

SOME AROMATIC COMPOUNDS PRESENT IN OVEN GASES¹

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ABSTRACT

The only compounds identified in condensates from bread oven vapors were ethanol, acetaldehyde, and acetic acid. Quantitative analysis of a representative condensate from twelve 1-lb. loaves yielded these values: ethanol, 3.9 g.; acetaldehyde, 55 mg.; acetic acid, 58 mg. A synthetic mixture of this composition, and several variants of it, failed to approximate the aroma of the oven gases. Mixtures to which furfural and acetylmethylcarbinol were added approached the natural aroma much more closely; an "optimum" composition is given. It is manifest that presently unidentified compounds, probably in trace amounts, must determine in large measure the aroma of oven vapors.

In a previous paper (6), some of the readily volatile compounds thought to be implicated in the aroma of fresh bread were characterized. Attempts to simulate the bread aroma with mixtures of these substances were not notably successful. It was thought distinctly possible that unidentified trace constituents might be of major importance in determining the aroma of bread, and further that the extremely appealing aroma of oven vapors might denote the presence of these unidentified substances in greater proportions. Baker and associates (1,2) reported the presence of a remarkable variety of organic compounds in bread oven vapors. In the present study, an attempt was made to collect as much as feasible of such substances by a variety of means, including condensation in cold traps and absorbing individual classes of compounds in suitable reagent solutions.

Materials and Methods

The first requisite was a source of oven gases, which would preferably be uncontaminated by gaseous products of combustion and be available on a large scale. In the bread shop of the American Institute School of Baking the indirect-fired Petersen "70" oven was fitted with a high-capacity condenser as follows:

An aluminum sampling tube, 1½ in. o.d., was inserted through the wall of the 14-in. duct which vents the baking chamber of the oven, as close as possible to the oven itself. The sampling tube connected with a condenser comprising 9 ft. of 1½-in. o.d. aluminum tubing jacketed with 8 ft. of 2½-in. galvanized steel pipe. The ends of the

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pipe were threaded to take pipe caps, and the latter were drilled out to pass the aluminum tubing. Neoprene stoppers were bored with $1\frac{1}{2}$ -inch holes and slipped over the ends of the aluminum tube, with their narrow ends just entering the reamed ends of the pipe. When the drilled pipe caps were drawn up snugly, the stoppers were seated firmly and sealed the jacket perfectly. The jacket was drilled near the ends and ordinary pipe nipples were brazed on to receive garden-hose couplings for circulation of cooling water. A curved and a straight section of $1\frac{1}{2}$ -in. tubing, joined with short sleeves of Tygon tubing, led the condensate into a wide-mouthed 5-gal. bottle through a thick Neoprene gasket, into which was also inserted a $\frac{1}{2}$ -in. copper tube serving as a vacuum line. The latter was fitted with a $\frac{1}{2}$ -in. brass gate valve to control the amount of vacuum applied and prevent excessive entrainment of spray. An industrial vacuum cleaner was found to provide ample suction.

The 5-gal. receiver bottle was at first packed in chopped ice during operation; but this was found to accomplish little in trapping highly volatile materials. It had been planned to insert a Dry Ice trap between the receiver and the vacuum source, until calculation showed that at the normal range of vapor flow rates the dimensions of such a trap, to be of any benefit, would have to be impossibly large. Adding about 10 lb. of chopped ice inside the bottle before beginning a run helped to chill the condensate for a short time, at the cost of diluting the condensate considerably. In normal operation, the exhaust of the vacuum cleaner discharged a considerable concentration of acetaldehyde vapor; this seemed to be the only compound being lost to any great extent.

For more precise quantitative work, baking was done in a Blue M Model OV 18S electric laboratory oven. One of the two top vents was plugged; the second was fitted with a vapor draw-off tube leading to the condensers or scrubbing solutions. Mild vacuum was applied in either case to assure that the oven gases would be drawn into the collecting devices; normal air leakage around the door seal assured that the pressure inside the oven would not be measurably below atmospheric. Condensation of the vapors was done in a system comprising a water-cooled Friedrichs condenser, two trap flasks surrounded with ice and salt, and a large Dry Ice trap. On one run a liquid nitrogen trap was added to the foregoing, but did not condense anything that might have passed through the Dry Ice stage.

No attempts were made to absorb organic acids from the vapors by means of alkaline solutions, with one exception noted below, since the acids are all readily condensable. Carbonyl compounds in the

vapors from the electric oven were absorbed by bubbling the vapors through a long tube filled to a depth of around 18 to 24 in., either with 2,4-dinitrophenylhydrazine in 2N hydrochloric acid or with dilute sodium bisulfite solution. On one occasion, barium hydroxide solution was used to trap the volatile acidic material for identification. Using the large gas-fired oven, no attempts were made to scrub the vapors.

Qualitative analysis of the oven-vapor constituents generally followed the procedures described in a previous paper (6). After separation of carbonyl compounds as their 2,4-dinitrophenylhydrazones and acids as the sodium or barium salts, the remaining material from the condensate was saturated with sodium sulfate and extracted at 0°C. with ethyl chloride. The ethyl chloride (b.p. 12°C.) was distilled off through a short Vigreux column without the use of heat, and vapor-phase chromatography was used to study the residual organic material. Samples were applied to a 10-ft. column containing a polyester (diethylene glycol succinate) on Chromosorb as the packing. The instrument (Aerograph Model C-100) was operated at 100°C. with a helium carrier gas flow rate of 25 ml. per minute.

Quantitative analyses were simplified considerably when it was determined that ethanol, acetic acid, and acetaldehyde were by far the most predominant components of the oven vapors, apart from water. Ethanol was estimated by oxidation with acid dichromate and measurement of excess dichromate, using the micro-method of Neish (4). Acetic acid was estimated by ordinary titration with 0.05N potassium hydroxide solution, using a mixed phenolphthalein-thymolphthalein indicator. Acetaldehyde was estimated by its bisulfite-binding capacity, using both the unmodified method of Neish (4) and a variant in which the excess unbound bisulfite rather than that bound by the aldehyde is determined. The details in which this latter method differs are pointed out under "Results."

Results

Examination of Condensates. During a typical run with the large oven, about 2 gal. of condensate were collected in one morning. Unfortunately, the oven was opened at intervals to load and unload, so that there was considerable loss of vapors through the doors; quantitative collection was obviously out of the question. When a day's run was completed, the condensate was transferred to glass-stoppered flasks which were filled completely and stored in a refrigerator. Five gallons of condensate were pooled, and distillation at atmospheric pressure yielded about 1¼ gal. of distillate plus a completely odor-

less residue. The distillate was redistilled through a Vigreux column fitted with a total-reflux, partial-takeoff stillhead, yielding 1,400 ml. of distillate and an odorless residue. This second distillate was then distilled again through the same apparatus to yield 300 ml. of highly odorous distillate and an odorless residue. This final distillate was saturated with sodium sulfate, chilled to 0°C., and extracted with ethyl chloride.

Individual portions of the extract were treated with 2,4-dinitrophenylhydrazine in 2N hydrochloric acid; 3,5-dinitrobenzoyl chloride in toluene; and *p*-phenylphenacyl bromide, according to standard procedures for preparation and identification of organic derivatives of carbonyl compounds, alcohols, and acids respectively (3,5). The results indicated that only acetaldehyde, ethanol, and acetic acid were present.

Using the electric oven, it was felt that the findings would be more trustworthy. For example, one run using the large oven yielded an apparently wide range of volatile compounds, which proved to be due to prior lubrication of the oven. Runs were made using the electric oven with the system of condensers described above, and also using the scrubbing tower filled at different times with solutions of 2,4-dinitrophenylhydrazine, sodium bisulfite, and barium hydroxide. In the case of the condensates the procedure described under "Methods" was followed, and the sole 2,4-dinitrophenylhydrazone detected was that of acetaldehyde, while the sole acid isolated as its barium salt proved to be acetic acid, by its unique *p*-phenylphenacyl ester and by its single peak on the vapor-phase chromatograph. The ethyl chloride extract yielded a single peak on the polyester column, corresponding to ethanol. Confirmation was obtained by preparing the 3,5-dinitrobenzoate and checking against an authentic sample. The scrubbing tower was used purely in the hope of trapping organic volatiles other than those noted, but without success.

Quantitative Analysis of Condensate. (1) Acetic Acid. The total condensate collected (using Dry Ice and liquid nitrogen traps) from the baking of 12 loaves in the electric oven was made to 250 ml. and 25-ml. aliquots were titrated with potassium hydroxide solution.

KOH used:	2.04, 2.03 ml. at 0.0472N
Acetic acid in aliquots:	$2.04 \times 0.0472 \times 60 = 5.8$ mg.
Total acetic acid in condensate:	$5.8 \times 10 = 58$ mg.

(2) Ethanol. A 10-ml. portion of the condensate was diluted to 100 ml., and 2.0-ml. aliquots were treated with 10.0 ml. of the dichromate reagent (0.0400N potassium dichromate in 18N sulfuric acid). The titers on duplicate aliquots were 0.270 and 0.269 meq.

of dichromate, giving ethanol contents of 3.1 mg. in the aliquots,

$$\text{or } 3.1 \times \frac{250 \times 10}{2 \times 1000} = 3.9 \text{ g. total.}$$

(3) Acetaldehyde. Using the unmodified Neish method (4), and titrating bisulfite regenerated from the complex with 0.05N iodine, meq. acetaldehyde per 10 ml. aliquot = 0.0357. In total condensate,

$$\text{acetaldehyde} = \frac{250}{10} \times 44 \times 0.0357 = 39.3 \text{ mg.}$$

This method was suspected of yielding low results, as the release of bisulfite from the aldehyde complex by sodium bicarbonate seemed very gradual. Using 2 ml. of 1% sodium bisulfite solution (about 0.1M) and adding 10.0 ml. of 0.05N iodine to destroy the excess, the unconsumed iodine was back-titrated with 0.04N thiosulfate. Milliequivalents acetaldehyde per 10 ml. aliquot = 0.0501, which

$$\text{gives a total content of } \frac{250}{10} \times 44 \times 0.0501 = 55 \text{ mg.}$$

It must be noted that these values are representative only of the particular condensate used; repetitions of these analyses on other condensates from the electric oven indicated only order-of-magnitude agreement with the ones given here. Doubt is thereby thrown on the extent to which the sampling of oven gases is quantitative. However, these order-of-magnitude results were considered valid enough to permit experiments on simulating the aroma of oven gases.

"*Synthetic Oven Vapors.*" Using the above proportions as a datum, several mixtures of 95% ethanol, acetaldehyde, and glacial acetic acid were made up. Holding the amount of ethanol constant, each of the other two components was varied, using the proportion cited and also one-half and twice this proportion. Aliquots of the nine mixtures were pipetted into varying volumes of hot water, and the odors were noted. In no instance did the odor resemble the oven vapors at all closely; the three organic compounds were clearly identifiable.

As a matter of curiosity, the mixture containing half the above proportion of acetaldehyde and the normal proportion of acetic acid was modified by additions of various amounts of acetylmethylcarbinol and furfural. Diacetyl was tried and rejected when it was found that its odor was too distinctive, even in the minutest traces. While no combination of acetylmethylcarbinol and furfural yielded an aroma very close to that of the oven gases, the improvement over the simple ethanol-acetaldehyde-acetic acid composition was notable. The optimum concentrations, arrived at by trial and error, were:

Ethanol	4.0 g.
Acetaldehyde	10.0 mg.
Acetic acid	40.0 mg.
Furfural	20.0 mg.
Acetylmethylcarbinol	6.0 mg.

One milliliter of this mixture in about 150 ml. of warm water produced a very pleasant aroma, though not quite that of the oven gases.

Discussion

In the experiments described, the apparent composition of the oven gases from the baking of white bread was very simple. That this composition does not account fully for the aroma is manifest from the attempts to reproduce the aroma synthetically, especially in view of the improvement afforded when furfural and acetylmethylcarbinol were incorporated. It must be concluded that the analytical methods used here did not detect traces of extremely important substances which, together with those which were detected, produce the characteristic and appealing aroma of baking bread. In Baker's studies (1,2), a large variety of substances was reported as occurring in the oven vapors; the work reported here failed to detect most of these substances, even with the use of a commercial-type oven to provide large volumes of condensed vapors.

Since the bulk of the condensable material in the oven vapors is water, efficient concentration of the organic components requires either very thorough extraction of the aqueous condensate or selective removal of water from the vapors. Experiments on the preferential sorption of water vapor on a glycerol-impregnated porous granular support are under way, using dilute aqueous solutions of the lower aliphatic alcohols, aldehydes, and acids as "synthetic" vapor sources.

Literature Cited

1. BAKER, J. C., and MIZE, M. D. Some observations regarding the flavor of bread. *Cereal Chem.* **16**: 295-297 (1939).
2. BAKER, J. C., PARKER, H. K., and FORTMANN, K. L. Flavor of bread. *Cereal Chem.* **30**: 22-30 (1953).
3. McELVAIN, S. Characterization of organic compounds. Macmillan: New York (1947).
4. NEISH, A. C. Analytical methods for bacterial fermentations. National Research Council of Canada, Report No. 46-8-3 (2nd rev.). Saskatoon, Sask. (November 25, 1952).
5. SHRINER, R. L., and FUSON, R. C. Systematic identification of organic compounds. Wiley: New York (1940).
6. WISEBLATT, L., and KOHN, F. E. Some volatile aromatic compounds in fresh bread. *CEREAL CHEM.* **37**: 55-66 (1960).