constitute a greater proportion of the body weight of the fish just prior to spawning than at other stages in their cycle of maturation.

In relation to the other fish (Table VI) both the herring and salmon appear to have increased in weight less than might have been expected from the extent of the changes in their sodium and potassium levels. Whether this means that the osmotic pressure of the intracellular fluids is lower in these fish than in the others or that the higher fat content of the two species specifically impeded the uptake of water cannot be determined from the data.

The fact that storage of fish in refrigerated sea water produces an uneven distribution of sodium ion in the flesh indicates that analyses based on the official method of sampling (*1*) in this case provide insufficient information for marketing purposes. A situation could conceivably arise wherein the outer layer of flesh of a fish contained an unpalatable level of sodium ion, the inner layer remained almost unchanged, while a value based on the cross-sectional sample specified in the official method indicated a level of sodium ion within the limits of palatability.

There have been many studies in which hydration of mammalian tissues has been observed in salt solutions isoosmotic with blood and tissue fluids, and there are conflicting explanations to account for the phenomenon (*8, 16, 18*). In this study, where the ion concentrations of the immersing solution were adjusted to maintain the flesh levels constant, water uptake must have been due primarily to the hypertonicity of the intracellular fluids of the flesh. This was further substantiated by the observation that a nondiffusible substance capable of increasing the osmotic pressure of the immersing solution prevented water uptake by the fish.

Polyvinylpyrrolidone is a chemically inert, hydrophilic, water-soluble macromolecule essentially nontoxic for humans by all routes of administration. The compound is widely used in the formulation of pharmaceuticals and has been recommended for use as a beverage clarifier (*5*).

In the practical application of the results reported here it would be feasible to premix and package sodium chloride, potassium chloride, and polyvinylpyrrolidone for convenient addition to tanks of fresh water on fishing vessels or in shore plants.


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**COFFEE VOLATILES**

# Analysis of the Volatile Constituents of Coffee


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A METHOD OF SAMPLING roast and ground coffee for analysis of coffee volatiles by gas chromatography has previously been reported (*3*). A few modifications in procedure and equipment have made it possible to obtain quantitative data on 19 volatile constituents of coffee.

Data on the green beans and beans roasted at various temperatures have been obtained for seven trade varieties of coffee. Analysis of 13 retail brands of coffee has been performed and the data presented for comparative purposes.

Brewed coffee has been analyzed using the same sampling technique. By use of comparative analysis of brewed coffee and coffee suspended in water, it has been possible to calculate the percentage of each constituent which is extracted and retained in freshly brewed coffee. Concentrations of volatiles in brewed coffee are shown to be in the range of a few parts per billion to 1 to 2 p.p.m.

Eighteen of the chromatogram peaks have been assigned tentative identifications.

Evaluation of the final roast data for the seven trade varieties indicates a possible relationship between the degree of roasting and the ratio of diacetyl to acetyl propionyl. The green bean analysis shows differences which may be helpful in typing or grading green coffee.

### Experimental

**Apparatus and Procedure.** The apparatus used in this work is essentially that previously described (*3*). The major modifications are: Original column replaced by a 4-meter column of 15% Carbowax 1500 on 30- to 60-mesh Chromosorb. Recorder sensitivity increased from 10 mv. full scale to 2.5 mv. full scale.

The sampling procedure was changed only to the extent of a decreased carbon

Studies on the roasting of seven varieties of coffee show that generally the concentration of volatiles in the bean increases with increased roasting. Hydrogen sulfide, methyl formate, and acetyl propionyl reach a maximum concentration within the normal roasting temperatures. The concentration of dimethyl sulfide remains essentially constant during the roasting process. Analysis of green beans shows differences which may be useful in typing or grading green coffee. In roasted coffee, the ratio of diacetyl to acetyl propionyl may be indicative of the degree of roast. Analysis of brewed coffee shows the concentration of volatiles to be in the range of 1 to 2000 p.p.b.

dioxide venting time, which then allowed a recollection of hydrogen sulfide without excessive recollection of carbon dioxide. The over-all sensitivity of the instrument was checked by use of a standard injection of acetone prior to the analysis of a coffee sample instead of using toluene as an internal standard.

The trade variety coffee beans were prepared by use of the following equipment. Gas-fired Thermalo roaster (Burns) with Foxboro controllers of 500-pound green bean capacity. Stir-flex coolers (Jabez Burns and Sons, Inc.), vacuum coffee can closing machine (Canco).

The beans were extracted from the roaster at predetermined temperatures, cooled, and the whole beans were vacuum packed under approximately 29 inches of vacuum.

The cans were opened and the beans were ground, using a coffee grinding attachment on a Waring Blendor, just prior to analysis. The green beans, being too tough for the coffee grinding attachment, were reduced to 20- to 40-mesh with the conventional Waring Blendor blades.

A 10-gram sample was used for the analysis of the green bean, the 300°, and the 325° F. roast. All other analyses were performed using a 5-gram sample.

**Chromatograms and Calculations.** The method of determining peak areas by multiplying the peak height by the peak width at half peak height requires prior knowledge of the sample so that each peak may be properly attenuated for best chart presentation. Many of the coffee samples would therefore have required a separate determination merely to establish the attenuator settings to be used in the actual analysis. Attenuation of peaks, when the instrument is not at recorder zero, results in base line shifts and makes peak height determinations difficult, especially when separations are not complete.

In order to eliminate these problems and to avoid time-consuming reruns, the chromatograms were obtained with peak bases always recorded at the most sensitive setting, and attenuating as necessary to obtain the peak maximums. With the peak bases all recorded at the same sensitivity, it is then relatively simple to establish the base line for the entire chromatogram. By knowing the recorder zero position, it is a simple matter to establish what the base line would be at the attenuation setting used to record a peak maximum. If a peak maximum was obtained at an attenuation factor of four, then the base line to use for measurement of peak height would be one-quarter of the distance up from the recorder zero to the base line established at the most sensitive setting. The true peak height is then determined by multiplying the measured peak height by the attenuation factor. The relative peak areas are calculated from the product of peak height and retention time.

Results obtained by this method were in good agreement with the results of a rerun of the same coffee in which the areas were determined by peak height times peak width at half peak height.

**Materials.** The trade varieties of coffee were roasted and vacuum packed (Jos. Martinson and Co., Inc.) under the direction of personnel of the Coffee Brewing Institute. The 13 retail brands of coffee were obtained from the Coffee Brewing Institute and coffee for brewed analysis was purchased locally.

Analysis was performed on the green bean and on samples roasted to 300°, 325°, 350°, 375°, and 400° F. and at varying final temperatures for each trade variety. The varieties and final roasting temperature are as follow:

| Variety | Final Roasting Temperature, ° F. |
|---|---|
| Santos | 402 |
| Maracaibo Cuban | 419 |
| Medellin Armenia | 421 |
| Past crop Colombia | 430 |
| Old crop Bucaramanga | 431 |
| Peruvian | 413 |
| Central America | 407 |

### Results and Discussion

Acetaldehyde, acetone, and methanol have been definitely identified previously by infrared spectra of the collected component (*3*). Methyl formate, furan, propionaldehyde, isobutyraldehyde, methylfuran, butyraldehyde, methyl ethyl ketone, isovaleraldehyde, and ethyl alcohol were tentatively identified on the basis of retention times. Hydrogen sulfide, isoprene, methyl mercaptan, dimethyl sulfide, diacetyl, and acetyl propionyl were tentatively identified on the basis of their distinctive odors and retention times.

A study of the complete data indicates that the concentration increases with increasing roasting temperature for a majority of the compounds analyzed. The exceptions to this steady increase are: Hydrogen sulfide reaches a maximum concentration at about 350° F. and then rapidly decreases. Methyl mercaptan shows a slight decrease be-

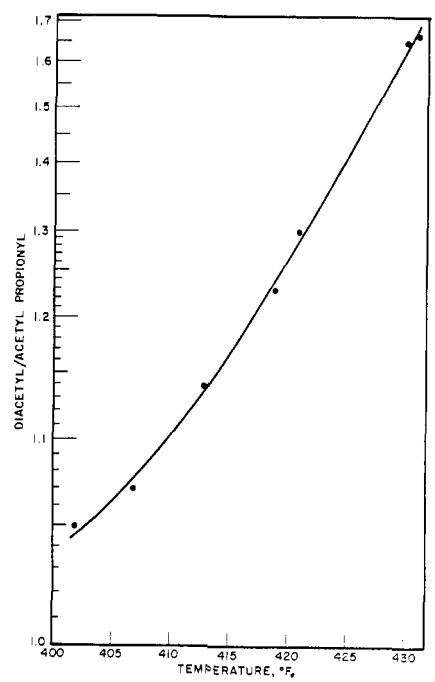


Figure 1. Relationship between degree of roast and the ratio of diacetyl to acetyl propionyl

tween 350° and 375° F. and then continues to increase. This decrease is attributed to the onset of physical changes in the bean which permits a greater rate of loss. Dimethyl sulfide shows a constant concentration during roasting. Methyl formate reaches a maximum at about 400° F. in four of the seven varieties. Acetyl propionyl appears to reach a maximum concentration at about 425° F.

Prior to the assignment of tentative identifications, the peaks were assigned numbers according to their relative retention times, on the basis of toluene as 1000. Table I, consisting of only a portion of the data, shows the results obtained for the green bean, the 350° F. roast, and the final roast, for four of the varieties analyzed.

Although there are insufficient data on the green beans to form any definite conclusions, a few interesting results are evident. Of the 19 compounds found in roasted coffee, 16 were detected in the green bean of one or more of the seven varieties analyzed. Dimethyl sulfide, although occurring at a constant concentration during the roasting process for a given variety (exception is old crop Bucaramanga), differs considerably in amount from one variety to another. Medellin, noted for its aromatic nature, has seven times as much as Santos and would indicate that a measure of the dimethyl sulfide content of green beans may be indicative of the aromatic nature of the beans in question. The green bean data for Maracaibo, Medellin, Peruvian, and Central America is sufficiently different from the other varieties for a number of compounds as to indicate a type or class difference. Only a statistical analysis of green bean data and organoleptic tests of the roasted coffee could satisfactorily determine if a relationship exists between green bean data and flavor or aroma.

A study of the final roast data indicates that the degree of roasting cannot be determined by the absolute amount of any particular volatile constituent. For the 400° F. roasts of six of the varieties studied, the ratio of diacetyl to acetyl propionyl is constant at 0.84 ± 0.04. Santos was not sampled at 400° F. The ratio of diacetyl to acetyl propionyl constantly increases with roasting for temperatures over 400° F. as shown below:

| Variety | Final Roast, ° F. | Ratio Diacetyl/ Acetyl Propianyl |
|---|---|---|
| Santos | 402 | 1.05 |
| Central America | 407 | 1.07 |
| Peruvian | 413 | 1.14 |
| Maricaibo, Cuban | 419 | 1.23 |
| Medellin, Armenia | 421 | 1.30 |
| Past crop Colombia | 430 | 1.65 |
| Old crop Bucaramanga | 431 | 1.67 |

This relationship is graphically presented in Figure 1 and indicates a possible method for determining the degree of roast. For a double-roasted demitasse coffee (data not included) the ratio was 2.77. An approximate assignment of these ratio values might be made as follows:

| Ratio | Degree of Roast |
|---|---|
| <1.1 | Light |
| 1.1 to 1.3 | Medium |
| >1.3 | Dark |

**Table I. Results of Analyses for Green Beans, 350° F. Roast, and Final Roast for Four Varieties**

| Source[a] | ° F. | Peaks and Compounds: 44 Hydrogen Sulfide | 69 Isoprene | 86 Methyl Mercaptan | 105 Acet-aldehyde | 130 Dimethyl Sulfide | 150 Methyl Formate | 170 Furan | 190 Propion-aldehyde | 220 Isobutyr-aldehyde | 250 Acetone |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Toluene Equivalents, γ/G. | | | | | | | | | |
| Col. | 430 | 1.64 | 1.01 | 3.82 | 48.8 | 1.21 | 10.9 | 4.40 | 8.58 | 19.9 | 80.0 |
| Med. | 421 | 1.98 | 1.21 | 2.43 | 55.1 | 3.44 | 13.2 | 4.95 | 10.1 | 16.3 | 79.1 |
| Cen. | 407 | 1.53 | 1.06 | 1.56 | 56.9 | 0.71 | 12.5 | 3.42 | 8.16 | 12.8 | 53.7 |
| San. | 402 | 4.26 | 0.69 | 2.30 | 50.3 | 0.48 | 9.70 | 2.20 | 6.20 | 15.0 | 42.2 |
| Col. | 350 | 12.2 | 0.04 | 3.02 | 12.6 | 1.13 | 0.71 | 0.37 | 0.73 | 19.0 | 8.17 |
| Med. | 350 | 6.46 | 0.10 | 1.75 | 12.6 | 3.74 | 1.50 | 0.56 | 0.91 | 14.2 | 11.2 |
| Cen. | 350 | 4.88 | 0.13 | 1.35 | 13.3 | 0.72 | 2.09 | 0.57 | 0.93 | 10.8 | 11.5 |
| San. | 350 | 13.2 | 0.08 | 2.30 | 15.0 | 0.46 | 1.30 | 0.35 | 0.73 | 13.0 | 9.10 |
| Col. | Green | 0.50 | ... | 0.26 | 3.97 | 1.05 | ... | 0.03 | 0.08 | 1.10 | 4.02 |
| Med. | Green | 0.56 | ... | 0.10 | 1.60 | 3.54 | ... | ... | 0.05 | 0.18 | 0.90 |
| Cen. | Green | 0.93 | ... | 0.12 | 1.86 | 0.55 | ... | 0.02 | 0.08 | 0.20 | 0.90 |
| San. | Green | 0.28 | ... | 0.19 | 3.70 | 0.50 | ... | 0.02 | 0.14 | 0.66 | 4.90 |

| | | Peaks and Compounds: 290 Methyl-furan | 350 Butyr-aldehyde | 450 Methyl Ethyl Ketone | 470 Isovaler-aldehyde | 540 Unknown | 630 Methanol | 780 Diacetyl | 850 Ethanol | 1420 Acetyl Propionyl |
|---|---|---|---|---|---|---|---|---|---|---|
| | ° F. | Toluene Equivalents, γ/G. | | | | | | | | |
| Col.[a] | 430 | 13.8 | 0.68 | 22.5 | 2.82 | 0.87 | 100 | 16.5 | 1.95 | 10.0 |
| Med. | 421 | 14.7 | 0.73 | 19.9 | 3.60 | 1.00 | 91.0 | 18.8 | 4.00 | 14.5 |
| Cen. | 407 | 8.79 | 0.51 | 14.9 | 2.47 | 0.53 | 87.9 | 19.7 | 1.93 | 18.4 |
| San. | 402 | 4.90 | 0.34 | 15.1 | 2.00 | 0.32 | 119 | 16.0 | 0.60 | 15.2 |
| Col. | 350 | 0.39 | 0.06 | 15.3 | 1.79 | ... | 77.5 | 1.24 | 1.06 | 1.59 |
| Med. | 350 | 0.67 | 0.07 | 12.2 | 1.97 | 0.07 | 101 | 1.73 | 4.08 | 2.53 |
| Cen. | 350 | 0.83 | 0.10 | 9.87 | 1.18 | ... | 107 | 1.77 | 2.20 | 3.24 |
| San. | 350 | 0.42 | 0.07 | 10.2 | 1.20 | 0.07 | 96.1 | 1.60 | 0.26 | 2.10 |
| Col. | Green | ... | 0.03 | 1.10 | 1.57 | ... | 7.41 | 0.27 | 0.65 | ... |
| Med. | Green | ... | 0.04 | 0.19 | 0.28 | ... | 12.4 | 0.08 | 3.51 | ... |
| Cen. | Green | 0.06 | 0.06 | 0.21 | 0.25 | ... | 13.4 | 0.09 | 1.72 | ... |
| San. | Green | 0.16 | 0.07 | 0.62 | 0.80 | 0.17 | 14.0 | 0.27 | 0.46 | ... |

[a] Col., past crop Colombia; Med., Medellin Armenia; Cen., Central America; San., Santos.

The complete data on the 13 retail brands of coffee are presented in Table II and include the diacetyl-acetyl propionyl ratio for each coffee. No attempt has been made to evaluate these data as no information on the roasting of these coffees was available.

Table III summarizes the data on green beans and several roasted coffees giving the normal concentration ranges of the various volatile compounds in the dry coffee.

### Brewed Coffee. Experimental Results

The ability of helium sweep gas to strip coffee volatiles from an aqueous solution was demonstrated as follows: A 5-gram sample of dry coffee was first analyzed to determine the total amount of each volatile constituent present. The dry coffee sampler was then replaced with a 100-ml. flask containing 5 grams of the coffee in 80 ml. of distilled water. The flask and contents were heated to 100° C. and the helium sweep gas was bubbled through the suspension of coffee in water at the same rate as with the dry coffee sample. The stripped volatiles were collected and analyzed in the usual manner. The data from these two analyses are presented in Table IV (A-1, A-2). Neglecting alcohols, the recovery of volatiles is comparable with the exception of an increase in hydrogen sulfide from the aqueous sample, and a slight decrease in diacetyl and acetyl propionyl from the aqueous sample. The general agreement in recovery of volatiles from these two analyses indicates the sampling method is applicable to aqueous coffee solutions within the afore-mentioned limitations.

By increasing the sampling time of the aqueous sample to one and one half hours (50% increase), the diacetyl and acetyl propionyl values approach the values obtained by analysis of the dry coffee. The hydrogen sulfide value, however, increased by 50%, or in direct proportion to the increased sampling time. It would therefore appear that hydrogen sulfide may well be a product of hydrolysis in the brewing of coffee.

Analysis of 5 grams of coffee in 80 ml. of distilled water and 80 ml. of tap water was performed to determine the effect of different water on coffee volatiles. The data on this test are shown in Table IV (B-1, B-2). The results of the two analyses are very similar with the single exception of hydrogen sulfide, which is markedly reduced in the tap water sample. This reduction in hydrogen sulfide is attributed to the type and/or amount of dissolved solids in the tap water.

Brewed coffee was prepared in a clean household drip coffee pot using 50 grams of coffee and 800 ml. of boiling distilled water. Two types of brewed coffee were prepared, one from a freshly opened can of coffee, and the other from a can which had been open for 6 days. The recovery of brewed coffee in each case was 665 ± 5 ml. An 80-ml. aliquot of each brewed coffee was then analyzed to determine the volatiles retained in the brew. A 5-gram sample of each coffee in 80 ml. of distilled water was also analyzed to determine the volatile content of the dry coffee equivalent to that required for the 80-ml. aliquot of the brewed coffee. The total amount of each volatile constituent in the 80-ml. aliquot expressed as a percentage of the total amount found in the corresponding 5 grams of dry coffee can then be calculated, and has been designated "per cent retained."

The results of the above analyses are reported in Table IV. Although the per cent retained in the brewed coffee

**Table II. Data on Thirteen Retail Brands of Coffee**

| Brand | Peaks and Compounds | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 44 Hydrogen Sulfide | 68 Isoprene | 86 Methyl Mercaptan | 105 Acet-aldehyde | 130 Dimethyl Sulfide | 150 Methyl Formate | 170 Furan | 190 Propion-aldehyde | 220 Isobutyr-aldehyde | 250 Acetone |
| | Toluene Equivalents, γ/G. | | | | | | | | | |
| A | 0.46 | 0.48 | 1.33 | 45.0 | 0.98 | 6.92 | 1.85 | 5.38 | 11.5 | 38.0 |
| B | 1.64 | 0.50 | 1.61 | 44.1 | 0.98 | 8.42 | 1.98 | 6.20 | 10.6 | 38.8 |
| C | 1.30 | 0.39 | 1.40 | 56.1 | 0.15 | 7.20 | 2.07 | 6.30 | 13.0 | 44.1 |
| D | 1.95 | 0.58 | 2.75 | 60.0 | 0.54 | 8.95 | 2.58 | 8.37 | 11.8 | 53.8 |
| E | 2.65 | 0.11 | 2.10 | 43.6 | 0.49 | 8.64 | 3.10 | 6.61 | 13.3 | 51.2 |
| F | 2.06 | 0.46 | 1.76 | 46.6 | 1.58 | 8.28 | 1.94 | 6.78 | 11.4 | 42 0 |
| G | 2.28 | 0.64 | 1.61 | 45.0 | 0.82 | 9.15 | 2.22 | 6.93 | 12.5 | 46.3 |
| H | 3.31 | 0.43 | 2.09 | 49.1 | 0.24 | 9.25 | 1.86 | 6.26 | 12.3 | 42.2 |
| I | 2.18 | 0.41 | 1.26 | 59.5 | 0.58 | 8.36 | 2.08 | 6.46 | 9.86 | 44.0 |
| J | 2.50 | 0.53 | 1.85 | 45.0 | 0.88 | 9.15 | 2.15 | 6.41 | 12.6 | 44.4 |
| K | 1.46 | 0.68 | 2.32 | 49.2 | 0.81 | 10.9 | 3.29 | 8.10 | 13.9 | 65.0 |
| L | 2.61 | 0.42 | 1.48 | 44.8 | 1.73 | 5.54 | 1.79 | 5.22 | 13.5 | 35.8 |
| M | 3.28 | 0.59 | 2.36 | 63.0 | 1.17 | 5.32 | 2.49 | 7.20 | 15.0 | 50.4 |

| Brand | Peaks and Compounds | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 290 Methylfuran | 350 Butyr-aldehyde | 450 Methyl Ethyl Ketone | 470 Isovaler-aldehyde | 540 Unknown | 630 Methanol | 780 Diacetyl | 850 Ethanol | 1430 Acetyl Propionyl | Ratio 780/1420 |
| | Toluene Equivalents, γ/G. | | | | | | | | | |
| A | 4.65 | 0.32 | 12.9 | 1.86 | 0.30 | 87.4 | 12.6 | 4.55 | 11.9 | 1.06 |
| B | 4.96 | 0.34 | 13.1 | 1.84 | 0.33 | 80.6 | 12.6 | 3.60 | 14.0 | 0.90 |
| C | 4.50 | 0.34 | 14.4 | 2.25 | 0.30 | 98.0 | 15.8 | 2.30 | 13.1 | 1.20 |
| D | 7.30 | 0.51 | 14.4 | 2.72 | 0.56 | 80.1 | 16.6 | 2.56 | 13.1 | 1.27 |
| E | 7.35 | 0.41 | 15.4 | 2.02 | 0.41 | 75.0 | 11.0 | 2.85 | 8.11 | 1.36 |
| F | 5.54 | 0.37 | 14.1 | 2.88 | 0.41 | 82.8 | 13.6 | 6.00 | 14.7 | 0.93 |
| G | 6.56 | 0.39 | 15.3 | 1.99 | 0.48 | 80.6 | 14.1 | 2.42 | 15.7 | 0.90 |
| H | 4.87 | 0.36 | 14.5 | 1.72 | 0.37 | 76.5 | 14.2 | 1.72 | 12.9 | 1.10 |
| I | 4.96 | 0.41 | 13.0 | 2.15 | 0.33 | 81.6 | 17.5 | 3.15 | 14.4 | 1.21 |
| J | 5.85 | 0.39 | 15.2 | 2.00 | 0.41 | 72.0 | 14.1 | 3.12 | 14.4 | 0.98 |
| K | 9.97 | 0.65 | 16.9 | 2.46 | 0.75 | 69.3 | 15.3 | 2.48 | 13.3 | 1.15 |
| L | 4.16 | 0.30 | 14.2 | 2.25 | 0.30 | 66.2 | 13.1 | 3.23 | 13.3 | 0.99 |
| M | 5.85 | 0.44 | 16.7 | 2.70 | 0.41 | 84.4 | 18.9 | 3.82 | 15.8 | 1.20 |

is variable for the different compounds, for the same compound the per cent retained in the two samples is generally in agreement. From these per cent-retained figures, it should therefore be possible to calculate, with reasonable accuracy, the amount of each constituent which would occur in a freshly prepared cup of coffee from the dry coffee data of Tables I and II.

Table V presents the data for brewed coffee, both fresh and 6-day-old, and the data for instant coffee at the concentrations found in normal preparation. Patton and Josephson (*2*) have determined the following taste threshold concentrations: methyl mercaptan, 0.002 p.p.m.; acetaldehyde, 1.3 p.p.m.; and dimethyl sulfide, 0.012 p.p.m.

Wales and Harmon (*5*) have determined diacetyl in cottage cheese in the range of 0.7 to 10.0 p.p.m. and Campbell *et al.* (*1*) give the taste threshold concentration of hydrogen sulfide as 0.05 p.p.m. in water and 0.12 p.p.m. in brewed coffee. These materials apparently occur in brewed coffee in the concentration ranges which could affect flavor or aroma, especially if one considers that the instrument was not calibrated for specific compounds.

Since completion of the work reported here, papers on the analysis of coffee volatiles have been presented by Sullivan, Robertson, and Merritt (*4*) and Zlatkis and Sivetz (*6*). Although Sullivan and Zlatkis each report the identity of about 30 compounds, only 14 compounds were identified by both. Twelve of these 14 compounds were also identified by this investigator. There are many quantitative differences which are probably due to the different methods of sample preparation and collection, as

**Table III. Data on Concentrations of Volatile Compounds of Green Beans, Several Roasted Coffees, and Dry Coffee**

| Peak | Compound | Trade Varieties: Green bean | Trade Varieties: Final roast | Retail Bronds |
|---|---|---|---|---|
| | | Concentration, γ/G. | | |
| 44 | Hydrogen sulfide | 0.1 - 1.0 | 0.7- 4.3 | 0.4- 3.3 |
| 69 | Isoprene | 0 | 0.6- 1.4 | 0.1- 0.7 |
| 86 | Methyl mercaptan | 0.1 - 0.3 | 1.5- 4.3 | 1.2- 2.8 |
| 105 | Acetaldehyde | 1.6 - 5.0 | 45.0- 70.0 | 44.0- 65.0 |
| 130 | Dimethyl sulfide | 0.1 - 3.5 | 0.5- 3.5 | 0.5- 1.8 |
| 150 | Methyl formate | 0 | 9.0- 13.5 | 5.0- 11.0 |
| 170 | Furan | 0 - 0.03 | 2.0- 6.0 | 1.8- 3.3 |
| 190 | Propionaldehyde | 0.05- 0.4 | 6.0- 11.0 | 5.0- 8.5 |
| 220 | Isobutyraldehyde | 0.2 - 1.2 | 15.0- 20.0 | 10.0- 14.0 |
| 250 | Acetone | 0.6 - 5.0 | 40.0-100.0 | 35.0- 55.0 |
| 290 | Methylfuran | 0 - 0.2 | 5.0- 20.0 | 4.5- 10.0 |
| 350 | Butyraldehyde | 0.02- 0.07 | 0.3- 1.0 | 0.3- 0.5 |
| 450 | Methyl ethyl ketone | 0.2 - 1.3 | 15.0- 25.0 | 13.0- 17.0 |
| 470 | Isovaleraldehyde | 0.2 - 2.0 | 2.0- 4.0 | 1.7- 2.8 |
| 540 | Unknown | 0 - 0.2 | 0.3- 1.0 | 0.3- 0.8 |
| 630 | Methanol[a] | 5.0 -15.0 | 60.0-100.0 | 65.0-100.0 |
| 780 | Diacetyl | 0.07- 0.3 | 16.0- 20.0 | 11.0- 19.0 |
| 850 | Ethyl alcohol[a] | 0.2 - 4.0 | 0.6- 4.0 | 1.7- 6.0 |
| 1420 | Acetyl propionyl | 0 | 10.0- 19.0 | 8.0- 16.0 |

[a] Data unreliable.

**Table IV. Analysis of Stripped Coffee Volatiles**

| | Peaks and Compounds: 44 Hydrogen Sulfide | 69 Isoprene | 86 Methyl Mercaptan | 105 Acetaldehyde | 130 Dimethyl Sulfide | 150 Methyl Formate | 170 Furan | 190 Propionaldehyde | 220 Isobutyraldehyde | 250 Acetone |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total Toluene Equivalents, γ | | | | | | | | | |
| A-1 | 8.46 | 1.51 | 8.05 | 199 | 6.40 | 22.6 | 6.71 | 24.6 | 54.7 | 162 |
| A-2 | 13.7 | 1.65 | 9.16 | 185 | 6.59 | 20.8 | 6.71 | 22.7 | 54.2 | 154 |
| B-1 | 13.9 | 1.51 | 9.08 | 187 | 6.40 | 20.2 | 6.40 | 22.0 | 51.6 | 162 |
| B-2 | 2.15 | 1.43 | 9.50 | 188 | 6.04 | 20.7 | 6.40 | 22.0 | 51.6 | 154 |
| C-1 | 11.4 | 2.51 | 9.66 | 190 | 10.7 | 26.0 | 9.00 | 23.2 | 57.8 | 152 |
| C-2 | 4.82 | 0.21 | 4.46 | 139 | 5.00 | 17.5 | 3.58 | 16.1 | 37.6 | 156 |
| Retained, % | 42 | 8 | 46 | 73 | 47 | 68 | 40 | 69 | 65 | 103 |
| D-1 | 9.90 | 0.96 | 8.75 | 159 | 2.76 | 14.5 | 5.10 | 18.6 | 41.3 | 108 |
| D-2 | 4.30 | 0.12 | 4.24 | 111 | 1.59 | 10.3 | 2.11 | 11.9 | 33.4 | 100 |
| Retained, % | 44 | 12 | 49 | 70 | 58 | 70 | 41 | 64 | 81 | 93 |

| | Peaks and Compounds: 290 Methylfuran | 350 Butyraldehyde | 450 Methyl Ethyl Ketone | 470 Isovaleraldehyde | 540 Unknown | 630 Methanol | 780 Diacetyl | 850 Ethanol | 1420 Acetyl Propionyl |
|---|---|---|---|---|---|---|---|---|---|
| | Total Toluene Equivalents, γ | | | | | | | | |
| A-1 | 17.7 | 1.35 | 62.0 | 10.9 | 1.12 | 292 | 69.1 | 10.2 | 64.2 |
| A-2 | 17.2 | 1.11 | 60.0 | 10.5 | 1.05 | 50 | 49.3 | 2.36 | 54.7 |
| B-1 | 16.0 | 1.10 | 58.3 | 10.3 | 0.92 | 47.0 | 50.8 | 1.75 | 57.8 |
| B-2 | 15.7 | 0.98 | 55.3 | 9.95 | 0.76 | 51.0 | 49.8 | 2.06 | 51.1 |
| C-1 | 21.9 | 1.22 | 60.4 | 10.5 | 0.94 | 57.5 | 46.0 | 2.34 | 49.3 |
| C-2 | 6.20 | 0.49 | 39.0 | 5.80 | 0.00 | 66.0 | 50.8 | 2.66 | 53.6 |
| Retained, % | 28 | 40 | 65 | 55 | 0 | 115 | 110 | 114 | 109 |
| D-1 | 11.7 | 0.73 | 42.0 | 7.22 | 0.0 | 38.2 | 32.5 | 1.75 | 32.8 |
| D-2 | 3.10 | 0.0 | 25.2 | 3.65 | 0.0 | 36.8 | 32.8 | 1.78 | 32.0 |
| Retained, % | 26 | 0 | 60 | 50 | 0 | 97 | 101 | 102 | 98 |

**Table V. Data for Brewed and Instant Coffee**

| Preparation | Peaks and Compounds: 44 Hydrogen Sulfide | 69 Isoprene | 86 Methyl Mercaptan | 105 Acetaldehyde | 130 Dimethyl Sulfide | 150 Methyl Formate | 170 Furan | 190 Propionaldehyde | 220 Isobutyraldehyde | 250 Acetone |
|---|---|---|---|---|---|---|---|---|---|---|
| | Concentration, P.P.M. | | | | | | | | | |
| 1[a] | 0.060 | 0.0026 | 0.056 | 1.74 | 0.063 | 0.22 | 0.045 | 0.20 | 0.47 | 1.95 |
| 2[b] | 0.054 | 0.0015 | 0.053 | 1.39 | 0.020 | 0.13 | 0.026 | 0.15 | 0.42 | 1.25 |
| 3[c] | 0.010 | 0.0000 | 0.022 | 0.71 | 0.000 | 0.02 | 0.004 | 0.038 | 0.14 | 0.55 |

| | Peaks and Compounds: 290 Methylfuran | 350 Butyraldehyde | 450 Methyl Ethyl Ketone | 470 Isovaleraldehyde | 540 Unknown | 630 Methanol | 780 Diacetyl | 850 Ethanol | 1420 Acetyl Propionyl |
|---|---|---|---|---|---|---|---|---|---|
| | Concentration, P.P.M. | | | | | | | | |
| 1[a] | 0.078 | 0.006 | 0.49 | 0.073 | 0 | 0.83 | 0.64 | 0.032 | 0.67 |
| 2[b] | 0.039 | 0.000 | 0.33 | 0.047 | 0 | 0.46 | 0.41 | 0.022 | 0.40 |
| 3[c] | 0.008 | 0.000 | 0.11 | 0.019 | 0 | 0.03 | 0.24 | 0.000 | 0.11 |

[a] Prepared from fresh coffee using 10.6 grams of coffee per 170 ml. of boiling, distilled water.
[b] Preparred from 6-day-old coffee using same proportion as 1.
[c] Prepared from an instant coffee using 1.91 grams per 170 ml. of distilled water.

well as to differences in analytical methods and procedures.


### Acknowledgment

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**VEGETABLE FLAVORS**

# Flash Exchange Gas Chromatography for the Analysis of Potential Flavor Components of Peas


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The technique of flash exchange gas chromatography was applied to the determination of aldehydes, ketones, and acids in the steam distillate of peas. The compounds identified were acetaldehyde, acetone, propionaldehyde, *n*-butyraldehyde, *n*-valeraldehyde, biacetyl, formic acid, acetic acid, and isovaleric acid. All these components occurred at a concentration of less than 3 p.p.m. on a fresh-weight basis. A mixture of these compounds at the concentration levels found did not reproduce the characteristic odor of pea steam distillate.


THE LONG-RANGE GOAL of flavor research is to improve flavor so that abundant, nutritious foods will be consumed at an increased rate. It is most desirable that rapid techniques be developed which could be applied to small, experimental quantities of material. Accuracy need not be greater than that required for a starting point in taste panel evaluation. With this type of research tool, studies of plant breeding, crop selection, harvesting practice, processing, and storage could be made with improved flavor as an objective.

A useful technique for the determination of carbonyl compounds and acids was developed which required only a few milligrams of compounds (*3*). Aldehydes, ketones, and acids are isolated as solid derivatives, regenerated in rapid exchange reactions, and volatilized