

The Loss of Volatile Esters from Cookies

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If we had to define two major consumer trends in the US food industry, one would have to mention convenience (long term) and “healthy” foods (more recent). The need for convenience has sparked the development of a host of frozen foods, including ready-made breakfasts, lunches, snacks and dinners. A current manifestation of this trend is the availability of takeout, prepared, complete meals by restaurants and grocery stores. While one would arguably say that cold breakfast cereals are convenient, recent data suggests that even cold ready-to-eat cereals lack the desired convenience and are being supplanted by meals that can be eaten on the go, such as breakfast bars, toaster tarts and other finger foods. This need unquestionably fueled the development of a large range of microwave foods, many of which were short-lived due to poor sensory quality.

The trend towards healthy eating, a mostly recent trend, may have peaked. A backlash toward compromising sensory quality for “healthiness” is beginning to appear. The term “healthy” often has been associated with low-fat qualities; the sensory quality of these foods has not met expectations. It is becoming more and more obvious that the consumer is reluctant to purchase foods that offer “healthiness” at the cost of sensory quality.

The following study considers some of the flavor problems associated with low-fat and microwaved foods. We have evaluated the influence of dough formulation (fat content), flavor form (liquid, spray-dried and encapsulated/controlled release) and baking method (conventional oven vs. microwaved) on the retention of flavor in cookies during baking.

Materials and Methods

Aroma compounds: Five aroma compounds (selected esters) were added to each type of cookie dough. These esters differed from each other in carbon chain length: ethyl acetate, ethyl butyrate, ethyl caproate, ethyl caprylate and ethyl caprate (Aldrich Chemical Co., Milwaukee). Ethyl laurate was used as an internal standard. These compounds are components of fruit flavors and are not naturally present in the product. In addition, they have a low reactivity, are stable in most analytical analysis, and are not generated in significant quantities during thermal processes.

Flavor addition — liquid flavorings: Ethanol was chosen as a solvent for liquid flavorings. One ml of each ester/ethanol solution (6 ml of ester in 25 ml ethanol) was added to the liquid phase of the dough (to facilitate their dispersion). Another experiment was done adding the aroma compounds just before the baking in order to check the influence of the stage of incorporation on flavor retention. The initial concentrations of aroma compounds were chosen deliberately high (600 ppm of each ester [$g_{\text{ester}}/G_{\text{dough}}$]) because the residual concentrations had to be sufficient to enable accurate quantification.

Flavor addition — encapsulated/controlled-release flavorings: The encapsulated flavorings were produced by spray drying using two different carriers: N-Lok (National Starch Co.; 45 percent infeed solids for spray drying) and gum acacia (Colloides Naturelles; 30 percent infeed solids). These flavorings were produced by dispersing 2 kg of carrier in water half a day before drying. The gum acacia formulation included 6.67 kg of water, while 4.44 kg was used for the N-Lok. The carrier/water blends were kept in a cold room (5°C) until ready to dry. The flavor solution (0.222 kg; 28 percent ethyl acetate, 25 percent ethyl butyrate, 19 percent ethyl caproate, 14 percent ethyl caprylate and 14 percent ethyl caprate [%w/w]) was blended (Greenco high-speed mixer) into the carrier solution just before drying. The emulsion was spray dried (Niro Utility Dryer with a centrifugal wheel atomizer) using an inlet temperature of 200°C and an outlet temperature of 100°C. Cookies were flavored with the resultant powders during dough preparation (gum acacia: 7 percent $w_{\text{powder}}/w_{\text{wet dough}}$; N-Lok: 6 percent $w_{\text{powder}}/w_{\text{wet dough}}$).

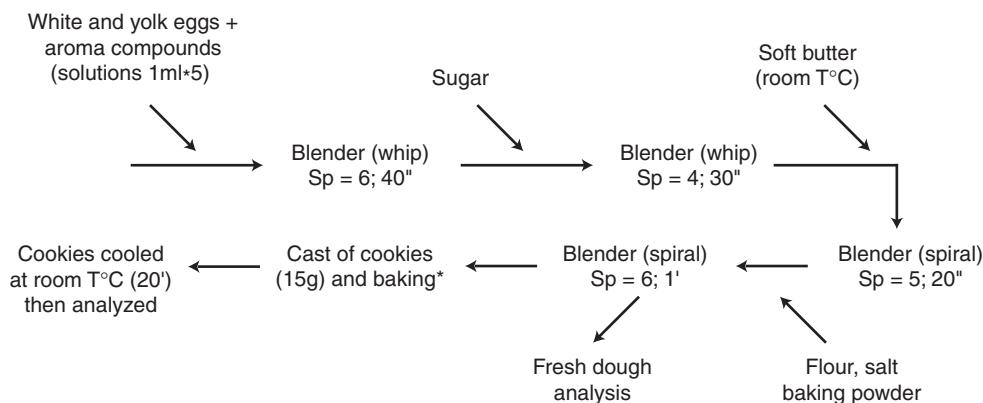
A portion of these spray-dried powders were sent to Robertet Flavors Inc. (Piscataway, NJ) for imparting controlled release properties. This process was done for us and is proprietary, thus, we have no information on the process itself. The encapsulated flavorings were analyzed for esters by gas chromatography and the amounts used to flavor the cookie doughs adjusted for flavor content.

Sample Preparation

Composition: Three different cookie formulations were used in these studies: regular, low-fat and meringue cookies.

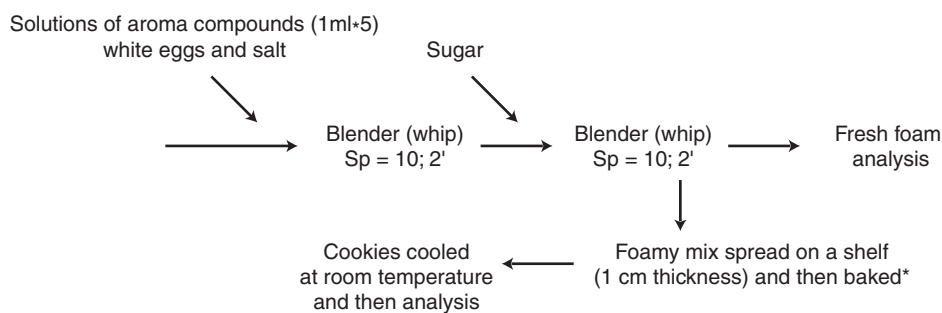
Figure 1. Methods for the preparation and analysis of cookies

Regular and low fat cookies



*(375°F/10') and (425°F/7') in conventional oven; (4'30"/high power) in microwave

Meringue cookies



*(275°F/55') and (325°F/35') in conventional oven; (2'30"/high power) in microwave

Table 1. Cookie formulations used in this study

Ingredients (percent total weight)	Regular Cookies (percent)	Low-Fat Cookies (percent)	Meringue (percent)
Flour	44.0	46.0	
Sugar	20.0	24.0	62.0
Butter	27.0	13.0	
Egg whites	5.0	12.0	37.5
Egg yolks	3.0	4.0	
Baking powder	0.5	0.5	
Salt	0.5	0.5	0.5
Moisture content	~8.0	~15.5	~36.5
Fat content	~27.0	~13.0	~0.0

Their formulations are provided in Table 1.

Cookie dough preparation: The steps in cookie making are summarized in Figure 1. A Kitchen Aid Model K45 blender (maximum bowl capacity: 2 kg; 10 rotation speeds available) was used for the blending of the dough. The cookie dough was baked in both a conventional oven (General Electric, maximum power: 9.1 kW) and a microwave (Litton Micro Browner). For each oven, different time/temperature combinations were tested.

Method of Analysis

Direct thermal desorption: Ester concentrations in the cookie dough and baked cookies were quantified using a Gerstel GC-Thermal desorption technique, which requires three dif-

ferent units connected together: a Thermal Desorption module (Gerstel TDS 2), where flavors were volatilized via a temperature program; a CIS module (Gerstel Controlled Injection system); a cryogenic trap that controlled the time and the duration of the injection into the column; and a Hewlett Packard 6890 gas chromatograph (DB5 column; 30 m x 320; 1 μ m film thickness capillary column, Figure 2).

In the first steps, the TDS unit was cooled to -20°C (using liquid nitrogen) and 4 mg of cookie dough or baked cookie was inserted in a glass desorption tube. Pieces of glass wool were placed at each tube extremity to avoid solid particles entering the GC column during the desorption cycle. Then 1 μ l of internal standard solution (240 μ l ethyl laurate in 100 ml ethanol) was injected via a syringe into the cookie sample and the sample was heated in a flow of helium (carrier gas, 50ml/min; ramp: $60^{\circ}\text{C}/\text{min}$; final temperature: 300°C ; final time: 3 min). During desorption, the CIS was kept at -50°C and the GC oven at 40°C . At the end of the desorption cycle, both CIS (ramp: $60^{\circ}\text{C}/\text{min}$; final temperature: 300°C ; final time: 3 min) and GC oven (ramp: $10^{\circ}\text{C}/\text{min}$; final temperature: 250°C ; final time: 4 min) were heated and desorbed volatile compounds were separated in the GC.

In order to check the recovery and precision of the thermal desorption method, three samples, varying in composition and analyzed in duplicate, were also analyzed using the Likens-Nickerson extraction method.

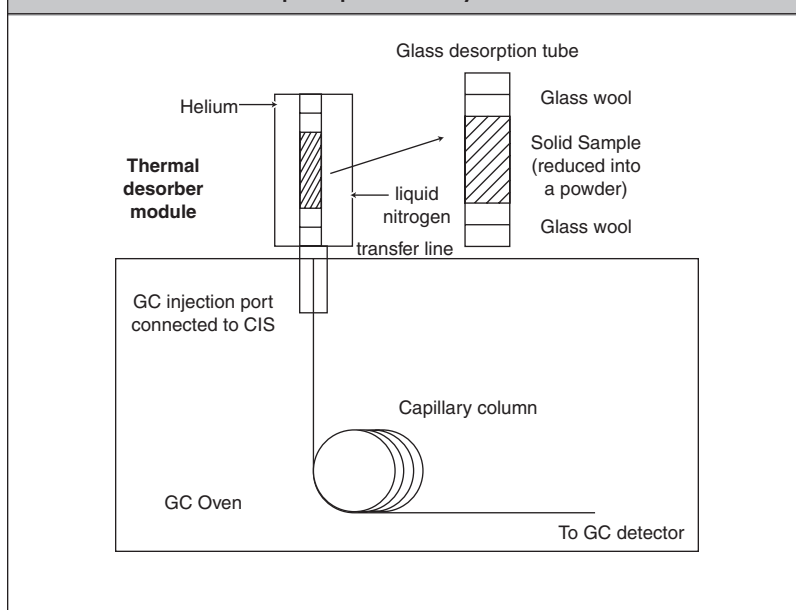
Likens-Nickerson extraction: Ten g of sample (cookie powder) was added to 100 ml of water, plus 1 ml of an internal standard solution (150 μ l ethyl laurate in 25 ml ethanol) and then heated to boiling for 2 h. Distilled diethyl ether (25 ml, $B_{p,760}=34.6^{\circ}\text{C}$) was used as a solvent for this extraction. The final extract was dried (anhydrous sodium carbonate) and injected (1 μ l) into the GC.

Results and Discussion of Liquid Flavoring

Quality and reproducibility of the thermal desorption method (TDS): While previous workers have studied both Likens-Nickerson and solvent extraction for flavor recovery from cookie doughs, we chose to work with a more rapid technique (direct thermal desorption) because we were able to add a large enough quantity of flavorings to our cookie dough to make this alternative method feasible.³ Initially, replicate experiments were done on our model aroma system by injecting 1 μ l of the esters (in an ethanol solution) onto glass wool in a thermal desorption tube, the esters desorbed and analyzed by GC. The results were very good, having a standard error of the mean <2 percent.

The initial results achieved by our analysis of the flavored regular cookie dough baked in a conventional oven were more

Figure 2. Schematic representation of the thermal desorption module mounted on a gas chromatograph, illustrating the features and operating principles of the system²



variable (standard error of the mean about 8 percent). This larger error was determined to be due to sampling problems. Parameters, such as the non-homogenous distribution of flavors in the cookie (especially between the crust and the crumb), the non-uniform temperature environment in the oven (results in different rates of loss depending upon the position of the cookie in the oven), and the small sample size, are likely to explain the poorer analytical precision. In order to improve the precision of the method, all cookies baked at one time were pooled and ground into a powder before sampling. This at least minimized some sample variability (standard error of the mean was reduced to ~5 percent).

The overall results achieved by the Likens-Nickerson method and the thermal desorption extraction were similar. However, the Likens-Nickerson extraction was less reproducible than the TDS method (standard error of the mean ~11 percent). The thermal desorption method appears to be rapid, quantitative and reproducible for this application.

Ester Retention in Cookies

Nature of aroma compounds: For aroma compounds of the same class (e.g. esters), aroma retention is inversely related to the boiling point of the ester. Across compound categories, previous studies have shown that Henry's law constants ($K=[c]_{\text{vapor phase}}/[c]_{\text{liquid phase}}$) give a better prediction for the loss of aroma compounds from solution. Henry's law accounts for solubility in the system continuous phase, which is a more valid consideration in many systems than boiling point. The physical properties, including Henry's law constants, of the esters used in this study are shown in Table 2.

Previous experiments have shown that partition coef-

Table 2. Physical and chemical properties of ester/water solutions⁴

Aroma Compounds	Molecular Weight (g/mol)	Boiling Point (°C)	Henry Constant [*] X = (-log)	Henry Constant [*] K = 10 ^x	Dielectric Constant
Ethyl butyrate	116	120	1.766	58.344	0.3
Ethyl caprylate	144	168	1.529	38.806	0.3
Ethyl caproate	172	208	1.283	19.187	0.3

^{*}Experiments done on flavor/water solutions (20°C)

ficients and resistance to mass transfers are fundamental parameters that explain flavor loss in cakes during baking.⁴ The solubility and the polarity of aroma compounds in aqueous and oil phases can strongly affect these parameters. This explains the differences in retention profiles, depending on the nature of aroma compounds and on the manufacturing process.

Matrix composition effects — conventional baking:

Recent studies have shown that water and oil are the main food components influencing the volatility and the release of flavor compounds. While binding of certain aroma constituents to proteins and polysaccharides occurs, this effect is generally considered minor relative to the influence of the ratio of oil to water in the food. As one would expect, our results show that the higher the fat content, the better the flavor retention was in cookies (Figure 3). We must point out that the meringue cookies were baked under very different time/temperature conditions, so the validity of comparison is questionable. However, the very high moisture content and the absence of fats in meringue cookies likely explain the poor retention of aroma compounds during baking.

Experiments on systems have shown that the higher the fat level, the better the overall retention of esters (see Figure 4; significant differences after 3 min of baking). It has been shown that aroma release is related to the amount of water that evaporates during cooking. High temperatures and steam formation facilitate mass transfer throughout the matrix. Steam also serves as a vehicle to transport volatile aromas across product/air boundaries. Thus, by decreasing the water loss from the matrix via steam distillation and reducing the vapor pressure of the fat-soluble volatiles, fats contribute to the retention of flavor in products.

Matrix composition effects — microwave baking:

While the absolute losses of esters were much greater during the microwave baking of cookies relative to conventional baking, the retention profile of aroma compounds during microwave baking followed similar trends based on composition (Figure 5). The full fat cookies retained the higher molecular weight esters to a greater extent, but the low fat and meringue cookies were similar.

Stage of flavor incorporation: Flavorings are usually premixed with either the fat or aqueous ingredients of the dough to facilitate better distribution. We found that ester

Figure 3. Influence of cookie formulation on the retention of esters during the baking of cookies (conventional oven)

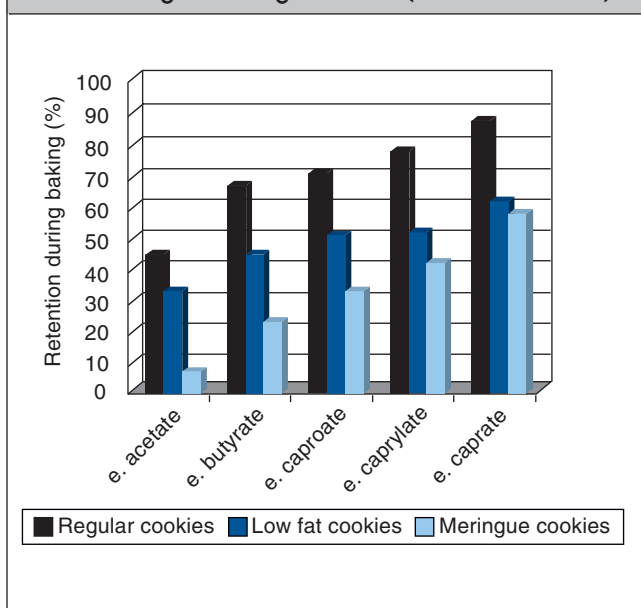
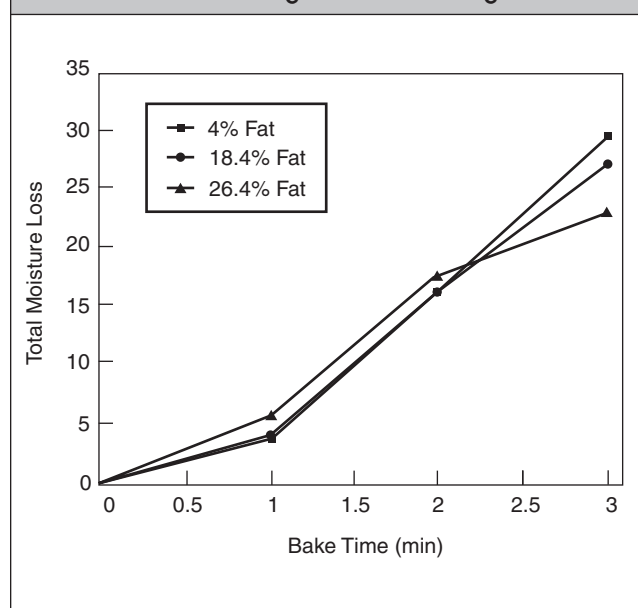


Figure 4. Effect of fat level on moisture loss from a cake during microwave baking¹



loss during dough preparation ranged from 42 percent (ethyl caprate) to 63 percent (ethyl acetate) if aroma compounds were added to the liquid components (egg whites and yolks) (Table 3). These losses were much greater than expected, and may be partially explained by the long mixing time. An alternative explanation is that esterases have been reported in flour, and we may have been getting some hydrolysis of our esters into the corresponding alcohols and acids. We did not conduct any experiments to determine if esterases were active in the dough.

In order to limit aroma loss during mixing via evaporation, it was possible to add the esters after the dry ingredients, i.e. just before baking. We assumed that a shorter blending time would still distribute the aroma in the dough, but reduce the losses during this process. Results show that this process significantly decreased aroma loss during preparation (Table 5). However, the addition of aroma compounds in the “solid phase” of the dough considerably increased aroma loss during baking (compare Tables 3 and 4) and, thus, little was gained by this change in procedure.

Results and Discussion: Influence of Baking Method on Aroma Retention

Microwave effects: Microwave baking consistently results in a greater loss of aroma compounds than conventional baking (Figure 6). For example, normal fat cookies ranged in ester retention from 45-87 percent (depending upon ester) during conventional baking while retention in microwave-baked cookies ranged from 7-72 percent (data not presented). The data in Figure 6 on low-fat cookies follows similar trends. Some of this effect is likely due to a non-uniform temperature profile of cookies baked in the microwave oven. The existence of hot spots would result in greater losses of volatiles than the lower temperature areas and result in a lower overall aroma retention. However, a major factor causing such differences in aroma retention relates to the inherently greater rates of moisture loss during microwave cooking, and the resultant effect this has on the loss of volatiles. This observation is consistent with previous studies and has been adequately discussed in the literature.^{1, 4, 5}

Influence of baking time/temperature on aroma losses during baking: Two different times/temperatures were used in a conventional oven. Flavor retention in cookies baked at a lower oven temperature over a longer period had approximately a twofold better ester retention in low-fat cookies (425°F vs. 375°F, Figure 6). A study of aroma loss kinetics gives a partial explanation. Cookies were analyzed at different stages of baking (after 1', 2', 3' and 10' of baking in a conventional oven at 375°F). The results (Figure 7) show that the aroma loss mainly occurs during the first minute of baking (97 percent loss of ethyl acetate after 1 min). This loss occurs before any surface crust forms, which may present a barrier to aroma loss. It appears that the higher baking temperature results in greater aroma losses before this barrier can form.

Figure 5. Influence of cookie composition on ester retention during microwave baking

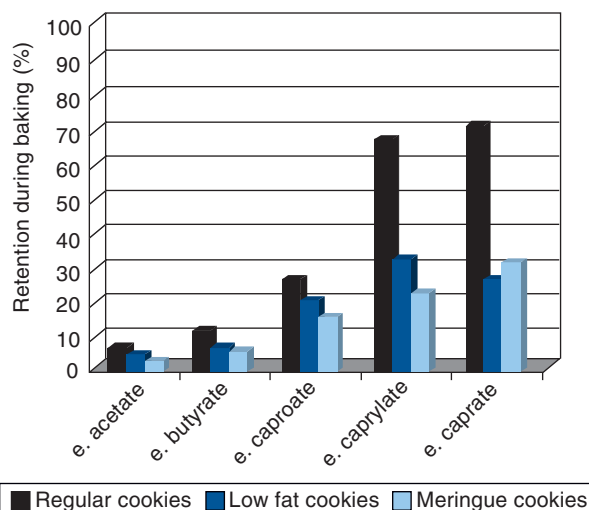


Table 3. Influence of the incorporation stage (liquid phase) of aroma compounds on their retention during baking (regular cookies; conventional oven (375°F/10'))

Flavors	Loss During Preparation ^a	Loss During Baking ^b	Total Loss ^c
Ethyl acetate	62.5	58.0	84.3
Ethyl butyrate	55.0	30.7	68.8
Ethyl caproate	59.4	30.1	71.6
Ethyl caprylate	41.4	17.8	51.8

^apercentage of the initial concentrations of aroma compounds
^bpercentage of concentrations before baking
^cpercentage of initial concentrations of aroma compounds

Table 4. Influence of the incorporation stage (before baking) of aroma compounds on their retention during baking (regular cookies; conventional oven (375°F/10'))

Flavors	Loss During Preparation ^a	Loss During Baking ^b	Total Loss ^c
Ethyl acetate	48.6	82.3	90.9
Ethyl butyrate	39.8	54.4	72.5
Ethyl caproate	31.1	42.7	60.5
Ethyl caprylate	25.3	43.8	58.0

^apercentage of the initial concentrations of aroma compounds
^bpercentage of concentrations before baking
^cpercentage of initial concentrations of aroma compounds

Figure 6. The influence of temperature/time and method of baking on ester retention in low-fat cookies

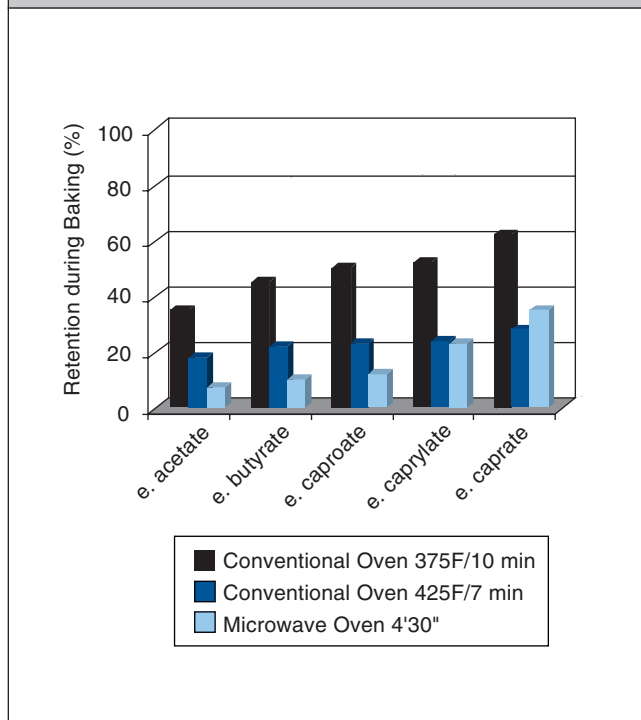
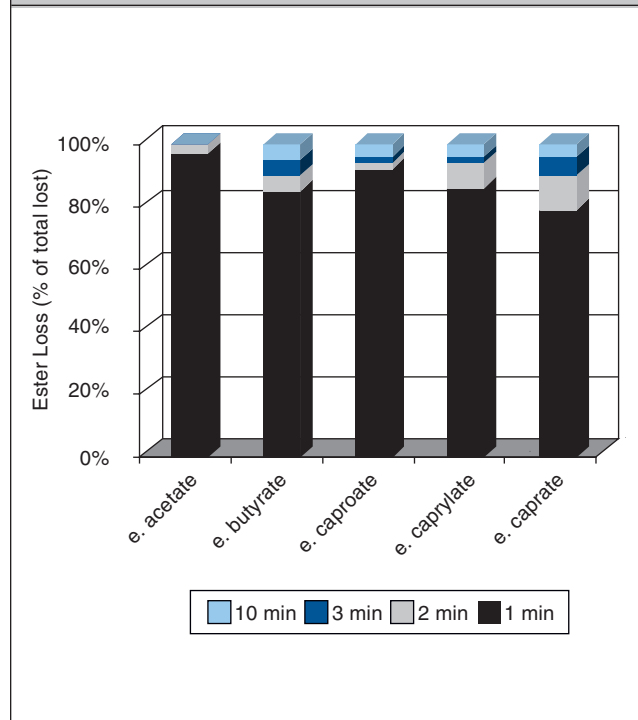


Figure 7. Losses of esters from full-fat cookies as a function of baking time



Encapsulation to Protect from Aroma Loss During Baking

The previous results have shown that flavor loss during cookie preparation and baking can be very significant. In order to minimize these losses, we evaluated flavor losses using different means of flavoring. We studied ester loss from the dough and during baking, when they were added in a liquid form (ethanol solvent), encapsulated form (spray dried with N-Lok or gum acacia as carrier), and two controlled release forms (done by Robertet Flavors Inc.). Results showed that the utilization of encapsulated flavorings considerably increased flavor retention during dough preparation (Figure 8). Adding the esters in an encapsulated form improved retention, the magnitude depending on the ester considered.

Adding the flavoring in an encapsulated form also resulted in improved retention of the esters during baking (Figure 9). While the encapsulated flavorings are soluble in water and one would expect their release in the cookie dough, they were retained substantially better during subsequent baking. It appears that there was not enough moisture in the cookie dough to release the flavoring until later in baking and thus, they were retained better. The carrier used in encapsulation influences the retention of esters as well. Gum acacia appears to provide better retention of all of the esters compared to using N-Lok as the encapsulating matrix. We do not have any data to aid in speculation as to why this difference in performance is observed.

The addition of controlled release properties to the spray dried flavorings again increased their retention dur-

ing baking. The effect was most pronounced for the most volatile esters (ethyl acetate and ethyl butyrate), and was insignificant for the least volatile. The implications of this are that often the most volatile aroma compounds carry the freshness of a flavoring, strawberry for example, and these notes are very readily lost during baking. This leaves the baked good flavor. Thus, the differences we observed for encapsulated flavorings (or those with controlled release properties) may have significant implications in how one achieves fresh flavors in baked products.

Conclusion

Direct thermal desorption appears to be a good way to analyze solid samples, such as cookies: this method is rapid (it does not require any sample preparation; a run is about 35 min long) and gives reliable and reproducible results. The most important limitation of the TDS was the sensitivity. Indeed, the usual candidates for a TDS/GC analysis are samples with a volatile level in the range of 1-100,000 ppm (w/w) and a moisture content of less than 5 percent. Since our cookie dough had a high water content (about 10-40 percent w/w, varying with formulation), this caused freezing and plugging of the column during cryofocusing. In order to adapt the TDS extraction to our samples, it was necessary to reduce the sample size and use relatively high flavor concentrations (600 ppm [w/w]).

We have demonstrated that the cookie formulation (increased fat content improves flavor retention), method of baking (conventional oven is superior to microwave baking), time/temperature of baking (lower temperature and

Figure 8. The retention of esters during dough preparation — influence of using esters in alcohol solvents vs. encapsulated forms

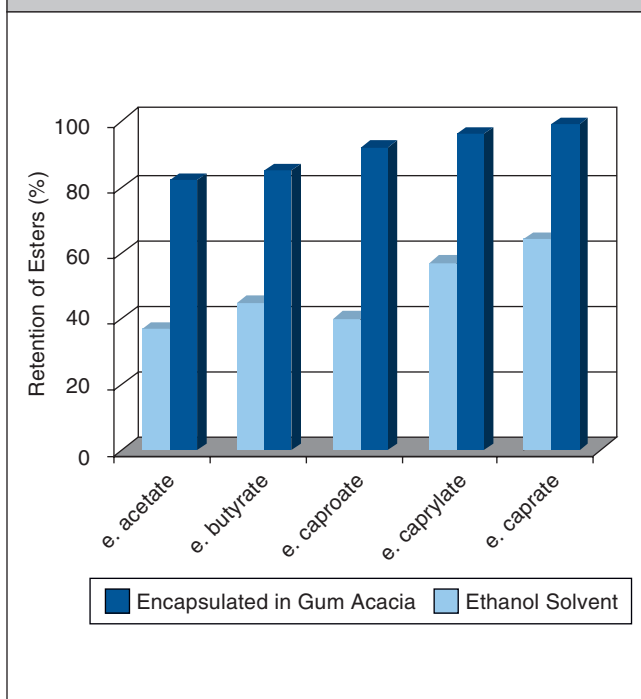
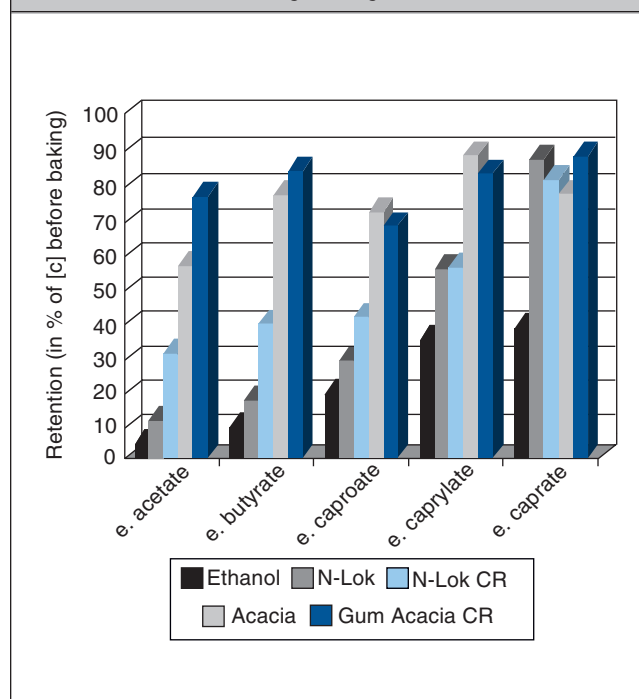


Figure 9. Influence of flavor form (liquid, spray dried and controlled release (CR)) on the retention of esters during baking of cookies



longer time is better than higher temperature and shorter time) and means of flavoring (spray fried with controlled release>spray dried>liquid flavorings) all influence the retention of flavorings both during cookie dough preparation and the baking of dough. We expect that the use of encapsulated flavorings will permit imparting fresh notes to baked goods.

References

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