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# FLAVOR CHARACTERIZATION OF DENTIFRICES USING EQUILIBRIUM HEADSPACE GAS CHROMATOGRAPHY

R. S. ROBINSON, E. A. TAVSS*, J. SANTALUCIA and D. L. CARROLL
*Research and Development Division, Colgate-Palmolive Company, 909 River Road, Piscataway, NJ 08854 (U.S.A.)*
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## SUMMARY

Equilibrium headspace gas chromatography was used to measure quantity and composition of flavor released from dentifrices into the headspace of sealed vials. Dentifrice formulations varying in composition were analyzed for volatile flavor components after thermodynamic equilibrium between the gas (headspace air) and liquid phase (dentifrice) was established. Comparison of dentifrice formulations allowed for determination of the effect of individual components on flavor binding. This information is useful to formulators, since knowing the extent of the effect of dentifrice components on flavor release allows the formulator to intelligently modify the dentifrice components/flavor. This technique is advantageous over the previously reported kinetic procedure in that the results of equilibrium headspace gas chromatography are not complicated by the effect of varied viscosity.

## INTRODUCTION

Flavor is the most important factor affecting human perception of dentifrice taste. Flavor oil has been demonstrated to bind to dentifrices to various extents[1], thereby affecting taste. An instrumental procedure whereby the degree of binding of flavor oil to the dentifrice could be quantitatively measured, would be of benefit to the formulator. With this knowledge the dentifrice and/or flavor oil could be modified to achieve a desired degree of flavor binding, thereby optimizing the dentifrice taste.

Due to the composition of dentifrices, *i.e.*, volatile flavor components within a matrix of non-volatile organic and inorganic materials, headspace gas chromatography (GC) was the appropriate method of analysis. Similar applications utilize headspace analysis such as the determination of trace organic substances in water and sewage[2,3]; ethanol and other compounds of toxicological interest in biological samples[4–7]; residual monomers in polymers[8]; bacterial metabolites[9]; and flavors in foods and beverages[10–13].

One headspace method[11] which approached the goal suffered from the fact that the measurements were made prior to attaining equilibrium. In this kinetic technique, the rate of diffusion of flavor from the dentrifrice core to the surface, which varies

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inversely with viscosity, becomes an important contributing factor, especially since dentifrices vary significantly in rheological properties. A procedure was required in which the complicating effect of viscosity was not a factor. This was accomplished by developing a quantitative instrumental method in which the flavor released was measured at equilibrium.

## EXPERIMENTAL

### *Instrumental headspace*

A Perkin-Elmer Sigma 2000 gas chromatograph equipped with an HS-100 automated headspace sampler and a flame ionization detector (Perkin-Elmer, Norwalk, CT, U.S.A.) was used throughout this work. The dentifrices were laboratory batch samples, typically containing the following ingredients: dicalcium phosphate dihydrate, water, glycerin, sodium lauryl (dodecyl) sulfate (SDS), cellulose gum, flavor, sodium monofluorophosphate, sodium benzoate, tetrasodium pyrophosphate and sodium saccharin. The flavor was a spearmint/peppermint blend containing excess menthol and carvone, plus anethole. A 140-mg amount (approximately 0.10 ml) of dentifrice was dispensed into a 22-ml headspace vial (Perkin-Elmer) and weighed to the nearest 0.0001 g. The vial was hermetically sealed by crimping an aluminum cap containing an aluminum-coated silicone rubber septum (Perkin-Elmer) onto the vial. The sealed vial was placed into the sample carriage of the HS-100 headspace sampler which was programmed to maintain each vial at 40°C for 5–7 h, achieving equilibrium of the contents. An aliquot of the headspace was then automatically injected onto a Supelcowax 10 bonded-phase fused-silica capillary column, 30 m × 0.32 mm with a 0.25 -$\mu$m film thickness (Supelco, Bellefonte, PA, U.S.A.). The carrier gas was helium; the flow-rate was 5 ml/min; the split ratio was 20:1 and the column was held at 50°C for 2 min, then programmed to 150°C at a rate of 10°C/min. Use of the HS-100 automated headspace sampler allowed for unattended analysis of up to 100 samples. The chromatograms were processed by an LCI-100 computing integrator (Perkin-Elmer). Analysis of each dentifrice was replicated six times.

### *Instrumental viscosity*

Relative viscosity measurements of the dentifrices varying in gum concentration were made with a Brookfield (Stoughton, MA, U.S.A.) digital viscometer model RVTD. Measurements were made directly in the dentifrice tube, two per sample.

## RESULTS

Four sets of flavored dentifrices were tested in this study. A representative equilibrium headspace gas chromatogram of a flavored dentifrice is shown in Fig. 1. The first set of dentifrices contained six concentrations of a detergent, SDS. Table I shows the effect of increasing the SDS concentration on flavor released into headspace. As the SDS concentration increased from 0.3 to 1.8%, the equilibrium headspace flavor decreased by 35%.

The degree of binding of flavor in a dentifrice to $\beta$-cyclodextrin was determined (Table II). A flavor–$\beta$-cyclodextrin complex was prepared and added to the dentifrice in place of flavor oil. The $\beta$-cyclodextrin significantly decreased the amount of flavor

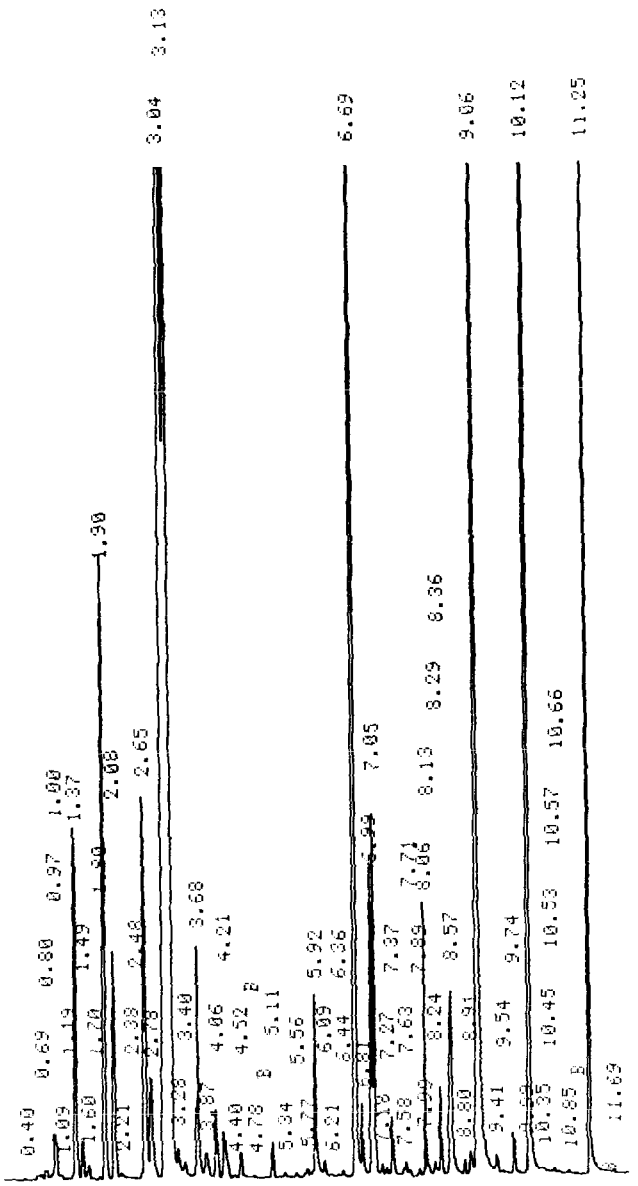


Fig. 1. Equilibrium headspace gas chromatogram of a flavored dentifrice. (Numbers indicate retention times in min.)

released into headspace, demonstrating the binding of flavor to $\beta$-cyclodextrin within the dentifrice. Also, the reproducibility of this method is exhibited by the coefficient of variation values of less than 3% for six replicate analyses per sample.

A series of dentifrices with eight different levels of flavor from 0 to 3.0% were tested by equilibrium headspace GC (Fig. 2, Table III). Results showed a strong

TABLE I

EFFECT OF DETERGENT (SDS) CONCENTRATION ON EQUILIBRIUM HEADSPACE FLAVOR

| *SDS Concentration (%)* | *Total area (GC units)** | |
|---|---|---|
| | *Mean ± standard error of the mean (n = 6)* | *Coefficient of variation (%)* |
| 0.3 | 17.14 ± 0.318 | 1.86 |
| 0.6 | 16.71 ± 0.082 | 0.49 |
| 0.9 | 16.55 ± 0.061 | 0.37 |
| 1.2 | 14.89 ± 0.237 | 1.59 |
| 1.5 | 12.30 ± 0.331 | 2.69 |
| 1.8 | 11.14 ± 0.073 | 0.66 |

* Electronic integrator counts (relative to component concentration).

TABLE II

EFFECT OF β-CYCLODEXTRIN ON EQUILIBRIUM HEADSPACE FLAVOR

| *Sample* | *Total area (GC units)* | |
|---|---|---|
| | *Mean ± standard error of the mean (n = 6)* | *Coefficient of variation (%)* |
| Control | 6.32 ± 0.159 | 2.52 |
| Flavor + β-cyclodextrin | 3.53 ± 0.057 | 1.61 |
| 1.2 × flavor + β-cyclodextrin | 4.30 ± 0.049 | 1.14 |
| 1.5 × flavor + β-cyclodextrin | 4.24 ± 0.049 | 1.16 |

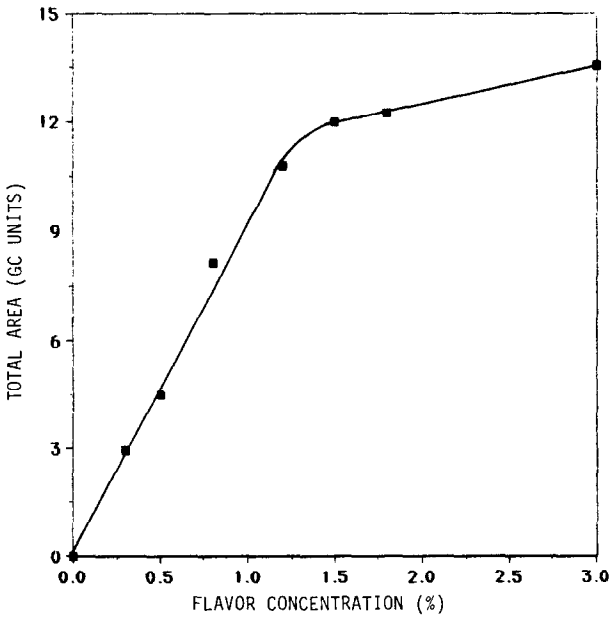


Fig. 2. Equilibrium headspace of dentifrices varying in flavor concentration.

TABLE III

EFFECT OF DENTIFRICE FLAVOR CONCENTRATION ON EQUILIBRIUM HEADSPACE FLAVOR

| *Sample (% flavor)* | *Total area (GC units)* | |
|---|---|---|
| | *Mean ± standard error of the mean (n = 6)* | *Coefficient of variation (%)* |
| 0 | 0 ± 0 | 0 |
| 0.3 | 2.95 ± 0.041 | 1.39 |
| 0.5 | 4.48 ± 0.094 | 2.10 |
| 0.8 | 8.17 ± 0.294 | 3.60 |
| 1.2 | 10.79 ± 0.302 | 2.90 |
| 1.5 | 12.01 ± 0.196 | 1.63 |
| 1.8 | 12.27 ± 0.098 | 0.80 |
| 3.0 | 13.54 ± 0.229 | 1.69 |

positive linear relationship between flavor concentration and headspace flavor from 0 to 1.2% (linear regression correlation coefficient = 0.998). Above 1.2% flavor, the flavor release continued to rise, but at a lower slope.

The fourth set of dentifrices tested contained six different concentrations of carboxymethyl (CM) cellulose thickening gum (from 0.3 to 2.0%). Table IV summarizes the results of this study, showing a 13.0% decrease in flavor release as the CM-cellulose concentration increased. Measurements by a Brookfield digital viscometer showed an increase of over two orders of magnitude in the viscosity of the dentifrices from 0.3 to 2.0% CM-cellulose (Fig. 3). Analysis of these dentifrices by kinetic headspace GC[1] resulted in a 28% decrease in released flavor over this range.

## DISCUSSION

This analysis on four sets of dentifrices provides a simple, reproducible method for determining absolute effects of dentifrice compositional differences on flavor released into headspace, independent of viscosity. Analysis of flavor released into head-

TABLE IV

EFFECT OF CM-CELLULOSE CONCENTRATION ON EQUILIBRIUM HEADSPACE FLAVOR

| *Sample (% cellulose)* | *Total area (GC units)* | |
|---|---|---|
| | *Mean ± standard error of the mean (n = 6)* | *Coefficient of variation (%)* |
| 0.3 | 7.95 ± 0.176 | 2.21 |
| 0.5 | 7.83 ± 0.159 | 2.03 |
| 0.9 | 7.81 ± 0.216 | 2.77 |
| 1.3 | 7.55 ± 0.196 | 2.60 |
| 1.7 | 7.37 ± 0.094 | 1.28 |
| 2.0 | 6.91 ± 0.118 | 1.71 |

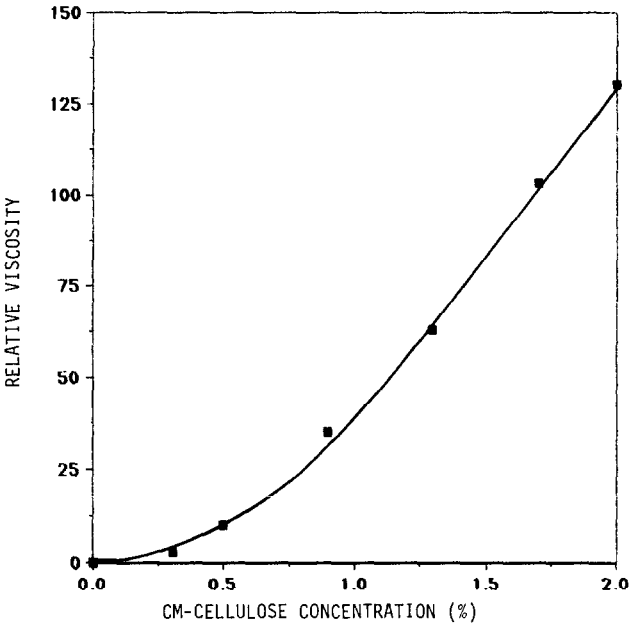


Fig. 3. Viscosity of dentifrices varying in CM-cellulose concentration.

space after thermodynamic equilibrium is attained reveals the binding affinity of a dentifrice component for flavor. Excellent reproducibility is illustrated by the low coefficient of variation data.

It was of interest to investigate the effect of SDS on flavor release in a dentifrice. SDS serves to form foam in a dentifrice, as well as to help dissolve the flavor oil. The results (Table I) demonstrated that the SDS has a rather substantial effect of complexing the dentifrice flavor, retarding its release. This is probably caused by the flavor oil being trapped in SDS micelles.

A complexing agent, $\beta$-cyclodextrin, was investigated for its ability to bind flavors as clathrates. The results (Table II) prove that it was effective.

The measured relationship (Fig. 2) found between flavor concentration and equilibrium headspace areas (within practical range) allows for quantitative modification of flavor levels in dentifrices to match desired flavor release.

The equilibrium CM-cellulose study (Table IV), when combined with the corresponding kinetic CM-cellulose study[1], allows for determination of the contribution of viscosity to flavor release. Since the equilibrium results are independent of viscosity, the 13% decrease found by equilibrium headspace GC is due to an interaction between CM-cellulose and flavor which inhibits flavor release. The 28% decrease found by kinetic headspace GC is a combination of two factors: a 13% decrease caused by the flavor–CM-cellulose interaction and a 15% decrease due to viscosity inhibiting the flavor migration from dentifrice to headspace.

Equilibrium headspace GC is of great value in analyzing large numbers of dentifrice formulations to determine the effect of dentifrice processing and formula-

tion changes on flavor. The results of these studies should be very useful to formulators, since knowing the effect of components such as SDS on flavor release would allow for corrections in detergent level, and flavor concentration and/or composition to be made.

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