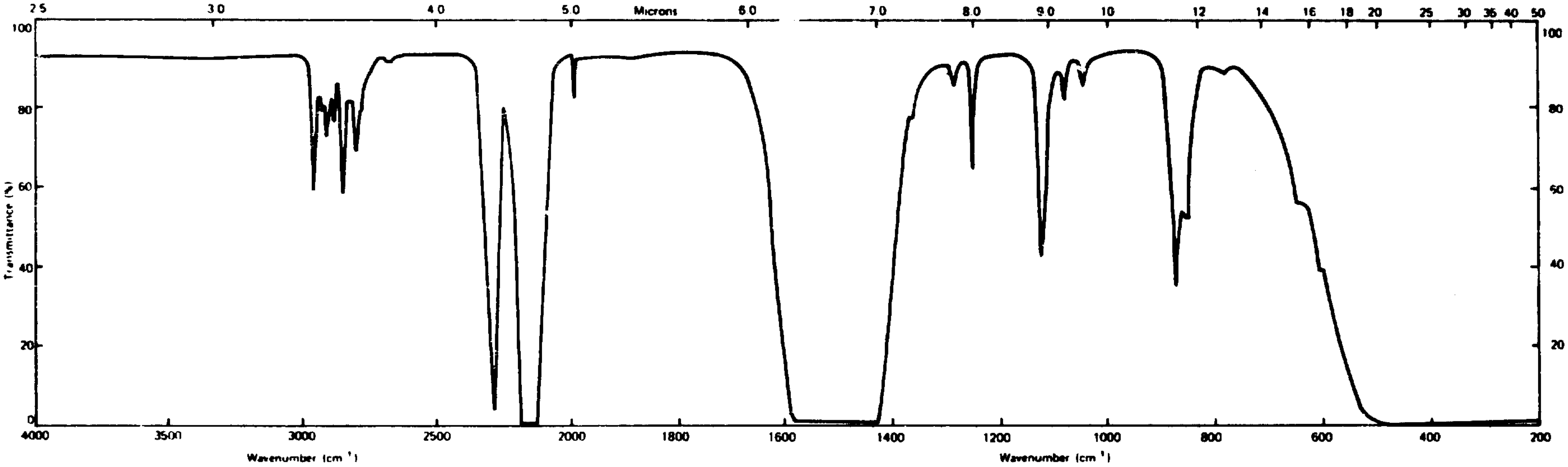


**Figure 3a. Infrared Spectra of Unknown**



| | |
|---|---|
| SAMPLE | Unknown in $CS_2$ |
| ORIGIN | Trapped from headspace of bottle of Biopal VRO 20 |
| SOLVENT | $CS_2$ |
| CELL PATH | ~ 0.05 mm |

Figure 3b. Infrared Spectra of Dioxane



SAMPLE Dioxane in $CS_2$ (10 µl in 4 ml $CS_2$)
ORIGIN Mallinckrodt Scintillar grade
SOLVENT $CS_2$
CELL PATH ~0.05 mm

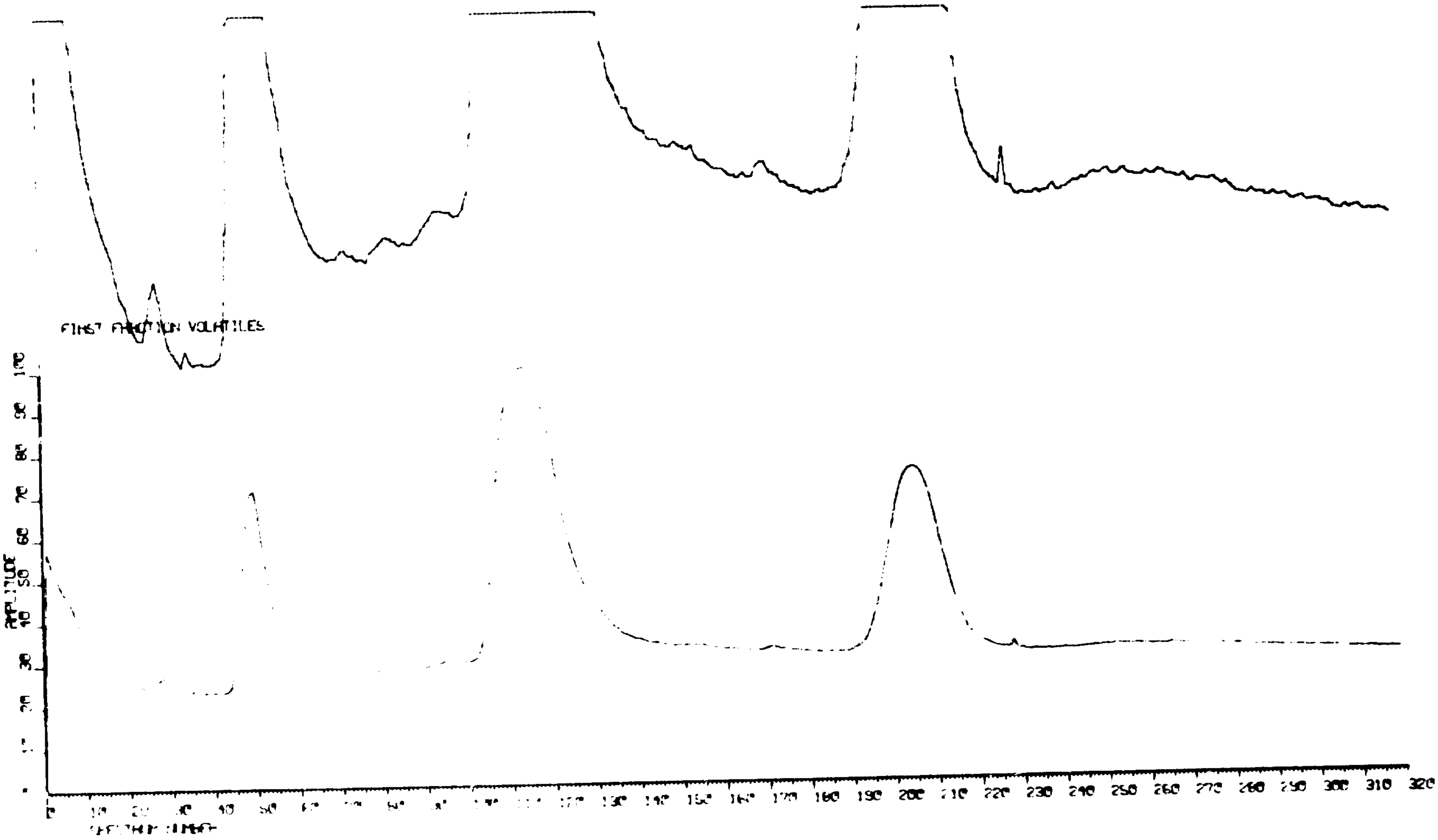
an eluting peak on a second gas chromatographic column, held at room temperature outside of the instrument oven, then heating the second column after it had been connected to the flame ionization detector. Through the use of the pair, Column 5 and Column 3, additional evidence was obtained that acetone, acetaldehyde, and methyl alcohol were present in the headspace of the distillates. This two-column technique was of limited value, however, for the same reasons hampering infrared analysis.

"Best guess" compounds were assembled and their vapors were injected to see if the peaks obtained matched any peaks on the chromatogram of headspace volatiles from the urine distillate. This single column technique, while providing only a very tentative identification, was pursued to its practical limits, also. Matching retention times were obtained for these compounds: propionaldehyde, methyl ethyl ketone, 3-methyl-2-butanone, 2-pentanone, diacetyl, toluene, methyl disulfide, 4-heptanone,and ethyl alcohol.

The next step was to subject the headspace volatiles of the distillate to analysis by a gas chromatograph-mass spectrometer complex, made available through the courtesy of the Department of Pharmacology, University of Texas at San Antonio Medical School. The first attempt using Column No. 6 was unrewarding for two reasons: (1) the concentration of volatiles was too low — near the lower limit of detection — and (2) bleed from Column No. 6 interfered with and complicated the interpretation of the mass spectral data.

Further laboratory work resulted in a column with a lower bleed rate (Column No. 7), but with slightly reduced separating capacity, and a vapor concentrate estimated to be from 100 to 1000 times more concentrated than that generated by the headspace analysis technique alone. The concentrate was obtained by flowing a small stream (approximately 20 ml/min) of nitrogen through distillate heated to its boiling point, then through a water cooled condenser, and finally through a cold-finger type glass trap, submerged in dry ice-solvent. By this means, the concentrate used in the second GC-mass spec analysis was obtained from 300 ml of first fraction distillate (i. e., 6 x 50-ml fractions) in the course of an hour of heating, sweeping, and trapping. The concentrate was kept in the dry ice-solvent bath during transport to the analytical site, then the trap was opened on one end to the atmosphere and allowed to warm up to near room temperature. Expansion of the cold vapors and nitrogen prevented outside air from entering the trap during the warming period. A gas syringe, fitted with a small Teflon tube extending from the syringe needle, was used to procure a 2-ml sample from inside the trap by feeding the Teflon tubing through the sidearm and downward to the lower half of the trap. The 2-ml injection provided an adequate amount for the analysis. Figure 4 shows the chromatogram generated by the GC-mass spec combination. Figures 5-10 show the mass spectral data for the six compounds unequivocally identified: acetaldehyde, acetone, methyl ethyl ketone, methyl alcohol, ethyl alcohol, and dioxane. Two more

Figure 4. Vapor Concentrate from Distillate from Urine
Which Contained BioPal VRO-20, Antifoam, and Acid
GC Column No. 7
GC-Mass Spec Combination



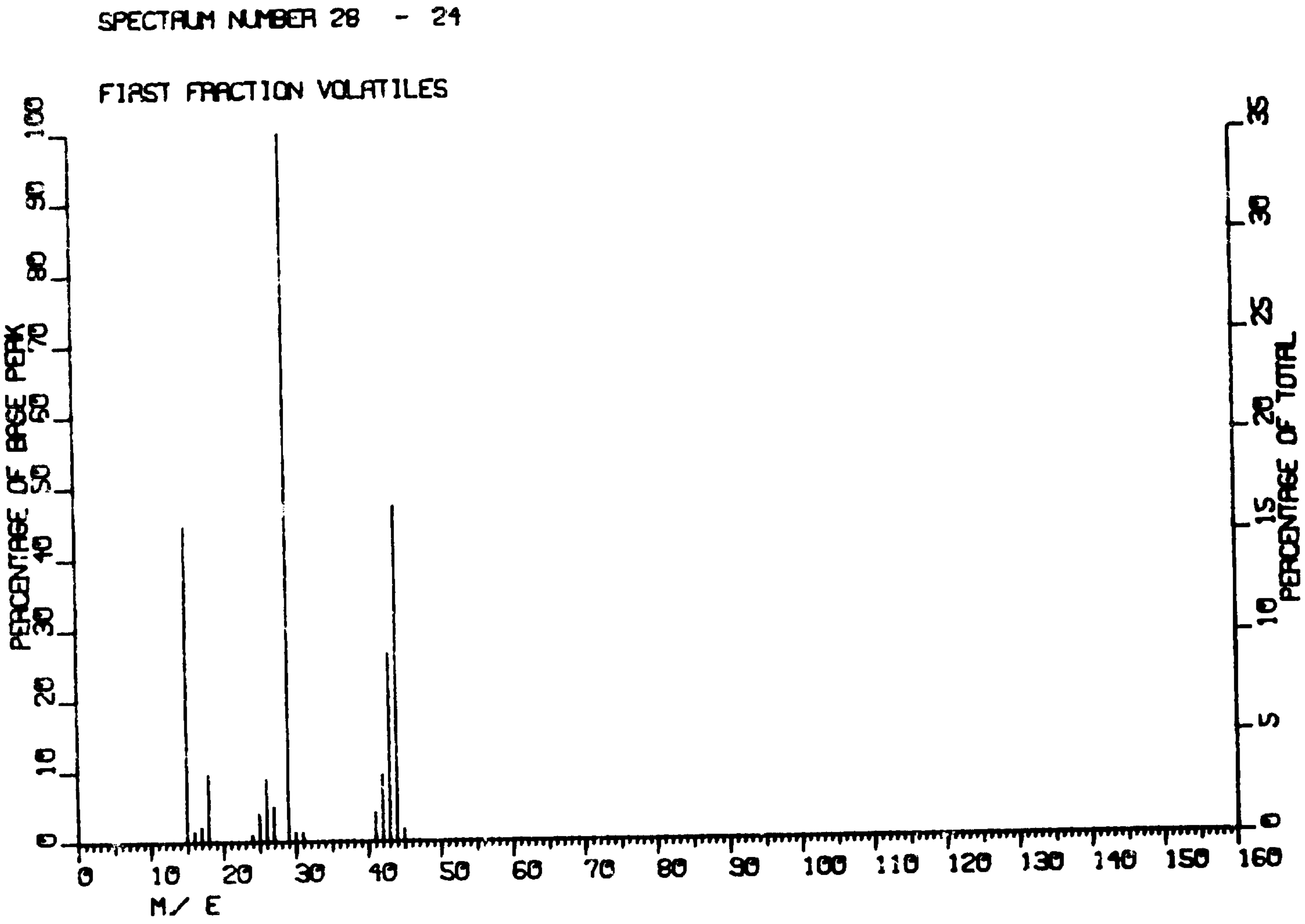


Figure 5. Acetaldehyde

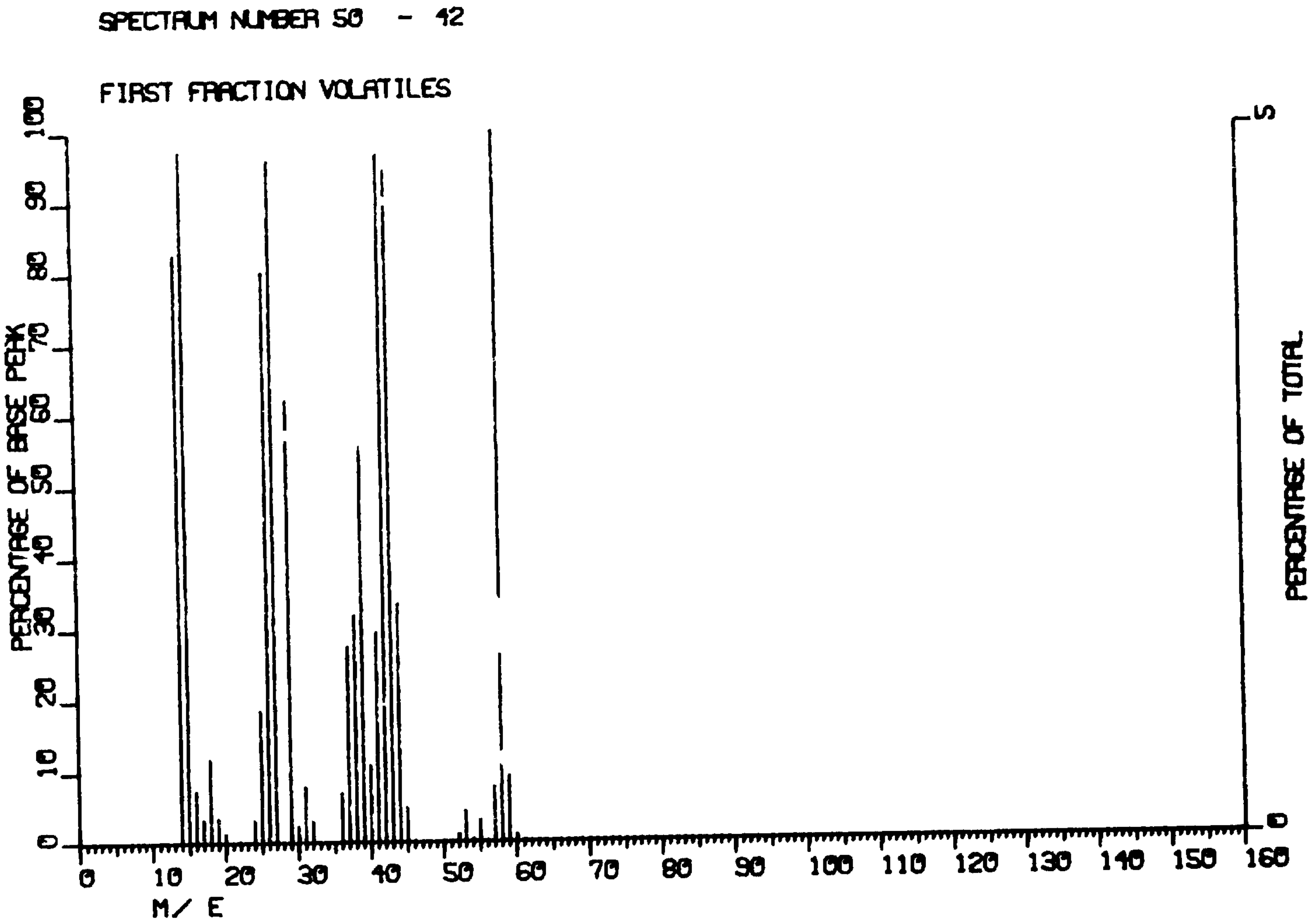


Figure 6. Acetone

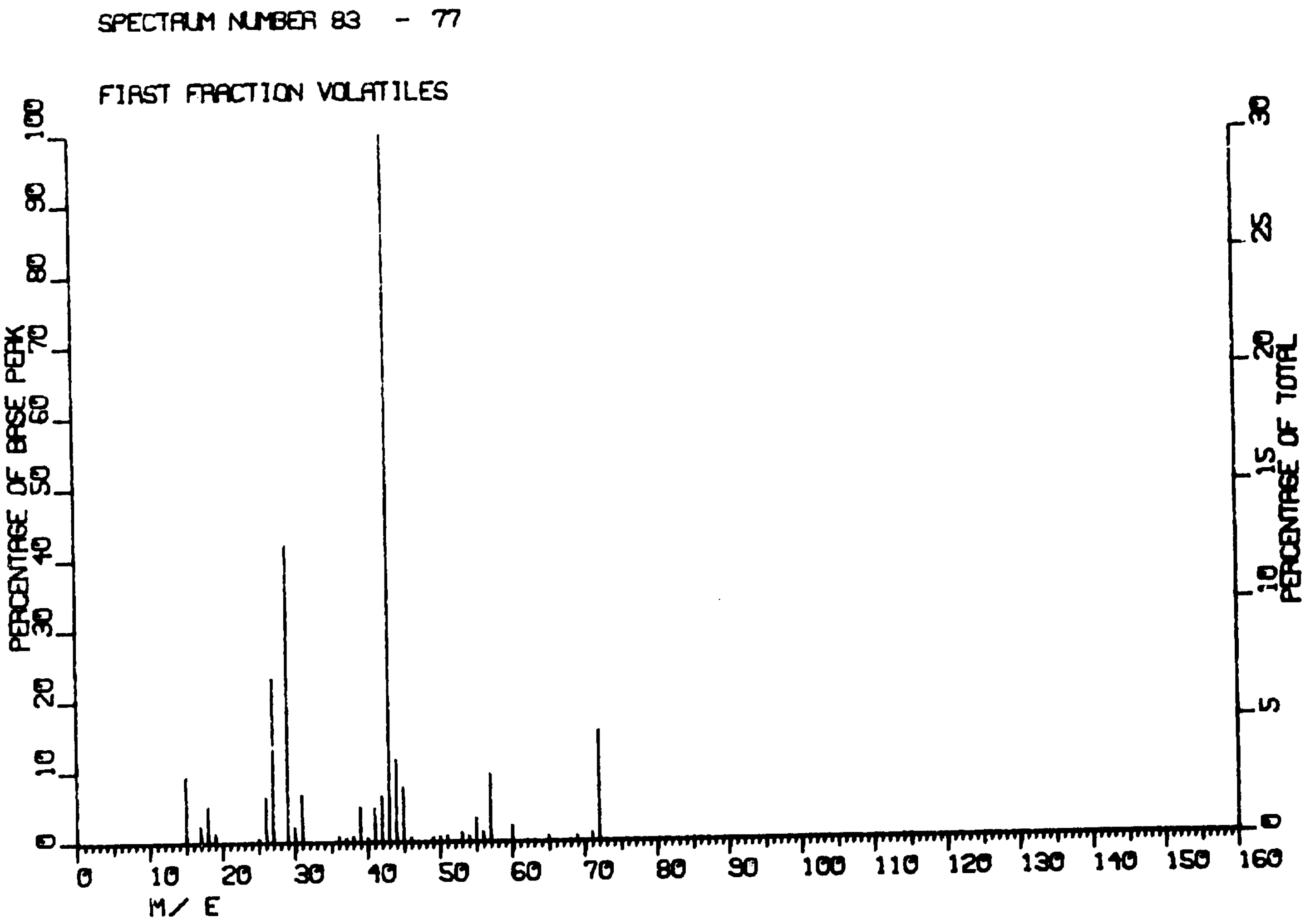


Figure 7. Methyl Ethyl Ketone

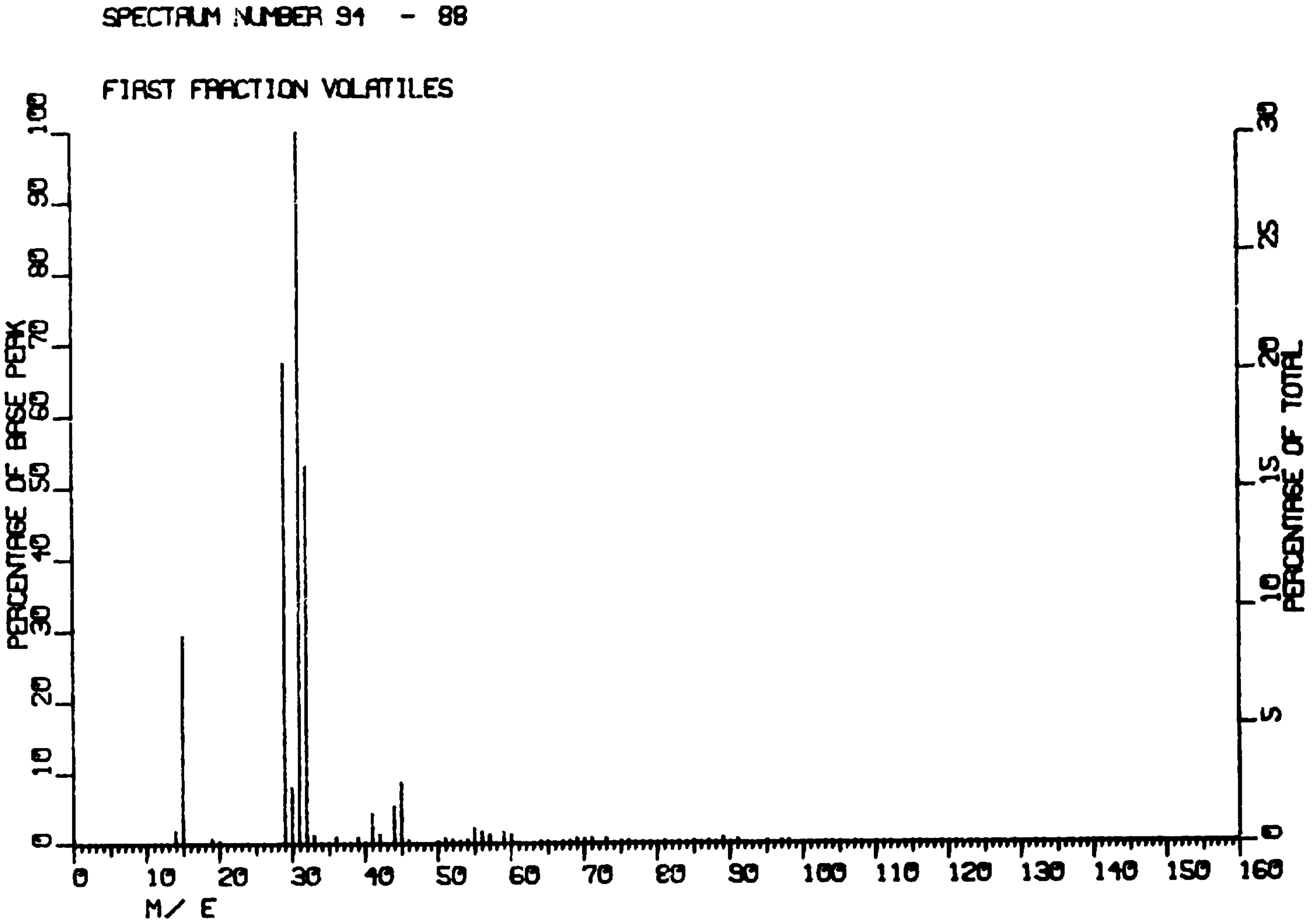


Figure 8. Methyl Alcohol

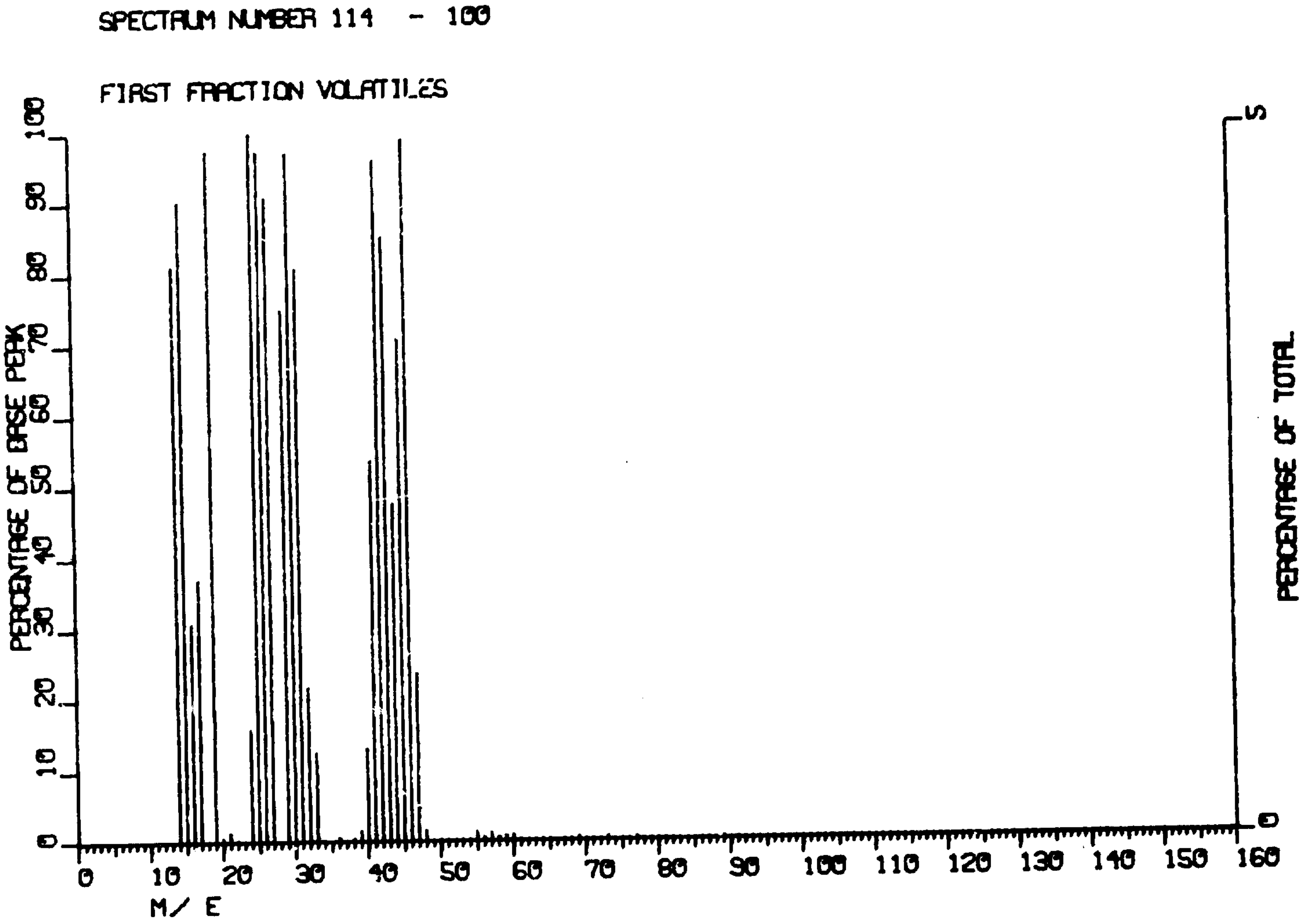


Figure 9. Ethyl Alcohol

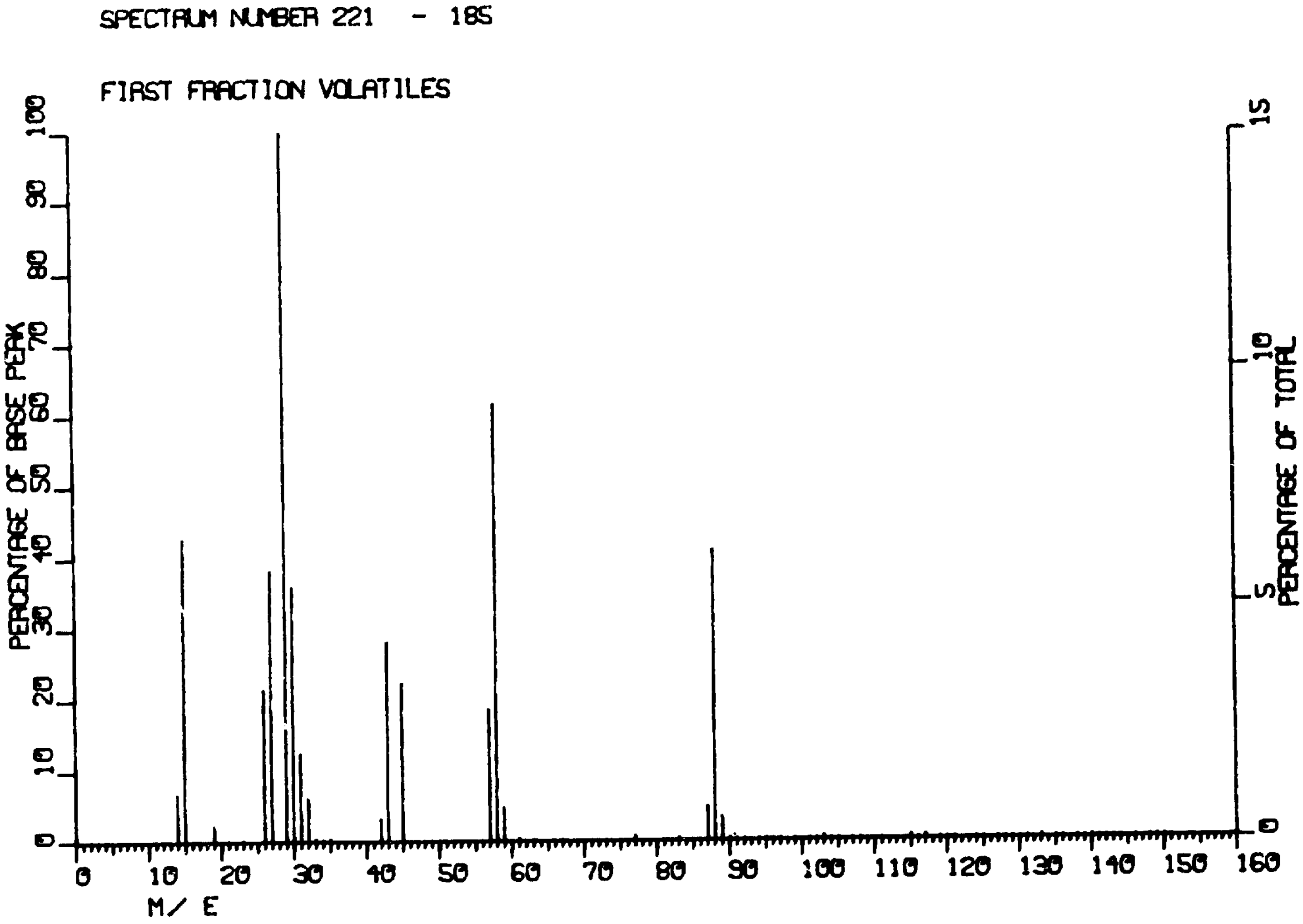


Figure 10. Dioxane

compounds were very probably present: 2-pentanone and 3-methyl-2-butanone. This same concentrate was injected into a gas chromatograph equipped with Column No. 7 and a flame ionization detector, and the chromatogram shown as Figure 11 resulted. Attempted retention time matching resulted in coincidence of times for 2-pentanone but not for 3-methyl-2-butanone. However, 3-methyl-2-butanone had been previously observed to coincide with an unknown peak produced through the use of Column 6.

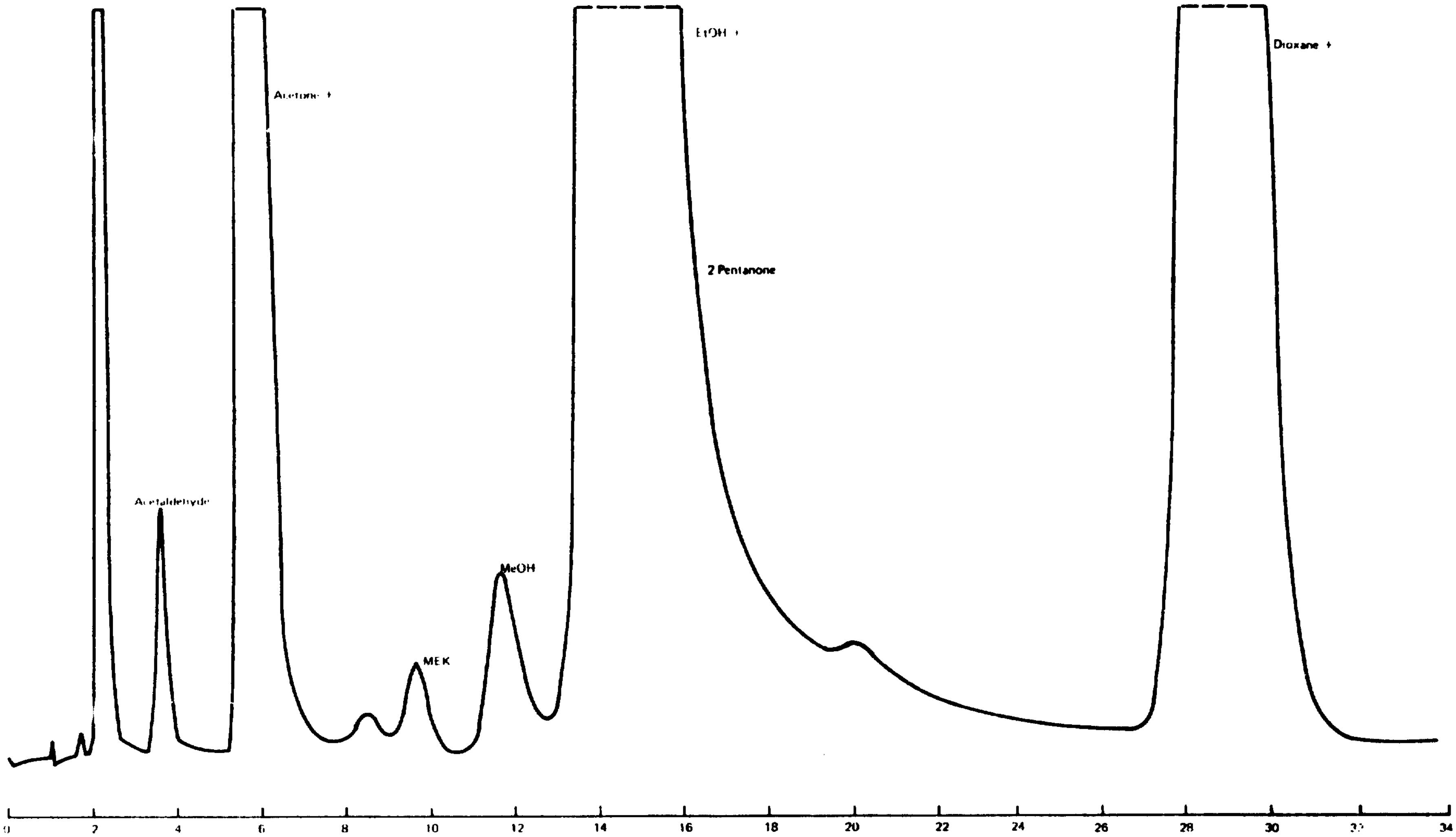
Wherever possible, concentrations of identified compounds in the distillate have been estimated, using the gas chromatograph. These estimates were made in one of two ways: (1) injection of a solution of known concentration, followed by comparison of peak heights, or (2) injection of headspace vapor, using the referenced technique, over an aqueous solution of known concentration, followed by comparison of peak heights.

Table IV summarizes the analytical results which were obtained in this work.

### C. Discussion

The most significant result is the finding of dioxane in the distillate and the identification of its source, BioPal premix. Not only is it probably the most toxic of the volatiles identified, but it is present in a concentration almost a hundred times greater than the next most abundant volatile compound under the conditions tested. This premix

Figure 11. Vapor Concentrate from Distillate from Urine Which Contained BioPal VRO-20, Antifoam, and Acid GC Column No. 7



## Table IV. Results of Analysis of Volatile Compounds In the First Fraction of Distillate

| Compound | Method(s) of Identification | Degree of Certainty of Identification | Estimated Concentration, ppm |
|---|---|---|---|
| Dioxane | GC - 1 column; IR; Mass spec | unequivocal | 340 |
| Acetone | GC - 1 col, 2 col; Mass spec | unequivocal | 4 |
| Acetaldehyde | GC - 1 col, 2 col; Mass spec | unequivocal | 0.3 |
| Methyl alcohol | GC - 1 col, 2 col; Mass spec | unequivocal | 3.8 |
| Ethyl alcohol | GC - 1 col; Mass spec | unequivocal | 0.08 |
| Methyl ethyl ketone | GC - 1 col; Mass spec | unequivocal | |
| Propionaldehyde | GC - 1 col | probable | 0.014 |
| 3-Methyl-2-butanone | GC - 1 col? ; Mass spec? | possible | |
| 2-Pentanone | GC - 1 col; Mass spec? | probable | |
| Diacetyl | GC - 1 col | possible | |
| Methyl disulfide | GC - 1 col | possible | |
| 4-Heptanone | GC - 1 col | possible | |
| Toluene | GC - 1 col; Mass spec - neg | improbable | |

procedure was used because it duplicates the anticipated procedure for water recovery during space flight. However, the occurrence of dioxane in recovered water suggests that some re-examination of this procedure might be warranted.

The results obtained pertain only to the first fraction of distillate (the first 20% distilled). Subsequent fractions, representing the same percentage of the charge, have already been shown to contain lesser amounts of the volatiles. Work was restricted to the richest fraction because of the severe analytical problems encountered at these, the highest, concentrations.

The compounds identified are not the only volatile compounds present in the distillate. Mass spectral data indicate that one or two peaks, caused by minor components, lie buried in each of the major peaks shown in Figure 11. A number of these unknowns could probably be identified but only at a high cost of effort. Additional expenditures for such an effort do not seem justified. Rather, the next work undertaken will be devoted to evaluating various techniques that might be used to remove volatile constituents from distillate.