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THE DETERMINATION OF THE VOLATILE COMPONENTS OF FOODSTUFFS
III. COFFEE AROMA

By

James H. Sullivan, Donald H. Robertson and Charles Merritt, Jr.

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TABLE OF CONTENTS

	<u>Page</u>
Abstract	iv
Introduction	1
Methods	1
Results and Discussion	7
Summary	10
Figure 1	2
Figure 2	4
Table I	6
Table II	8

ABSTRACT

Mass spectrometric analysis has led to the identification of several components of coffee aroma.

The volatile compounds from ground roasted coffee are collected by distillation under high vacuum at room temperature into a receiver at liquid nitrogen temperature. Direct fractionation of a "center cut" on the mass spectrometer and subsequent analysis has shown the presence of more than twenty compounds. Among the compounds identified are furans, aldehydes, esters, alcohols, nitriles and sulfur compounds.

The techniques which have been used offer the following advantages: (1) The method of collection by vacuum distillation in a closed system is superior to other methods of collection. (2) A minimum of sample handling reduces greatly any loss of material. (3) Direct analysis on the spectrometer permits a complete qualitative analysis in a rapid, efficient manner and also provides for the extension to quantitative analysis, if desired.

INTRODUCTION

The interest in the chemical composition of coffee aroma has been increasing greatly in recent years. This interest arises mainly from the desire to improve the acceptability of soluble coffee products and also to afford a means of quality evaluation and control. Since coffee-like flavors can be produced by roasting various beans and nuts, the knowledge of the chemical components which comprise coffee aroma might also lead to the development of a more desirable wholly synthetic coffee should the need arise.

The early work on coffee aroma was carried out more than 50 years ago, employing coffee roaster condensates as samples. In general, the complexity of these condensates and the lack of sensitive analytical methods made the complete analysis extremely difficult, if not impossible. In the past decade several papers have appeared reporting further attempts to gain more complete information about the volatile components which comprise a coffee aroma (1-9). In reviewing the rather voluminous literature which has appeared on this subject, one finds a wide divergence with respect to the nature of the samples taken, the methods of analysis used, and the results obtained. In one report (10) as many as 70 compounds are listed as having been identified. Consideration of the methods employed, however, raises considerable doubt concerning the reliability of some of the identifications. The answer to this complex and perplexing problem appears to lie in the utilization of more modern instrumental methods of analysis. The results reported here are based entirely on mass spectrometric analysis. In other current research (1, 5) gas chromatography and mass spectrometry are also being used.

METHODS

In this study volatile components are considered to be those compounds which may be distilled under vacuum at room temperature from the dry, ground, roasted coffee. This method of obtaining the sample was employed for a number of reasons. First, it was believed that heating the coffee should be avoided. In all the studies of coffee aroma reported in the literature the references available indicate that heat has been employed with the objective of effecting more complete distillation and collection of aroma. The possibility for chemical change inherent in a heat-induced or

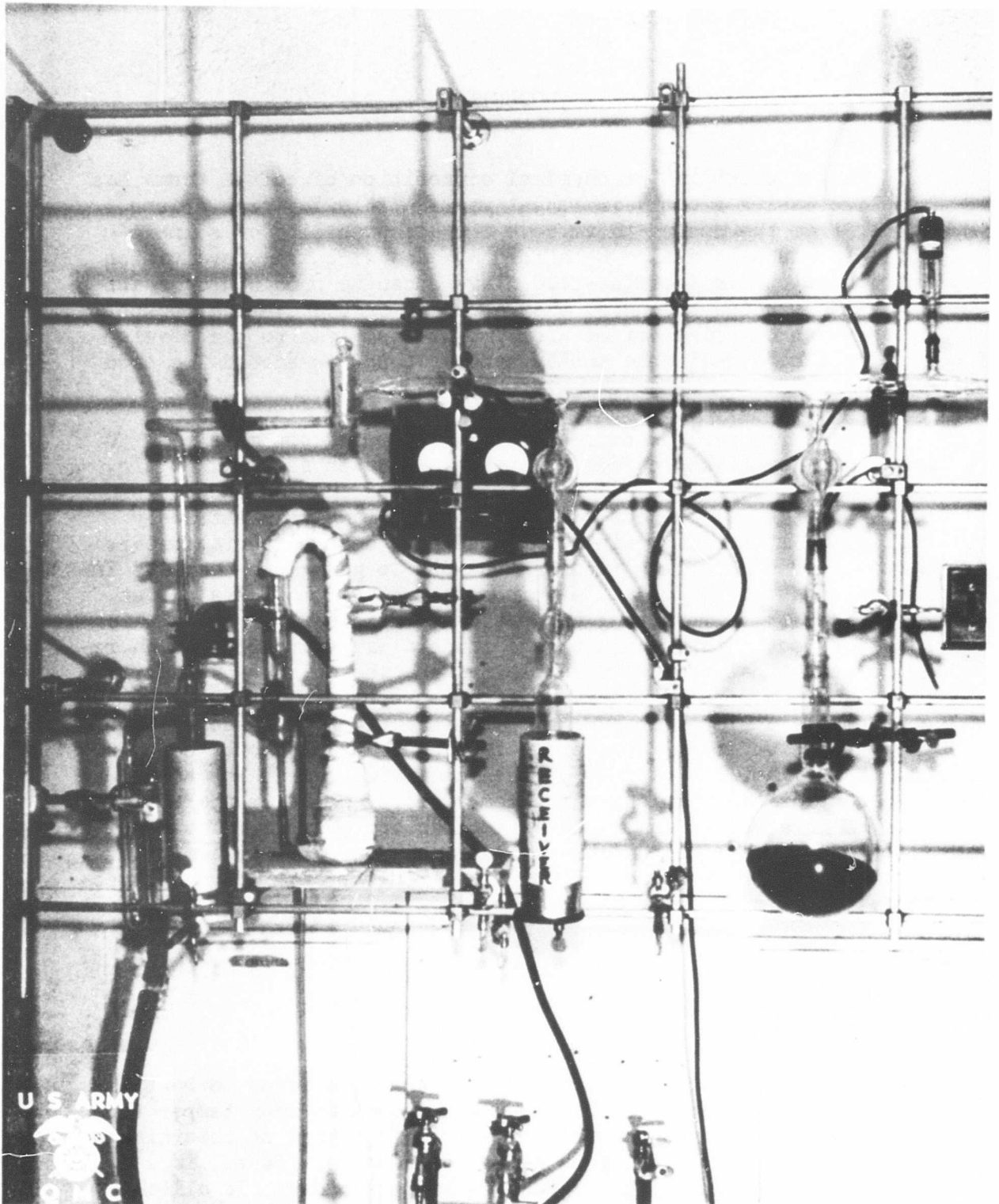


Figure 1. Collection Apparatus for Coffee Volatiles.

heat-accelerated distillation has been considered great enough to discourage its use. In these studies, therefore, no heat above that of room temperature was applied. Furthermore, it is believed that samples collected without heating are more representative of a characteristic sample of aroma.

The chemical changes responsible for development of coffee flavor and aroma are generally conceded to be effected exclusively in the roasting process. The majority of previously reported studies on coffee aroma have, therefore, been made in connection with these "roasting products," and the sampling procedures have employed heat, steam, water extraction, or solvent extraction, individually or in combination. The introduction of solvents and the use of steam or water might also be expected to cause chemical alteration of the volatile components. In addition, steam, water, or solvent extraction methods of obtaining a sample all suffer the disadvantage that nonvolatile but extractable materials may be collected, and the problem of subsequent separation of these impurities as well as solvents needlessly complicates the procedure. The method of sampling which employs a carrier gas to sweep out the coffee sample is apparently a satisfactory one, but it suffers the disadvantage that it requires considerable extra time and affords the possibility that very volatile components may be lost by failure to be condensed in the cold trap. The methods which have been employed are basically those which have been described previously for the analysis of volatile components from irradiated meat (11).

A picture of the apparatus which was employed to collect the sample of total condensate from coffee is shown in Figure 1. One pound of freshly ground, medium grade coffee is placed in the flask, the flask is attached to the vacuum manifold, cooled to liquid nitrogen temperature, and the air is pumped from the system until a final pressure of about one micron is attained. The stopcock to the vacuum pump is then closed and the coffee is allowed to come to room temperature. A dewar of liquid nitrogen is placed around the receiver flask and the distillation is allowed to proceed for five days or approximately 120 hours. Since this investigation was concerned mainly with qualitative results, no studies were made of exact collection times and the sample was simply allowed to distill for a relatively long period of time in order to insure exhaustive collection of the volatile materials. The mass spectral data from which ultimately 30 volatile components were identified were based on analysis of two such one-pound samples of coffee.

Fractionation of the total condensate was accomplished by means of usual procedures employing low temperature-high vacuum

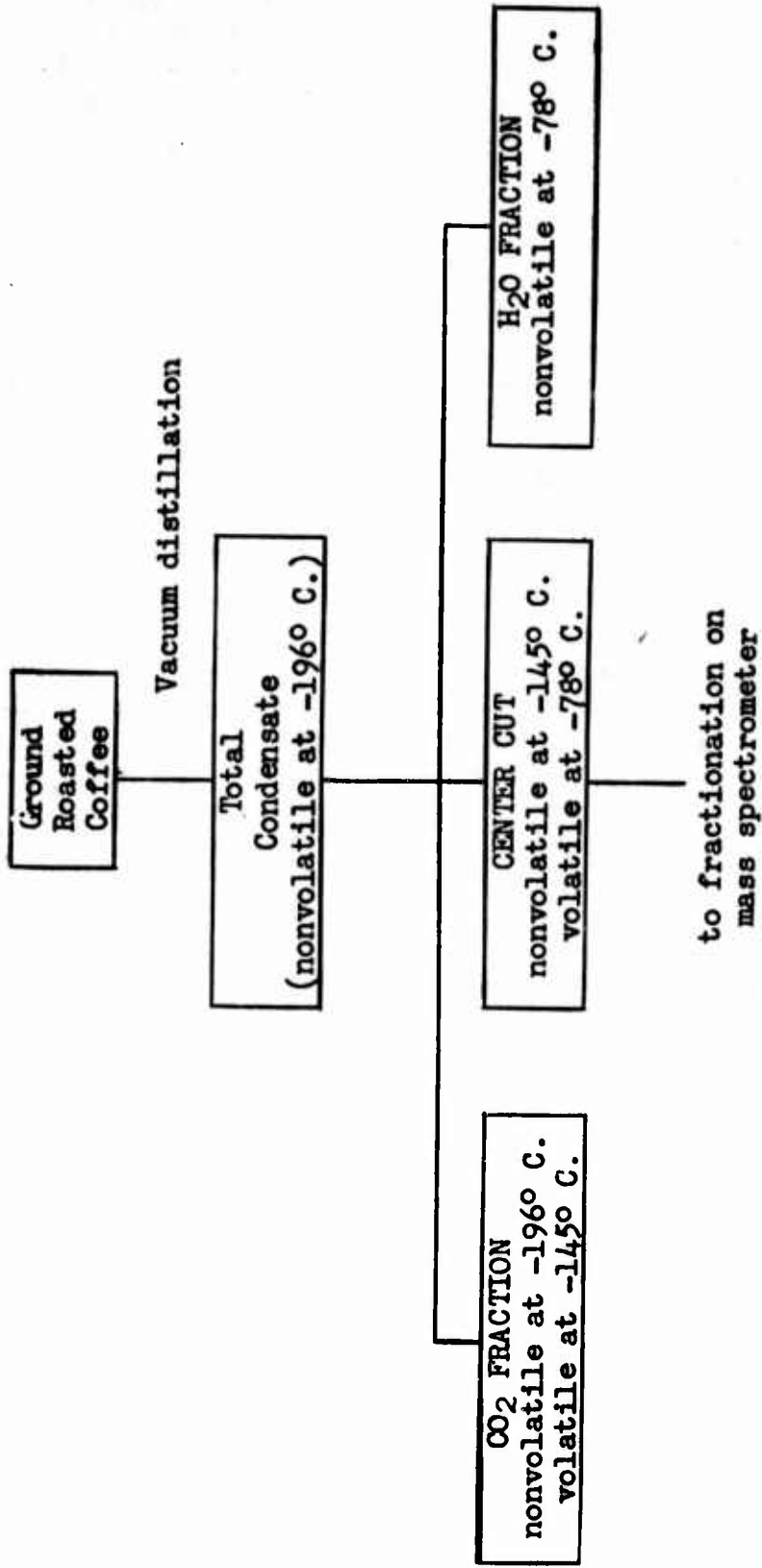


Figure 2. Diagram of the Fractionation of a Sample of Coffee Aroma.

distillation into a water fraction, a carbon dioxide fraction, and a center cut (11). A schematic diagram of the fractions obtained is shown in Figure 2.

The carbon dioxide fraction was by far the largest fraction obtained from the total condensate, and comprised about 95% of the total volatiles collected. The carbon dioxide fraction, however, contains only compounds which are volatile at a temperature below -145° C. and, therefore, only low molecular weight gases are expected to be found in this fraction. No systematic analysis of the carbon dioxide fraction was made because of the relative unimportance of compounds expected to be found in this fraction, but a qualitative analysis with lead acetate paper indicated the presence of trace amounts of hydrogen sulfide. The water fraction was much smaller than that usually obtained from foodstuffs having higher moisture contents. The water fraction had a pale yellow color which subsequently turned darker on standing. The volume of the water fraction was about 10 ml. Since our techniques for the analysis of water fractions have not yet been fully developed, no attempts were made to identify the compounds present at this time. Accordingly, the analyses which we are reporting here are based entirely on the analysis of the center cut which contains the components of intermediate volatility.

Some interesting observations were made of the character of the aroma of the various fractions which were obtained. The total condensate retained a highly characteristic and typical coffee aroma and appeared to be unchanged in character from the aroma observed over the fresh coffee before the collection was started. The CO_2 fraction was practically odorless but typical coffee-like aromas remained in the center cut and in the water fraction. In general, difference in aroma between the center cut and the water fraction appears to be that the center cut has the character of the so-called fines, whereas the water fraction retains the more heavy bodied aroma.

The analysis of the center cut was accomplished by direct fractionation on the mass spectrometer using the procedure which has been previously described (12). The fractionation was accomplished in steps of 5° C. from -145° to room temperature and a mass spectrum was obtained for each fraction. For some of the fractions which contained as many as 8 or 10 compounds, the interpretation of the spectrum was simplified by employing the low ionization voltage technique (12).

TABLE I
TABLE OF COMMON CONSTITUENTS OF COFFEE AND THEIR IDENTITY

<u>Compound</u>	<u>Method of Identification</u>	<u>Investigators</u>
Acetaldehyde	2,4-Dinitrophenylhydrazine	Clements and Deatherage (6)
"	"	Johnson and Frey (13)
"	Vapor phase chromatography	Rhoades (1)
Diacetyl	2,4-Dinitrophenylhydrazine	Clements and Deatherage (6)
"	Diacetyl dioxime τ Ni salt and H_2NOH	Prescott, et al. (14)
"	Bis-semicarbazone	Johnson and Frey (13)
"	Ni dimethylglyoxime precipitate	Schmalfuss and Barthmeyer (15)
Diethyl ketone	2,4-Dinitrophenylhydrazine	Clements and Deatherage (6)
"	"	Prescott, et al. (14)
Methyl ethyl ketone	2,4-Dinitrophenylhydrazine	Clements and Deatherage (6)
Acetone	2,4-Dinitrophenylhydrazine	Clements and Deatherage (6)
"	Salicylaldehyde reaction	Hughes and Smith (16)
"	Vapor phase chromatography	Rhoades (1)
Propionaldehyde	2,4-Dinitrophenylhydrazine	Clements and Deatherage (6)
Ethanol	Naphthylcarbamate derivative	Prescott, et al. (14)
Methanol	Vapor phase chromatography	Rhoades (1)
Dimethyl sulfide	No proof offered	Reichstein and Staudinger (3)
Furan (?)	Green pine splinter reaction, brown ppt. τ conc. HCl	Johnson and Frey (13)

RESULTS AND DISCUSSION

A summary of the previously reported compounds and methods of analysis used to identify them is given in Table I.

The various carbonyl compounds have been identified by means of 2,4-dinitrophenylhydrazine derivatives (6, 13). The presence of diacetyl which is an ortho-dicarbonyl compound has also been confirmed by the nickel-dioxime reaction by Prescott (14), and by Schmalfluss and Barthmeyer (15). In addition, acetaldehyde, acetone, and propionaldehyde have been identified by gas chromatography by Rhoades (1). The presence of all these carbonyl compounds seems to be well established.

Ethanol has been identified as the naphthylcarbamate derivative (14), and methanol by gas chromatography (1).

Dimethylsulfide has been reported to be present by Reichstein and Staudinger (3) but no proof was offered. The presence of furan as suggested by Johnson and Frey (13) based on a green pine splinter reaction can hardly be considered conclusive.

Interpretation of all the mass spectra obtained has led to the positive identification of 24 compounds. These are listed in Table II. Although reference spectra are not available in our catalog to permit confirmation, the mass spectra also tentatively suggest the presence of 6 other compounds. Of the 24 compounds which have been positively identified, 10 have been previously reported. The remaining 14 compounds which have been identified and the six, tentatively identified, have not been previously reported.

The figures given at the right of the compounds listed in Table II are quantitative estimates of the relative amounts of the compounds in a center cut. The values are given as mole percentage based on an average value taken from the two coffee center cuts analyzed. More accurate quantitative data cannot be given because all the necessary reference spectra for which calibrations have been obtained are not at present available. On the other hand, exact quantitative information could be readily obtained if desired by making the necessary calibrations. Therefore, although the following data are not strictly quantitative, the relative abundance of the various compounds identified can be estimated.

Acetaldehyde and isovaleraldehyde are the two most abundant compounds present in the center cut and the aldehydes collectively comprise about half the compounds found. Methyl ethyl ketone and

TABLE II
THE COMPOSITION OF COFFEE AROMA

<u>Aldehydes</u>		<u>Esters</u>	
Acetaldehyde	26.4%	Methyl formate	5.3%
Isovaleraldehyde	13.7	Methyl acetate	<u>5.0</u>
Propanal	8.9		10.3%
Propenal	0.8		
α -Methyl, β -ethyl acrolein	<u>0.9</u>		
	50.7%		
*Dimethyl acrolein			
		<u>Nitriles</u>	
		Propene nitrile	0.6%
		3-Butene nitrile	<u>1.1</u>
			1.7%
<u>Ketones</u>		<u>Alcohols</u>	
Acetone	0.5%	Methanol	2.0%
Methyl ethyl ketone	12.7	Ethanol	<u>0.4</u>
Methyl vinyl ketone	0.4		2.4%
Biacetyl	7.8		
Acetylacetone	<u>0.1</u>		
	21.5%		
<u>Heterocyclic Compounds</u>		<u>Summary of Composition</u>	
Pyrrole	0.5%	Alcohols	2.4%
Furan	2.3	Aldehydes	50.7
2-Methyl furan	4.0	Esters	10.3
2,5-Dimethyl furan	<u>0.2</u>	Heterocyclic compounds	7.0
	7.0%	Ketones	21.5
*Propyl furan		Nitriles	1.7
*Butyl furan		Sulfur compounds	<u>4.3</u>
*Dimethyl pyrrole			97.9%
*N-Methyl pyrrole			
<u>Sulfur Compounds</u>			
Carbon disulfide	0.2%		
Dimethyl sulfide	0.7		
Methyl ethyl sulfide	0.2		
Dimethyl disulfide	<u>3.2</u>		
	4.3%		
*Methyl ethyl disulfide			

*Tentatively identified due to lack of calibration spectra.

biacetyl are the most abundant of the ketones. Methyl ethyl ketone is the third most abundant of all the compounds.

The most abundant of the various heterocyclic compounds are the furans with furan and 2-methyl furan representing about 2 and 4%, respectively, of the total composition. Both these compounds, i.e., furan and 2-methyl furan, are believed to be among the more significant compounds in the complex which makes up typical coffee aroma.

The most abundant of the sulfur compounds appears to be dimethyl disulfide. The other compounds occur to a lesser extent. Regarding the identification of the various sulfur compounds that might be present, the absence of any mercaptans is particularly significant. By mass spectrometric analysis it is a relatively easy matter to be able to distinguish between a sulfide and a mercaptan, and furthermore, mercaptans can be readily identified as a class of compound in the presence of many other functional group type compounds. Therefore, it is reasonably certain that no mercaptans of intermediate molecular weight are present in the samples of coffee aroma isolated from dry ground coffee. This does not exclude the possibility that some higher molecular weight mercaptans may be present in the water fraction, but this we have not as yet examined. Although mercaptans have been previously reported by other workers, in all cases the samples of volatiles have been obtained from brews or percolates. It may be reasonably assumed that the mercaptans found were formed from the disulfides during preparation of the beverage.

There are two methyl esters which are fairly abundant, namely, methyl formate and methyl acetate. Two nitriles have also been found, both of which are unsaturated, namely, propene nitrile and 3-butene nitrile.

A summary of the composition according to type of compound shows the aldehydes comprise about 51% of the sample and ketones 21-1/2%, thus indicating that the carbonyl compounds represent some 70 odd per cent of the total volatile materials found in the center cut. The two esters make up another 10%, and heterocyclic compounds 7%. The remainder of the sample is distributed among the sulfur compounds, nitriles, and alcohols. All the compounds identified account for 98% of the material in the center cut. The remaining 2% of the sample is distributed among those compounds which are only tentatively identified and some other compounds which at present cannot be determined because of the small amount present. The 6 tentatively identified compounds account for the bulk of this 2% remainder. From an indication of perhaps two or three other compounds which may be present, the amount unidentified

can be estimated to be probably less than a tenth of a per cent of the total.

SUMMARY

The approximate composition of a coffee aroma center cut has been determined by mass spectrometry. The methods of sampling and fractionation used, together with direct mass spectrometric analysis, offer the advantage of minimum sample handling and avoid the possibility of loss and/or contamination of the sample throughout the process. Furthermore, by using vacuum distillation without heat, a more representative sample has been obtained of the volatile components which contribute to the aroma of coffee.

LITERATURE CITED

1. Rhoades, J. W., Food Research 23, 254 (1958).
2. Farber, L., Food Research 24, 72 (1959).
3. Reichstein, T., and Staudinger, H., Perfume and Essential Oil Record 46, 86 (1955).
4. Rhoades, J. W., J. Agr. Food Chem., in press.
5. Zlatkis, A., and Sivetz, M., J. Agr. Food Chem., in press.
6. Clements, R. L., and Deatherage, F. E., Food Research 22, 222 (1957).
7. Reichstein, T., and Staudinger, H., Coffee and Tea Inds. 6, 91 (1955).
8. Moncrieff, R. W., Food 19, 124 (1950).
9. Moncrieff, R. W., Food 19, 176 (1950).
10. Lockhart, E. E., "Chemistry of Coffee," The Coffee Brewing Institute, Inc., New York (1957).
11. Merritt, C., Jr., et al., J. Agr. Food Chem. 7, 784 (1959).
12. Bazinet, M. L., and Merritt, C., Jr., Anal. Chem. Series Research Report No. 11, QM Research and Engineering Center, Natick, Mass. (1959).
13. Johnson, W. R., and Frey, C. N., J. Am. Chem. Soc. 60, 1624 (1938).
14. Prescott, et al., Food Research 2, 1 and 165 (1937).
15. Schmalfluss, H., and Barthmeyer, H., Biochem. Z. 216, 330 (1929).
16. Hughes, E. B., and Smith, R. F., J. Soc. Chem. Ind. (London) 68, 322 (1949).