



(86) Date de dépôt PCT/PCT Filing Date: 2004/12/16
(87) Date publication PCT/PCT Publication Date: 2005/07/28
(45) Date de délivrance/Issue Date: 2013/05/14
(85) Entrée phase nationale/National Entry: 2006/06/21
(86) N° demande PCT/PCT Application No.: EP 2004/014468
(87) N° publication PCT/PCT Publication No.: 2005/068601
(30) Priorité/Priority: 2004/01/13 (US10/756,617)

(51) Cl.Int./Int.Cl. *C11D 17/00* (2006.01),
C11D 3/50 (2006.01)
(72) Inventeurs/Inventors:
KERSCHNER, JUDITH LYNNE, US;
SHAFER, GEORGIA LYNN, US;
NUNN, CHARLES CRAIG, US;
FARRELL, TERENCE JAMES, US
(73) Propriétaire/Owner:
UNILEVER PLC, GB
(74) Agent: BERESKIN & PARR LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : COMPOSITIONS ET PROCEDE DE PREPARATION DE PAINS DE SAVON A FAIBLE TENEUR EN
TENSIOACTIF SOLUBLE PERMETTANT DE RENFORCER LE DEPOT/LONGEVITE DE PARFUM
(54) Title: COMPOSITIONS AND PROCESS FOR PREPARING CLEANSING BARS COMPRISING LOW LEVELS OF
SOLUBLE SURFACTANT FOR ENHANCED FRAGRANCE DEPOSITION/LONGEVITY

(57) **Abrégé/Abstract:**

The invention relates to perfume-containing bar compositions in which the effect of the perfume(s) (e.g., longevity) is enhanced relative to comparative bars in that perfume-containing bar of the invention, comprise less than about 35 % soluble surfactant. The invention further comprises a process for enhancing deposition/longevity of perfume, for example, by controlling the level of soluble active relative to insoluble active and/or by increasing levels of perfume.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
28 July 2005 (28.07.2005)

PCT

(10) International Publication Number
WO 2005/068601 A1

(51) International Patent Classification⁷: C11D 17/00,
3/50, A61K 7/00

New Jersey 07506 (US). **SHAFER, Georgia, Lynn** [US/US]; Unilever R & D Edgewater, 45 River Road, Edgewater, New Jersey 07020 (US). **NUNN, Charles, Craig** [US/US]; Unilever R & D Edgewater, 45 River Road, Edgewater, New Jersey 07020 (US). **FARRELL, Terence, James** [US/US]; Unilever R & D Edgewater, 45 River Road, Edgewater, New Jersey 07020 (US).

(21) International Application Number:
PCT/EP2004/014468

(22) International Filing Date:
16 December 2004 (16.12.2004)

(74) Agents: **MULDER, Cornelis, Willem, Reinier** et al.; Unilever Intellectual Property Group, Patent Department, Colworth House, Sharnbrook, Bedford Bedfordshire MK44 1LQ (GB).

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/756,617 13 January 2004 (13.01.2004) US

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for AE, AG, AU, BB, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NA, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only*): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London Greater London EC4P 4BQ (GB).

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, SY, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only*): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (*for IN only*): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

Published:
— *with international search report*

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **KERSCHNER, Judith, Lynne** [US/US]; 22 Ravine Drive W., Hawthorne,

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COMPOSITIONS AND PROCESS FOR PREPARING CLEANSING BARS COMPRISING LOW LEVELS OF SOLUBLE SURFACTANT FOR ENHANCED FRAGRANCE DEPOSITION/LONGEVITY

(57) Abstract: The invention relates to perfume-containing bar compositions in which the effect of the perfume(s) (e.g., longevity) is enhanced relative to comparative bars in that perfume-containing bar of the invention, comprise less than about 35 % soluble surfactant. The invention further comprises a process for enhancing deposition/longevity of perfume, for example, by controlling the level of soluble active relative to insoluble active and/or by increasing levels of perfume.



WO 2005/068601 A1

- 1 -

COMPOSITIONS AND PROCESS FOR PREPARING CLEANSING BARS
COMPRISING LOW LEVELS OF SOLUBLE SURFACTANT
FOR ENHANCED FRAGRANCE DEPOSITION/LONGEVITY

5 The present invention relates to delivery of perfume performance from cleansing bar systems. Specifically, it relates to a process for enhancing perfume performance (measured as perfume enhancement factor or "PEF") by formulating bars in such manner as to decrease the soluble
10 surfactant to perfume component(s) ratio.

The ratio of soluble surfactant to perfume component in a bar can in turn be controlled by decreasing the level of soluble surfactant (e.g., by controlling the amounts of
15 generally less soluble, saturated, longer chain length fatty acid or fatty acid soaps versus amounts of generally more soluble, saturated, shorter chain length fatty acid or fatty acid soaps); and/or by increasing level of perfume.

20 Soap bars consist of a blend of different chain length fatty acid soaps. Some of the fatty acid soaps (e.g., typically shorter chain length C₁₄, C₁₂ and below as well as some unsaturated soaps, such as oleate) from which the bars are made are soluble (by "soluble" is generally meant it
25 dissolves at greater than 1 wt.% level in water at less than about 40°C; it should be understood that solubility may refer to single soaps/surfactants or to mixtures/complexes of soaps and/or surfactants which, as a mixture or complex, have solubility within the defined parameters); and some
30 (e.g., C₁₆, C₁₈ and higher chain lengths) are insoluble or

- 2 -

substantially insoluble (again insolubility may refer to mixtures or complexes).

A "typical" soap bar consists of mixtures of saponified nut
5 oils (generally producing more lower chain length, soluble fatty acid soaps) and saponified non-nut oils (generally producing more higher chain length, insoluble fatty acid soaps) which will comprise the various chain length fatty acid and various saturated and unsaturated fatty acid soaps.
10 A typical 85/15 bar, for example, is 85 % tallow (comprising longer chain soaps generally required for the structuring when bars are extruded) and 15 % coconut (containing shorter, more soluble soaps which yield good foam and other attributes). Such 85/15 soaps will generally contain about
15 50-60 % soluble actives.

The applicants have now found that, when the level of soluble actives is kept low (e.g., below about 35 % by wt. of bar composition, more preferably below 30 % by wt., even
20 more preferably below about 25 % of final bar being soluble active, active being soap or synthetic surfactant), then the fragrance delivery is enhanced relative to delivery of fragrance from a bar having higher levels of soluble active in the final bar. In one embodiment of the invention, the
25 bar with low levels of soluble active is predominantly a soap bar or bar comprising a mixture of soap and free fatty acid but, as noted, the bar can be any bar where the amount of the soluble surfactant (e.g., soap, synthetic) is kept at a level of below about 35 % by wt. of final bar.

- 3 -

There are a number of references which disclose compositions having mixtures of short and long chain, saturated and unsaturated fatty acids possibly mixed with variety of ions to form soaps. No art of which applicants are aware, however, discloses the criticality of maintaining levels of soluble active below certain level (35 % of total active) to enhance perfume delivery or a process/method of enhancing such delivery using the specific compositions of the invention.

10

U.S. Patent No. 5,387,362 to Tollens et al. discloses compositions containing a tailored mixture of Mg, Na and K ions reacting with lauric acid, select C₁₄-C₁₈ fatty acids as well as oleic acid to generate soap base. A related reference is U.S. Patent No. 5,540,852 to KeFauver et. al. There is no disclosure in either reference of compositions with perfume and levels of soluble soaps which must be below certain levels, nor a disclosure of a process for enhancing perfume delivery (e.g., enhanced PEF). Indeed, there is no recognition of preparing bars to ensure the level of soluble soap must comprise no higher than 35 % of total surfactant.

15

20

25

30

U.S. Patent No. 5,262,079 to Kacher et al. discloses partially neutralizing fatty acids to form a network for a framed bar and also contains high levels of anionic surfactant plus nonionic firmness aids. There is no discussion of compositions with perfume and levels of soluble active below certain level or of processes to enhance perfume delivery. That is, there is no direction or suggestion to prepare bars to ensure final level of soluble active is no more than 35 % of total actives. The reference

- 4 -

also relates to framed bars versus extrusion bars of the subject invention.

U.S. Patent No. 6,121,216 to Narath et al. discloses a way to improve processing of a syndet bar which incorporates amphoteric as a mildness aid. Processing efficiency is increased by minimizing levels of soap, especially unsaturated soaps. That soluble active must comprise less than 35 % of the total active, and the influence of such low level on perfume enhancement are not disclosed.

According to the present invention there is provided a bar composition comprising:

- (a) 0.5 % to 35 % by wt. soluble surfactant active or actives;
- (b) perfume;
- (c) 0.5 % to 20 % by wt. water;
- (d) 0.1 % to 99 % by wt. filler, wherein the filler is a mixture of long chain saturated fatty acids and long chain saturated fatty acid soaps;

wherein solubility is defined by dissolution of surfactant active or active combination of greater than about 1 % by wt. in water at 40°C;

wherein the bar has performance enhancement factor ≥ 2.2 PEF based on ratio of perfume deposited from the bar relative to that deposited from a standard control; and

wherein the bar composition comprises 0 - 12.5 mol% unsaturated fatty acid and less than 5 % by wt. C₁₄ or lower chain length in final soap/fatty acid mixture.

- 5 -

The remainder of bar (e.g., 0.1 % to 65 % by wt.) may comprise 0.5 % to 20 %, preferably 0.5 % to 15 % by wt. water and 0.5 % to 99 %, preferably 1 % to 70 % by wt. of "filler materials".

5

Such filler materials may range from anything which can hold together or "structure a bar" including insoluble actives (insoluble soaps and/or fatty acids), organic and inorganic structurant materials and any one of thousands or more of materials which can be used as bar components.

10

The only criticality is that soluble surfactant comprises no more than 35 % of bar by wt., and that the bar is solid enough to function as a "bar" (e.g., have yield stress of at least 90 kPa as measured by standard cheese-wire method with a 200g weight and cheese wire diameter of 0.5 millimetres).

15

Also disclosed herein is a process for enhancing perfume retention/longevity of perfume which process comprises minimizing the level of soluble surfactant actives in a bar relative to a typical bar comprising greater than about 35 %, generally comprising 40 % to 70 %, soluble surfactant active.

20

Further disclosed are bar compositions comprising:

25

- (1) 20 % to 75 % fatty acid soap and free fatty acid mixture (most of which is insoluble but some of which may be soluble);
- (2) 0 to 20 % synthetic surfactant active; and

30

- 6 -

(3) balance water, minors and fillers/other bar components,

wherein the percent of active (1) and (2) which is soluble is less than about 35 % by wt. total bar composition; and wherein PEF \geq to about 2.2, preferably greater than 2.3, more preferably greater than 2.5 relative to a standard control (for example 85/15 soap bar).

10 The invention will be described by way of example only with reference to the accompanying figures, in which:

- Figure 1 is a graph showing the fraction of soap into which the perfume partitions. The graph shows that most perfume by far will partition into the soluble filtrate. While not wishing to be bound by theory, it is for this reason that it is believed the percent of soluble surfactant should be minimized, i.e., to minimize loss of perfume through soluble component, thereby making it unavailable for good perfume performance;

- Figure 2 is a graph of surfactant to perfume ratio and it's impact on two different perfume components. Both components partition into the surfactant phase and therefore provide higher surfactant to perfume ratios (i.e., greater surfactant content), and perfume impact is reduced;

- Figure 3 is a graph of the effect of surfactant to perfume ratio on perfume performance for a 2:1 sodium oleate:sodium laurate system. Increasing surfactant:perfume ratio results in decreased perfume impact;

- 7 -

- Figure 4 is a graph of predicted impact measurements for benzyl acetate and limonene in surfactant solutions with increasing surfactant to perfume ratios. The higher the ratios, the lower the perfume impact;

5

- Figure 5 is a graph comparing GC head space data of soap systems having different solid levels. Generally, those with "high solids" (i.e. less amount of soluble soap) have significantly higher fragrance headspace. As such, again, bars with a lower amount of soluble soap will have greater perfume impact;

10

- Figure 6 shows GC data of two bar solutions at different dilutions, one with 1 % perfume compared to one with 4 % perfume. Raising the level of perfume relative to surfactant also enhances perfume impact above the solution.

15

- Figure 7 shows GC data from a SPME measurement of perfume deposited on the skin. This graph compares the deposition of perfume from a bar formulated with "high solids" (low soluble surfactant) and a control bar with low solids (high soluble active). Clearly the graph indicates more fragrance deposited to the skin from the "high solids" bar; and

20

25

- Figure 8 shows the GC data from a SPME measurement of perfume deposited on the skin. This graph compares the deposition from a bar containing 1 % perfume and a bar containing 4 % perfume (same high soluble active formulation). Again the graph indicates that increasing the

30

- 8 -

perfume:soluble surfactant ratio provides greater perfume deposition.

The present invention relates to bar compositions comprising perfume and to processes for enhancing perfume retention/longevity using bar composition having no more than a defined amount of soluble active as a percent by wt. of total bar. The soluble surfactant active is believed to enhance perfume partitioning into the active, thereby reducing available perfume and decreasing perfume performance.

Another way of defining a low level of soluble active is to define a soluble surfactant:perfume ratio. Specifically, activity or impact of perfume can be seen to increase as the ratio of surfactant to perfume decreases. While such a ratio from a "typical" soap bar may be 60:1, the compositions of the subject invention have ratios less than 40:1, preferably lower than 35:1, more preferably less than 30:1 and more preferably lower than 25:1. The lower the ratio, the greater the perfume impact.

The ratio in turn can be decreased either by decreasing the level of soluble surfactant (including synthetics and/or soluble soap), as has been noted, and/or by increasing the level of perfume.

The crux of the invention is therefore really that the total amount of soluble surfactant in the final bar composition be below about 35 % of the bar composition because it is into the soluble surfactant (rather than any insoluble surfactant) that perfume will more readily partition in use,

- 9 -

more readily wash off and ultimately reduce the perfume performance.

The type of soluble surfactant is therefore really
5 irrelevant, other than the fact that a soluble surfactant
(or mixtures or complexes of surfactants) is/are defined as
one(s) that have/has a solubility in water greater than 1
wt.% at temperature of 40°C. If the surfactant(s) does not
meet this solubility limitation, there is therefore no limit
10 on the amount of "insoluble" surfactant which can be used.
It is for this reason that increasing the amount of
insoluble surfactant relative to soluble surfactant (or
conversely decreasing the amount of soluble surfactant in
the bar composition) is one way of increasing the fragrance
15 performance (e.g. fragrance deposition or fragrance
longevity in use).

An example of how this works is if we consider a blend of
different chain length fatty acid soaps. As indicated above,
20 shorter chain length fatty acid/fatty acid soap (e.g.,
typically shorter than C₁₆, particularly shorter than C₁₄)
are "soluble" (and hence are also sometimes considered
"harsher") while, for example, C₁₆ and above chain length
saturated fatty acids/fatty acid soaps are typically
25 insoluble. By increasing the ratio of longer chain length to
shorter chain length saturated soaps (as the applicants have
done for different reasons in co-pending, co-filed
application relating to fatty acid/fatty acid soap based bars
with relatively low synthetic), it is possible to enhance
30 perfume longevity or effect.

- 10 -

In particular, in one embodiment the invention comprises:

- (1) 0.5 % to 35 % by wt. soluble surfactant/actives;
- (2) perfume;
- 5 (3) 0.5 % to 20 %, preferably 0.5 % to 15 % by wt. water; and
- (4) 0.1 % to 99 % by wt., preferably 1 % to 70 % by wt. fillers which may comprise structuring materials including insoluble actives and organic
10 and inorganic materials which structure and fill.

The amount of soluble active/surfactant of (1) comprises no more than 35 % by wt. of total bar, or the enhanced effect of the invention is not observed relative to bars having for
15 example greater than about 35 % soluble active. Stated differently, only those bars with soluble surfactant less than 35 % by wt. of bar composition have performance enhancement factor of ≥ 2.2 PEF, preferably ≥ 2.3 , more preferably ≥ 2.5 based on ratio of perfume deposited from bar
20 relative to that deposited from a standard control.

With regard to the surfactant/active, there is no constraint on what the active may be. It may be any of the myriads of anionic surfactants, nonionic surfactants,
25 amphoteric/zwitterionic surfactants, cationic surfactants well known to those skilled in the art with the only criticality being that no more than 35 % of active (including mixtures or complexes) may be soluble, wherein solubility is defined as at least 1% by wt. soluble in water
30 at 40°C.

- 11 -

Perfume molecules include but are not limited to:

acetanisol; amyl acetate; anisic aldehyde; anisole;
anisylalcohol; benzaldehyde; benzyl acetate; benzyl acetone;
5 benzyl alcohol; benzyl formate; hexenol; d-carvone;
cinnamaldehyde; cinnamic alcohol; cinnamyl acetate; cinnamyl
formate; cis-3-hexenyl acetate; Cyclal C (2,4-dimethyl-3-
cyclohexen-1-carbaldehyde); dihydroxyindole; dimethyl benzyl
carbinol; ethyl acetate; ethyl acetoacetate; ethyl
10 butanoate; ethyl butyrate; ethyl vanillin; tricyclo decenyl
propionate; furfural; hexanal; hexenol; hydratropic alcohol;
hydroxycitronellal; indole; isoamyl alcohol; isopulegyl
acetate; isoquinoline; ligustral; linalool oxide; methyl
acetophenone; methyl amyl ketone; methyl anthranilate;
15 methyl benzoate; methyl benzyl acetate; methyl heptenone;
methyl heptyl ketone; methyl phenyl carbonyl acetate; methyl
salicylate; octalactone; para-cresol; para-methoxy
acetophenone; para-methyl acetophenone; phenethylalcohol;
phenoxy ethanol; phenyl acetaldehyde; phenyl ethyl acetate;
20 phenyl ethyl alcohol; prenyl acetate; propyl butyrate;
safrole; vanillin; viridine; allyl caproate, allyl heptoate,
anisole, camphene, carvacrol, carvone, citral, citronellal,
citronellol, citronellyl acetate, citronellyl nitrile,
coumarin, cyclohexyl ethylacetate, p-cymene, decanal,
25 dihydromyrcenol, dihydromyrcenyl acetate, dimethyl octanol,
ethyl linalool, ethylhexyl ketone, eucalyptol, fenchyl
acetate, geraniol, gerynyl formate, hexenyl isobutyrate,
hexyl acetate, hexyl neopentanoate, heptanal, isobornyl
acetate, isoeugenol, isomenthone, isononyl acetate, isononyl
30 alcohol, isomenthol, isopulegol, limonene, linalool, linalyl
acetate, menthyl acetate, methyl chavicol, methyl octyl

- 12 -

acetaldehyde, myrcene, naphthalene, nerol, neral, nonanal, 2-
 nonanone, nonyl acetate, octanol, octanal, α -pinene, β -
 pinene, rose oxide, α -terpinene, γ -terpinene, α -terpinenol,
 terpinolene, terpinyl acetate, tetrahydrolinalool,
 5 tetrahydromyrcenol, undecenal, veratrol, verdox, allyl
 cyclohexane propionate, ambrettolide, AmbroxTM DL
 (dodecahydro-3a,6,6,9a-tetramethyl-naphtho[2,1-b]furan),
 amyl benzoate, amyl cinnamate, amyl cinnamic aldehyde, amyl
 salicylate, anethol, aurantiol, benzophenone, benzyl
 10 butyrate, benzyl iso-valerate, benzyl salicylate, cadinene,
 campylcyclohexal, cedrol, cedryl acetate, cinnamyl
 cinnamate, citronellyl isobutyrate, citronellyl propionate,
 cuminic aldehyde, cyclohexylsalicylate, cyclamen aldehyde,
 dihydro isojamone, diphenyl methane, diphenyl oxide,
 15 dodecanal, dodecalactone, ethylene brassylate, ethylmethyl
 phenylglycidate, ethyl undecylenate, exaltolide,
 GaloxilideTM (1,3,4,6,7,8-hexhydro,4,6,6,7,8,8-hexamethyl-
 cyclopenta- γ -2-benzopyran), geranyl acetate, geranyl
 isobutyrate, hexadecanolide, hexenyl salicylate, hexyl
 20 cinnamic aldehyde, hexyl salicylate, α -ionone, β -ionone, γ -
 ionone, α -irone, isobutyl benzoate, isobutyl quinoline, Iso
 E SuperTM (7-acetyl,1,1,2,3,4,5,6,7,8-octahydro,1,1,6,7-
 tetramethyl naphthalene), cis-jasmone, lilial, linalyl
 benzoate, 20 methoxy naphthalene, methyl cinnamate, methyl
 25 eugenol, γ -methylionone, methyl linolate, methyl linolenate,
 musk indanone, musk ketone, musk tibetine, myristicin, neryl
 acetate, δ -nonalactone, γ -nonalactone, patchouli alcohol,
 phantolide, phenylethyl benzoate, phenylethylphenylacetate,
 phenyl heptanol, phenyl hexanol, α -santalol, thibetolide,

- 13 -

tonalid, δ -undecalactone, γ -undecalactone, vertenex,
vetiveryl acetate, yara-yara, ylangene.

The "filler" material is everything else in the bar other
5 than "soluble" surfactant, water and perfume or perfume
ingredients. It should be understood that "filler" itself
may be soluble and, as indicated above, is defined only as
being something other than the specifically recited
surfactant, perfume or water.

10

The structurant can be long chain, preferably straight and
saturated (e.g., C₁₆-C₂₄) fatty acids, fatty acid soaps or
ester derivatives thereof; and/or branched long chain,
preferably straight and saturated alcohol or ether
15 derivative.

It may be polyalkylene glycol of MW 2000 to 20,000.

Other ingredients which may be used as structurants and or
20 fillers include starches, sugars, maltodextrins and other
polysaccharides. They may also include waxes and unsaponified
fats.

Inorganic fillers such as talc, kaolin, clays and calcium
25 salts may also be used.

Structuring aids can also be selected from water soluble
polymers chemically modified with hydrophobic moiety or
moieties, for example, EO-PO block copolymer,
30 hydrophobically modified PEGs such as POE(200)-glyceryl-

- 14 -

stearate, glucam DOE 120 (PEG 120 Methyl Glucose Dioleate), and Hodag™ CSA-102 (PEG-150 stearate), and Rewoderm^(R) (PEG modified glyceryl cocoate, palmate or tallowate) from Rewo Chemicals.

5

Other structuring aids which may be used include Amerchol™ Polymer HM 1500 (Nonoxynyl Hydroethyl Cellulose).

10 In addition, the bar compositions of the invention may include optional ingredients as follows; sequestering agents, such as tetrasodium ethylenediaminetetraacetate (EDTA), EHDP or mixtures in an amount of 0.01 % to 1 %, preferably 0.01 % to 0.05 %; and coloring agents, opacifiers and pearlizers such as zinc stearate, magnesium stearate, TiO₂, EGMS (ethylene glycol 15 monostearate) or Lytron™ 621 (Styrene/Acrylate copolymer); all of which are useful in enhancing the appearance or cosmetic properties of the product.

The compositions may further comprise antimicrobials such as 20 2-hydroxy-4,2'4' trichlorodiphenylether (DP300); preservatives such as dimethyloldimethylhydantoin (Glydant™ XL1000), parabens, sorbic acid etc.

25 The compositions may also comprise coconut acyl mono- or diethanol amides as suds boosters, and strongly ionizing salts such as sodium chloride and sodium sulfate may also be used to advantage.

- 15 -

Antioxidants such as, for example, butylated hydroxytoluene (BHT) may be used advantageously in amounts of about 0.01 % or higher if appropriate.

5 Cationic polymers as conditioners which may be used include Quatrisoft™ LM-200 Polyquaternium-24, Merquat Plus™ 3330 - Polyquaternium 39; and Jaguar^(R) type conditioners.

10 Polyethylene glycols as conditioners which may be used include:

Polyox™	WSR-205	PEG 14M,
Polyox™	WSR-N-60K	PEG 45M, or
Polyox™	WSR-N-750	PEG 7M.

15

Other ingredients which may be included are exfoliants such as polyoxyethylene beads, walnut shells and apricot seeds.

20 In a specific embodiment the invention relates to fatty acid soap/fatty acid based bars comprising:

- (1) 20 % to 75 % by wt. fatty acid/fatty acid soap;
- (2) 0 to 20 % synthetic active;
- (3) balance water and fillers (as defined);

25 wherein percent active of soluble active of (1) and (2) and (3) of if any) is less than about 35 % by wt. total bar; and

where $PEF \geq 2.2$ relative, preferred >2.3 , more preferably >2.5 to a standard control bar.

30

- 16 -

In a further embodiment, the invention relates to a process of enhancing perfume performance (e.g. deposited/longevity) from a bar comprising:

- (1) surfactant active;
- 5 (2) perfume;
- (3) water; and
- (4) filler

wherein said process comprises decreasing the level of soluble surfactant active relative to insoluble surfactant active and/or filler. Specifically, the bar should have
10 level of soluble active less than 35 %, preferably less than 30 %, of final bar composition and PEF \geq 2.2 relative to a standard control.

15 In a further embodiment of the invention, the invention relates to an process of enhancing perfume deposition/longevity from a bar comprising:

- (1) surfactant active;
- (2) perfume;
- 20 (3) water; and
- (4) filler

wherein said process comprises increasing level of perfume.

EXAMPLES

25

Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts or ratios of materials or conditions or reaction, physical properties of materials
30 and/or use are to be understood as modified by the word "about".

- 17 -

Where used in the specification, the term "comprising" is intended to include the presence of stated features, integers, steps, components, but not to preclude the presence or addition of one or more features, integers, steps, components or groups thereof.

The following examples are intended to further illustrate the invention and are not intended to limit the invention in any way.

10

Unless indicated otherwise, all percentages are intended to be percentages by weight. Further, all ranges are to be understood to encompass both the ends of the ranges plus all numbers subsumed within the ranges.

15

EXAMPLE 1

To better understand how bar compositions can affect longevity of perfume, studies were conducted on the overall effects of soluble and insoluble surfactant on fragrance properties using a standard 85/15 soap bar (85 % tallow and 15 % coconut oil). In considering fatty acid soap ratios in an 85/15 soap bar, it is easy to predict how much soap will be solubilized upon dilution or in use. Since 50-60 % of the bar is sodium oleate and sodium laurate (soluble soaps), it can be assumed at least this amount will solubilize with enough water.

Studies were performed to determine how much perfume partitioned into the soluble and the insoluble portions of the diluted soap systems. With these learnings, two model

30

- 18 -

"mortar" systems and three model soap systems were then investigated to determine the effects of soluble and insoluble surfactant in a bar on actual perfume performance.

5 To understand where the perfume partitioned during soap bar use, a 5 % dilution of fragrance 85/15 soap was made, filtered and solid rinsed. The three samples (solid, filtrate, rinse) were extracted (using a Soxtherm™ extractor) to see the amount of perfume in each phase. Extraction of
10 filtered 85/15 soap showed that about 74 % of the perfume was in the filtrate which contains about 45 % of the soap (soluble portion). Thus, upon dilution, the soluble soap to perfume ratio is actually 50 to 55:1 as could be predicted by the fatty acid distribution in a typical 85/15
15 (tallow/coconut oil) soap. This is seen from Figure 1. This thus clearly showed partitioning of perfume into the soluble fraction.

EXAMPLE 2

20 Using the perfume partitioning information of Example 1 (e.g., most perfume went with soluble surfactant and therefore was not available for the enhanced perfume effect), the applicants established a set of model studies
25 with a range of soluble soap systems having different soap:perfume ratios. Specifically, a soluble soap model with 1:1 ratio sodium laurate and sodium oleate was used with soap:perfume ratio 20:1 to 60:1 and compared to 85/15 soap bar containing 1 % perfume (1:1 benzyl acetate:limonene
30 mixture). Five soap dilutions were made for each sample, 40 %, 25 %, 10 %, 5 % and 1 %. Figure 2 shows the equilibrium

- 19 -

headspace measurements for each sample at every dilution point (graphed as mg perfume in sample instead of percent dilution).

5 As can be seen, as the surfactant:perfume ratio increase (a function of more soluble soap components) for each of these perfume components, perfume impact or GC (gas chromatography) area count decreases and that, at a soap:perfume ratio of 60:1, perfume impact approaches that of a 85/15 bar.

10

Without wishing to be bound by theory, it is believed that, since limonene is so volatile, it reaches perfume saturation at low perfume levels and thus, even in 5 % soap samples, perfume headspace plateaus. Benzyl acetate is less volatile
15 so, in most samples, headspace saturation has not yet been achieved. Even under these conditions, it is clear for both molecules that the amount of soluble surfactant greatly impacts perfume performance and that a soap:perfume ratio of 60:1 more clearly represents results from a bar than any
20 other total sample.

EXAMPLE 3

The experiments of Example 2 were repeated with a 2:1 sodium
25 oleate:sodium laurate system. The 2:1 base system showed similar trends in perfume performance, again indicating that increasing the surfactant:perfume ratio results in decreasing perfume impact of a benzyl acetate:limonene mixture (1:1) (Figure 3).

30

- 20 -

EXAMPLE 4

A mathematical model for similar dilution profiles as shown
Figures 4 was used to calculate the theoretical perfume
5 performance based on the perfume type and the
perfume:surfactant ratio. Dilution curves were calculated
for sodium dodecylsulfate (SDS)/benzyl acetate and
SDS/limonene. These curves correlate very well with the
experimental values obtained. The calculated data is
10 depicted as solid lines in the figures, while the symbols
represent actual data points (Figure 4). This validates the
assumption that the actual surfactant:perfume ratio achieved
during use with an 85/15 bar is ~50-60:1, and this is most
likely driving the perfume performance.

15

EXAMPLE 5 - Effect of Soluble/Insoluble Soap on Perfume
Performance in Bars

The GC analysis of model soap systems and theoretical
20 predictions indicate that the amount of soluble soap in a
bar directly correlates to the perfume performance. That
is, the higher the soluble soap content in a bar, the lower
the fragrance impact and hence deposition.

25 To test this theory in real soap bars, several simplified
soap systems were identified that contained varying levels
of soluble/insoluble soap. The simplest approach toward
preparing these bars was to add insoluble long chain soaps
(sodium stearate) to the 2:1 sodium oleate:sodium laurate
30 model mortar. Three model bar systems were chosen and
compared directly to a standard 85:15 soap. The first model

- 21 -

bar was a "low solids" sample composed of 20 % sodium stearate and 80 % 2:1 sodium oleate/sodium laurate and the second was a "high solids" sample composed of 80 % sodium stearate and 20% 2:1 sodium oleate/ sodium laurate. In
5 addition to these systems, an 85/15 model system composed of 47.5 % sodium ASAD (mixture of sodium stearate and sodium palmatate)/14.9 % sodium cocoate/37.6 % sodium oleate was prepared.

10 The addition of the 85/15 model system was to determine if small changes in the composition of soap with similar I.V. values (iodine values - relate to level of unsaturation) would effect perfume performance. The two perfumes tested in these bases were 1:1 benzyl acetate:limonene mix and a
15 standard perfume mixture, both dosed at 1 wt.%.

After preparation of these soap bar systems, equilibrium GC headspace measurements were conducted on the solid samples at different bar dilutions (40 %, 25 %, 10 %, 5 %, and 1 %).
20 As predicted, decreasing the level of soluble soap ("high solids" bar) directly enhances the perfume impact in the soap base. The GC results show that the 85/15, the 85/15 model system and the "low solids" bars all have similar perfume headspace profiles, while the "high solids" bar with
25 only 20 % soluble soap has significantly higher fragrance headspace (Figure 5).

EXAMPLE 6 - Decreasing Ratio by Adding Perfume

30 Another way to decrease the soluble soap:perfume ratio is to add more perfume to the bar. If the goal is to get

- 22 -

comparable perfume performance in a soap bar to that in a shower liquid, matching the soluble surfactant:perfume ratio is important. Typical shower liquids are formulated with 15-20 % surfactant and 1 % perfume, so the soluble
5 soap:perfume ratio is ~20:1.

To mimic this in a standard 85:15 soap bar in which the soluble soap: perfume ratio is ~65:1, 4 % perfume would have to be formulated in the bar (i.e. soluble soap:perfume ratio
10 of ~65:4). A standard 85:15 soap bar with 4 % perfume was prepared to test the theory. As expected, decreasing the ratio of surfactant: perfume from 85:1 to 20:1 significantly increases the perfume headspace over the product compared to an 85:15 soap bar with 1 % perfume (Figure 10).

15

EXAMPLE 7 - Solid Phase Microextraction Results

Perfume performance over washed skin is the ultimate test to determine if the experimental differences measured as impact
20 from diluted products can predict actually fragrance deposition in an in-use situation. Solid phase microextraction (SPME) is used to collect perfume over skin after it is washed with a product and the SPME needle is then injected in the GC for analysis.

25

This SPME experiment was performed with the "high solids" bar (~20:1 soluble soap:perfume ratio) versus an 85/15 control (~65:1 soluble soap:perfume ratio) both with 1 % perfume (Figure 6). The surfactant:perfume ratio is 20:1 in
30 the "high solids" bar, achieved by lowering the amount of soluble surfactant in the actual bar. Again, as expected,

- 23 -

the analysis results indicate that lowering the amount of soluble surfactant in a bar significantly increases perfume deposition.

5 Another way to decrease the soluble soap:perfume ratio is to add more perfume to the bar. If the goal is to get comparable perfume performance in a soap bar to that in a shower liquid, matching the soluble surfactant:perfume ratio is important. To mimic a low active bar with only 20 %
10 soluble active and 1 % perfume, a standard 85:15 soap bar in which the soluble soap: perfume ratio is ~65:1 would have to be formulated with 4 % perfume in the bar (i.e. soluble soap:perfume ratio of ~65:4).

15 A standard 85:15 soap bar with 4 % perfume was prepared to test the theory, and a similar SPME deposition experiment was conducted on arms washed with 0.5g of an 85/15 soap bar containing 1 % perfume and 0.12 g of an 85/15 bar with 4.25 % perfume (Figure 7). Therefore in both experiments, an
20 equal amount of perfume was dosed to the skin, with the only difference between the samples being the surfactant:perfume ratio. The results of this SPME analysis suggests that when formulated perfume amount was increased so that soluble surfactant:perfume ratio is ~20:1 in a soap bar, the amount
25 of perfume deposited on the skin increases significantly, although the results are not as great as lowering over soluble active content in the bar.

While increasing the perfume amount in a typical 85/15 soap
30 bars provides greater deposition, it does so at a prohibitive cost, and a standard soap bar with 4 % perfume

- 24 -

smells very strong (too strong for consumer liking). A more effective use of the 1 % perfume typically added to a soap bar would be the preferred technology option, and formulating soap bars with lower soluble active content achieves this goal.

EXAMPLE 8

One example of a bar cleansing composition with a low amount of soluble surfactant includes predominantly soap/fatty acid compositions which can be made by reacting components having a low mol% of unsaturated fatty acid (0-12.5 mol%) (unsaturates are generally quite soluble); 50 to 87.5 mol% fatty acid of chain length C₁₆ or greater; and 12.5 to 50 mol% caustic (50 % resulting in full neutralization) to form a bar precursor which can then be blended with up to 25 % synthetic. Such a final bar has high amounts of soap/fatty acid, yet processes well and lathers unexpectedly well.

One example of such compositions (which can be prepared by neutralizing fatty acid with caustic, as noted, or by simply blending pre-formed soap with fatty acid) is as follows:

25

- 25 -

Molar Ratio of Soap/Fatty Acid		
C_{16}/C_{18}	$C_{18:1}$	NaOH
75	0	25
Nominal Composition		Weight %
Soap		46
Fatty Acid		25
Anionic (Fatty Alcohol Ether Sulfate)		7.5
Sodium Cocoyl Isethionate		7.5
Water		9
Sodium LAS		5

EXAMPLE 9

5

Many different personal cleansing bars were prepared, and fragrance deposition was measured by collecting the fragrance above washed arms immediately after the wash using SPME, and then analyzing the absorbed fiber with GC.

10

If the deposition of fragrance from a standard 85/15 soap bar is set at 1.0, a perfume enhancement factor (PEF) can be calculated for each product by determining the ratio of perfume deposited from different personal cleansing bars compared to the standard control. Typically a consumer perceivable difference in fragrance deposition is noted if the PEF is $\geq 2.2-2.5$. The following table lists the perfume enhancement factors for different personal cleansing

15

- 26 -

formulations as averaged from several washes on different people with respect to the total soluble active content in the product. As the amount of soluble surfactant is reduced to <35 %, a perceivable consumer benefit is noted (PEF \geq 2.2).

Product #	% Soluble Active	PEF (ave.)
1	50	1
2	45	1.06
3	40	2.1
4	40	1.8
5	30	2.75
6	30	3.2
7	23	3.9
8	22	5.1
9	20	3.8
10	20	4.2
11	20	4.7
12	20	6.0
13	18	2.5
14	18	3.3
15	15	3.5

The formulation ingredients for products 1-14 are summarized as follows:

Product 1 (85/15 soap formulation) contains 84.75 % 85 (Tallow)/15 (Coconut) Soap, 14.25 % Water and 1 % Perfume;

- 27 -

Product 2 contains 80 % 85 (Tallow)/15 (Coconut) Soap, 8.57 % Sorbitol, 4 % Glycerine, 1 % perfume, 1.5 % triethanolamine, 1.5 % propylene glycol, 2.87 % water, 0.56 % sodium chloride;

5

Product 3 contains 65.50 % 85 (Tallow)/15 (Coconut) Soap, 20 % Sodium Stearate, 13.5 % Water and 1 % Perfume;

10 Product 4 contains 65.5 % 85 (Tallow)/15 (Coconut) Soap, 20 % saponified hardened tallow, 13.5 % Water and 1 % Perfume;

Product 5 contains 45.5 % 85 (Tallow)/15 (Coconut) Soap, 40 % Sodium Stearate, 13.5 % Water and 1 % perfume;

15 Product 6 contains 45.5 % 85 (Tallow)/15 (Coconut) Soap, 40 % saponified hardened tallow, 13.5 % water and 1 % perfume;

20 Product 7 contains 51.9 % Sodium sterate/palmate mixture, 10 % Dove noodles, 7.24 % Water, 7 % disodium lauryl sulfosuccinate, 7 % sodium laureth sulfate; 5 % glycerine, 4 % cocamidopropyl betaine, 3.11 % fatty acid, 3 % PEG 1450, 1.75 % perfume;

25 Product 8 contains 33.65 % stearic/palmitic acid mix, 18.28 % sodium soap, 10.57 % sodium citrate, 10 % fatty acid ester sulfonate (Alpha-Step PC-48), 10 % sodium cocoylisethionate, 9 % water, 5 % glycerine, 2 % sodium dodecylbenzene sulfonate, 1 % perfume and 0.5 % titanium dioxide;

- 28 -

Product 9 contains 45.4 % Stearic/Palmitic acid mixture, 24.53 % Sodium stearate/palmitate mixture, 20 % Sodium cocoyl glycinate, 9.07 % water and 1 % perfume;

5 Product 10 contains 42.8 % stearic/palmitic acid mixture, 23.16 % sodium stearate/palmitate mixture, 20 % primary alcohol sulfate sodium salt (Sasolfin™ 23S), 7.54 % water, 5 % glycerine, 1 % fragrance and 0.5 % titanium dioxide;

10 Product 11 contains 60 % saponified hardened tallow, 25.5 % 85 (Tallow)/15 (Coconut) Soap, 13.5 % water and 1 % perfume;

Product 12 contains 60 % sodium stearate, 25.5 % 85 (Tallow)/15 (Coconut) Soap, 13.5 % water and 1 % perfume;

15

Product 13 contains 55 % Sucrose, 5 % Polyvinylpyrrolidone 40K, 15 % Sodium laurate, 2 % Sodium dodecylsulfate, 1.75 % Perfume, 0.5 % TiO₂, 0.2 % EDTA, 0.5 % EHDP and 20.05 % Water;

20

Product 14 contains 40 % Sucrose, 20 % Maltodextran 250, 15 % Sodium laurate, 2 % Sodium dodecylsulfate, 1.75 % Perfume, 0.5 % TiO₂, 0.2 % EDTA, 0.5 % EHDP and 20.05 % Water;

25 Product 15 contains 42.6 % stearic/palmitic acid mixture, 23 % sodium stearate/palmitate mixture, 15 % primary alcohol sulfate sodium salt (Sasolfin™ 23S), 8 % talc, 5 % glycerine, 5.4 % water and 1 % perfume.

- 29 -

EXAMPLE 10 - Sensory Panel Results

To determine whether the increase in measured fragrance
5 release from skin is actually perceivable by humans, a
trained sensory panel was used to evaluate and measure the
fragrance intensity over arms washed with these products.
In this study, the two products compared were Product 1
(85/15 soap control) and Product 10 (a low active bar) from
10 Example 9. This study would provide information on whether
a PEF of >2.5 is perceivable by the human nose.

In this study all "washes" were washed with both products so
a direct comparison of the products could be assessed
15 without having to take into account the differences in
fragrance properties in the individual people (different
deposition, different fragrance smell and different
background odors). This will allow a comparison of the
product performance regardless of the characteristics of the
20 individual being washed. The results are shown in Table 2,
and the sensory responses were recorded as an average of the
magnitude estimation score recorded by the panelists for all
three washes at the different time points.

- 30 -

Table 2: Fragrance Intensity Sensory Scores for Product 1 and Product 10

	Time After Wash	Average Sensory Score
Product 1 (~50% soluble surfactant)	5 minutes	28.5
	60 minutes	12.2
Product 10 (~20% soluble surfactant)	5 minutes	51.5*
	60 minutes	26.5*

5 *different at the 95% confidence level

The results in Table 2 represent the average scores for the panel for all six washed arms, 5 minutes and 60 minutes after the wash. Each person was washed with both products, one product on one arm and the other product on the second arm (washed arms were randomized). As is quite evident from the results, the fragrance impact from skin washed with Product 10 was perceived greater than that washed with Product 1 and these differences valid to a 95 % confidence level. The sensory panel results correspond well with the analytical measurements and similar results were noted with the other products that provided a measurable PEF of greater than 2.5.

CLAIMS

1. A bar composition comprising:
 - (a) 0.5 % to 35 % by wt. soluble surfactant active or actives;
 - (b) perfume;
 - (c) 0.5 % to 20 % by wt. water;
 - (d) 0.1 % to 99 % by wt. filler, wherein the filler is a mixture of long chain saturated fatty acids and long chain saturated fatty acid soaps;wherein solubility is defined by dissolution of surfactant active or active combination of greater than about 1 % by wt. in water at 40°C; wherein the bar has performance enhancement factor ≥ 2.2 PEF based on ratio of perfume deposited from the bar relative to that deposited from a standard control; and wherein the bar composition comprises 0 - 12.5 mol% unsaturated fatty acid and less than 5 % by wt. C₁₄ or lower chain length in final soap/fatty acid mixture.
2. A bar composition according to claim 1 having no more than 30 % by wt. soluble surfactant active.
3. A bar composition according to claim 1 or claim 2, wherein the surfactant active is selected from anionic, non-ionic, amphoteric/zwitterionic/cationic surfactants and mixtures thereof.
4. A bar composition according to claim 1, 2 or 3, wherein said filler comprises everything in the bar composition other than said surfactant, said water or said perfume.

5. A bar composition according to claim 4, wherein the filler further comprises polyethylene glycol, starch, maltodextrin, polysaccharides or mixtures thereof.
6. A bar composition according to any one of claims 1 to 5, wherein the bar has $PEF \geq 2.3$.
7. A bar composition according to any one of claims 1 to 6, wherein the bar has $PEF \geq 2.5$.

Fig.1.

Perfume extraction data of the solution and solid phases of a 5% solution of 85/15 soap.

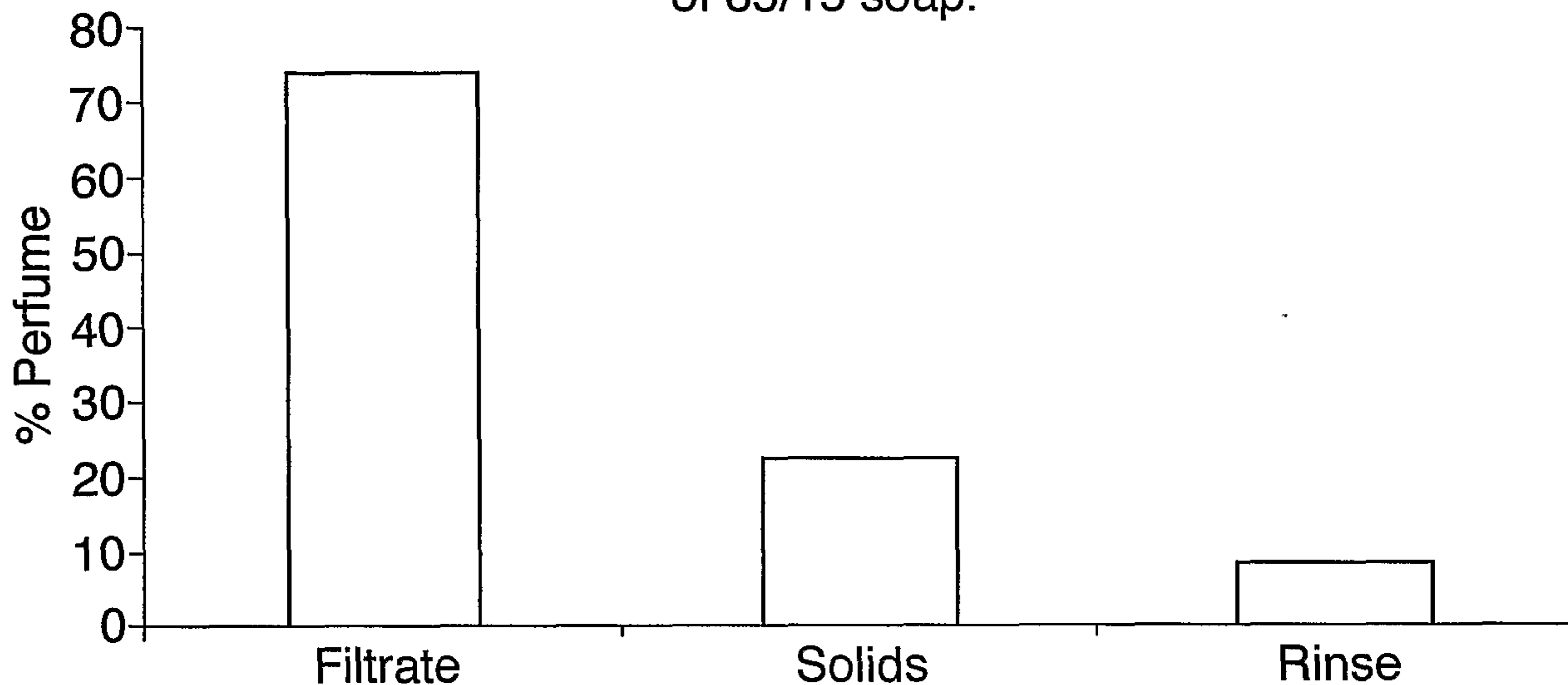
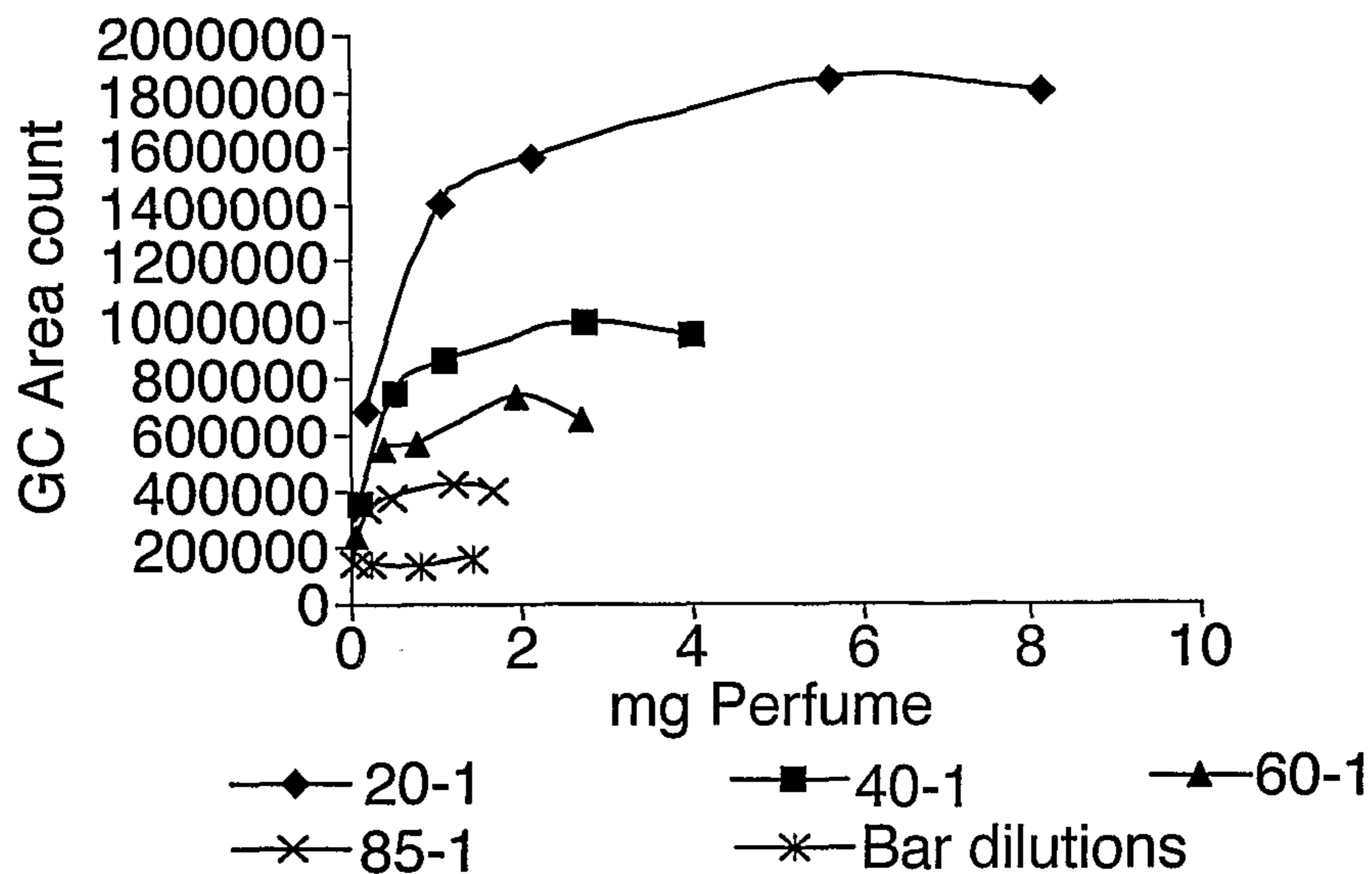


Fig.3.

Effect of surfactant:perfume ratio on perfume performance in 2:1 model system

1:1 Benzyl Acetate/Limonene



2/5

Fig.2.

Effect of surfactant:perfume ratio on performance of individual perfumes

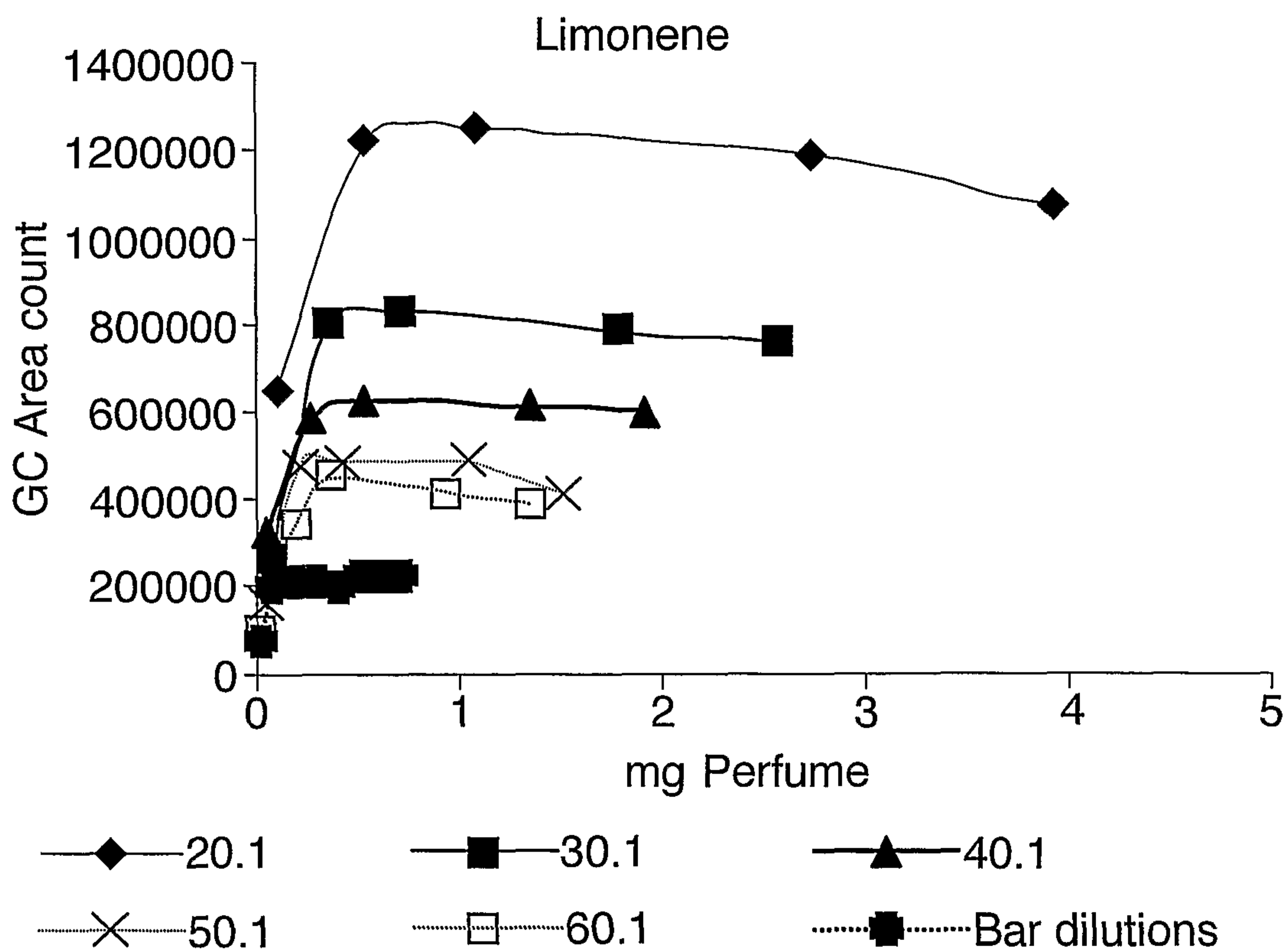
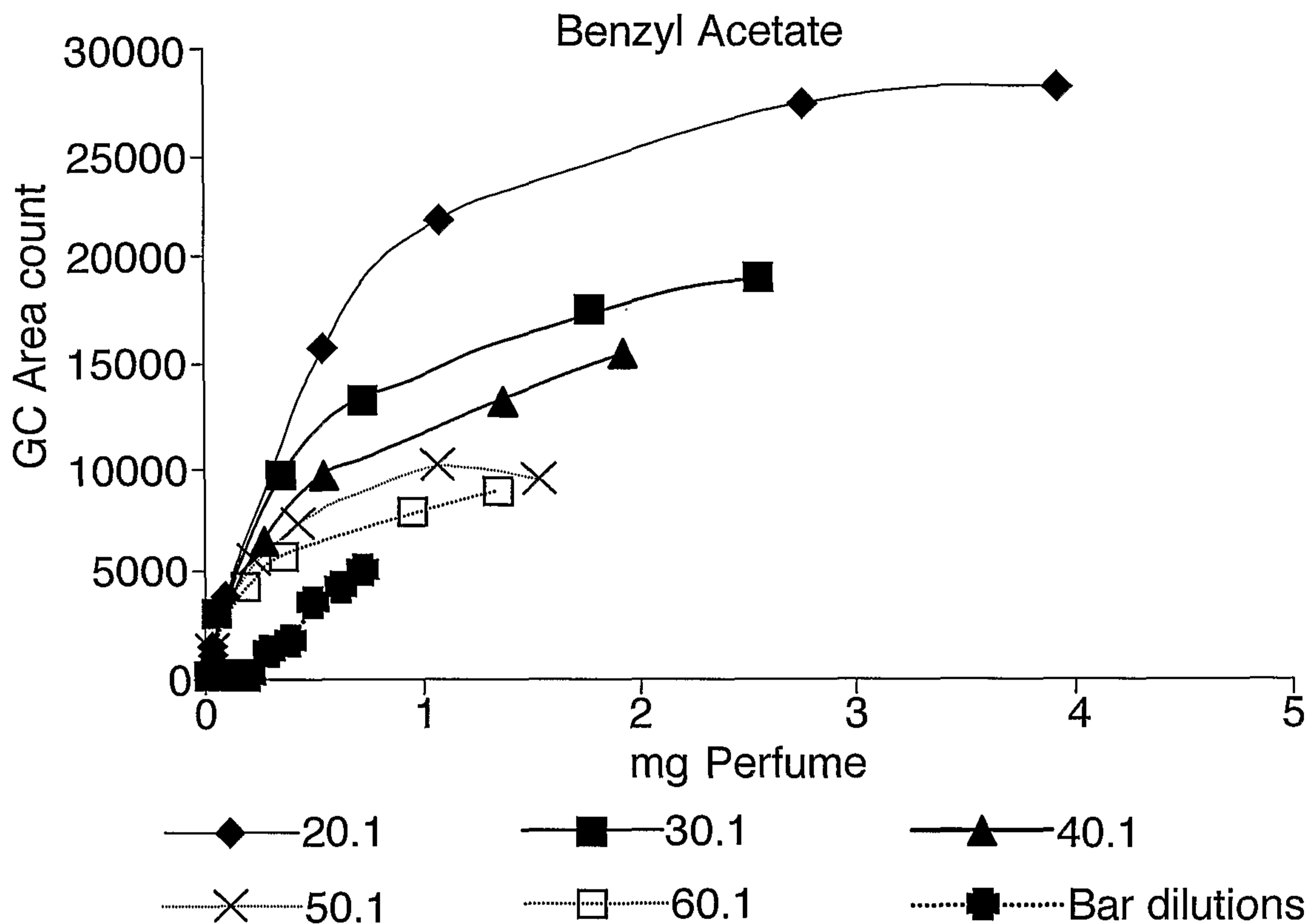
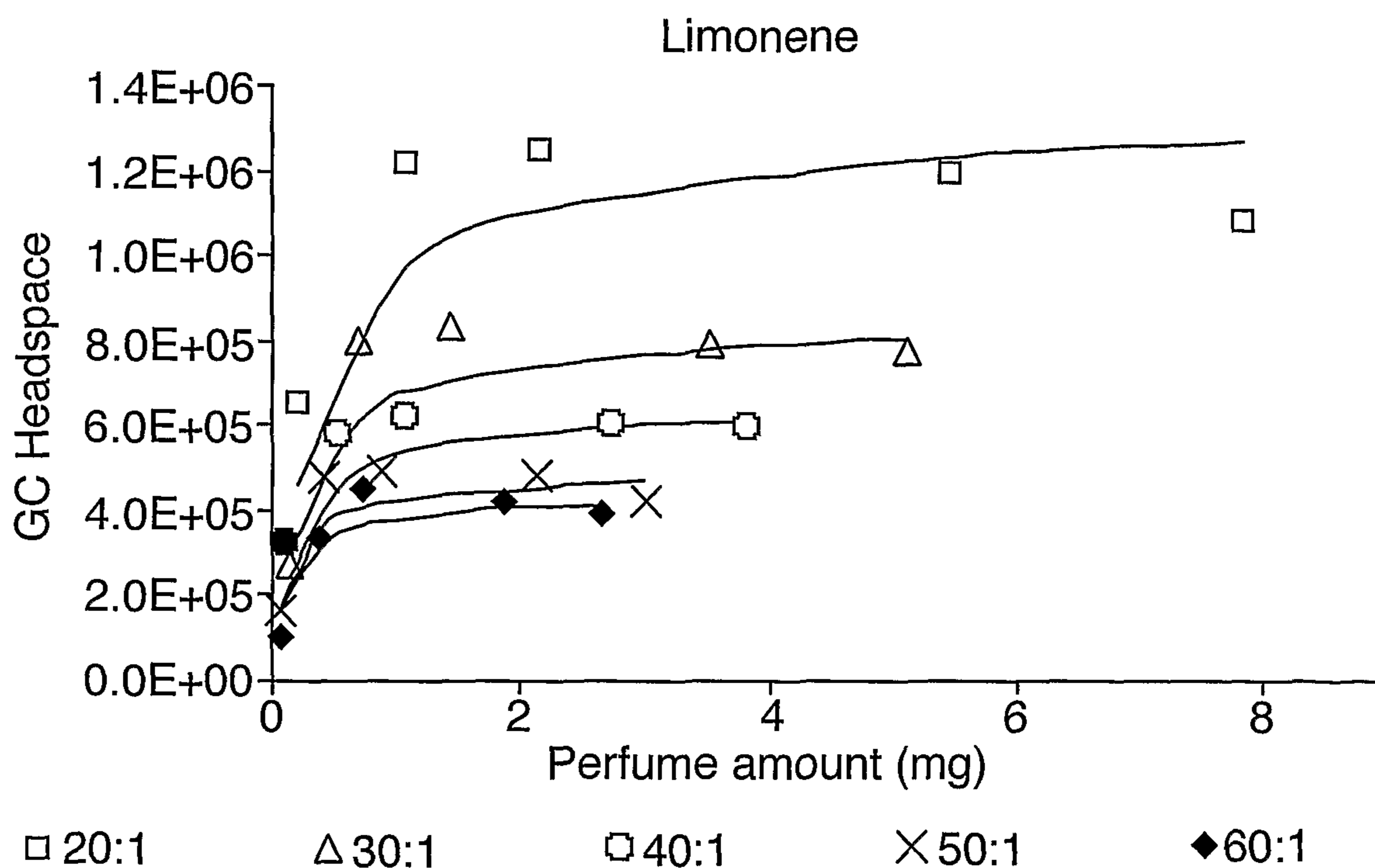
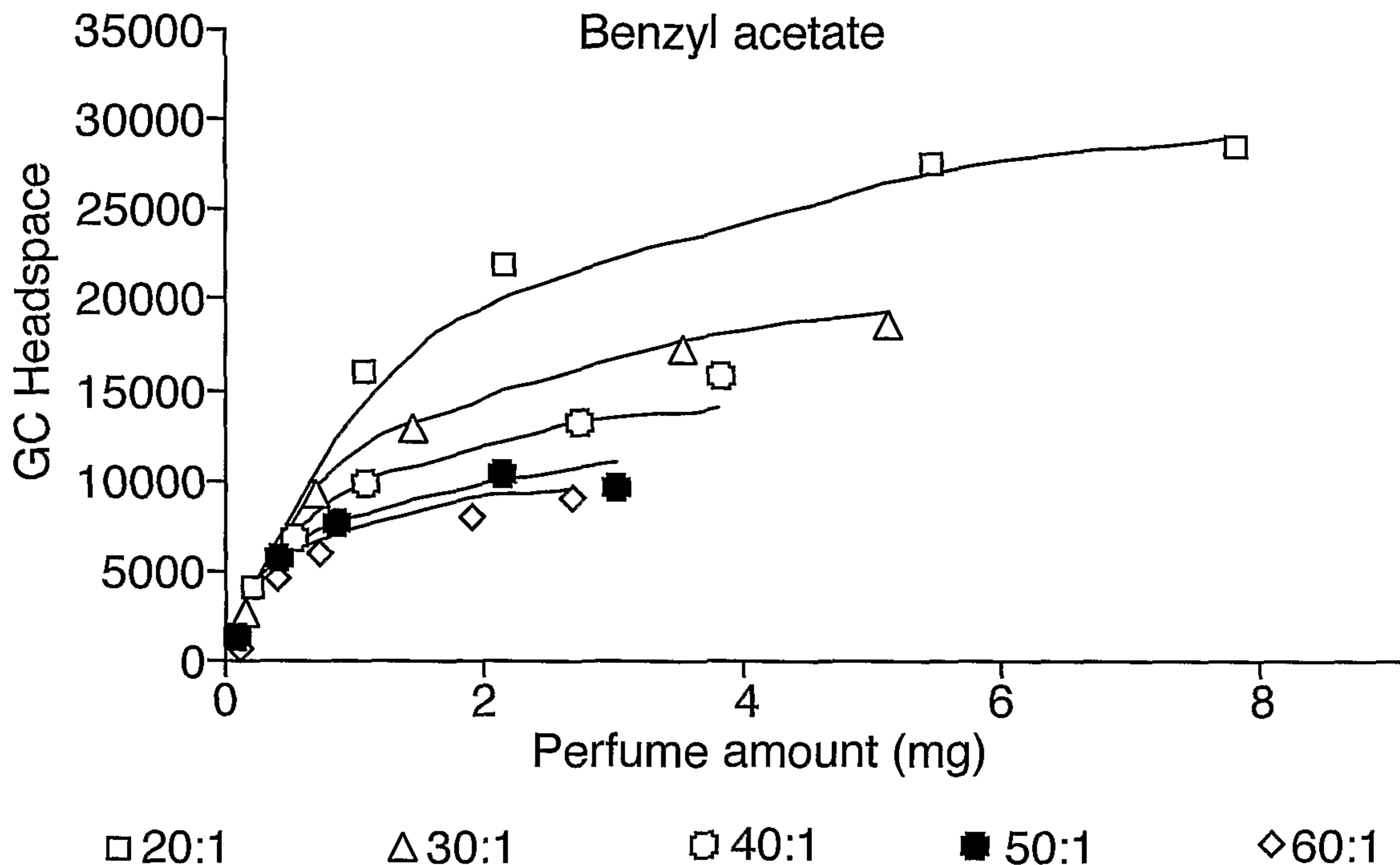


Fig.4.

Predicted values (solid lines) vs. experimental results (symbols) for benzyl acetate in surfactant solutions with increasing surfactant to perfume ratios



4/5

Fig.5.

GC Headspace data for soap systems with different solids levels

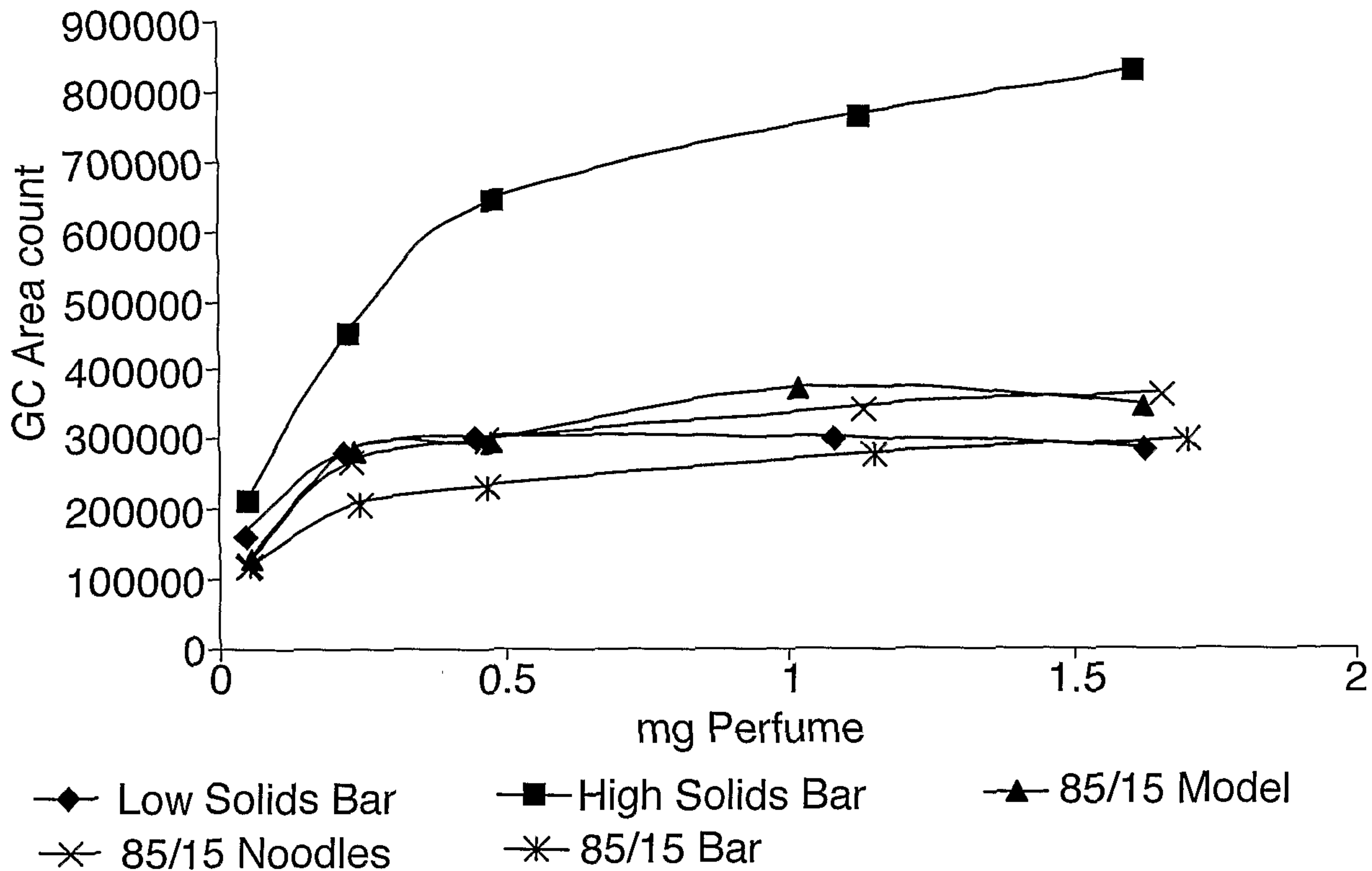
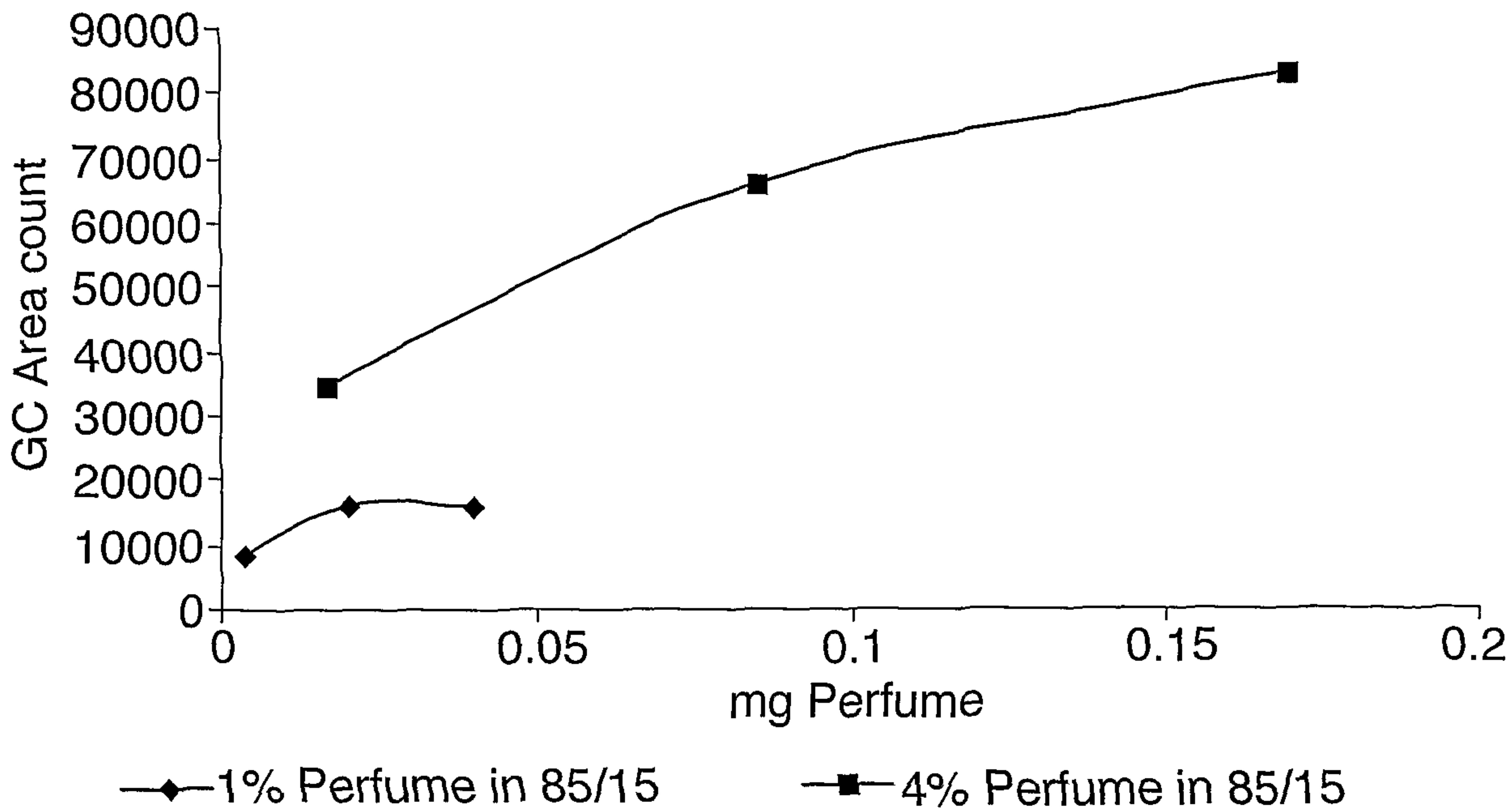


Fig.6.

GC Data comparing a soap bar with 1% perfume to a soap bar containing 4% perfume.



5/5

Fig.7.

SPME Data for arms washed with the "high solids" bar vs. an 85/15 bar

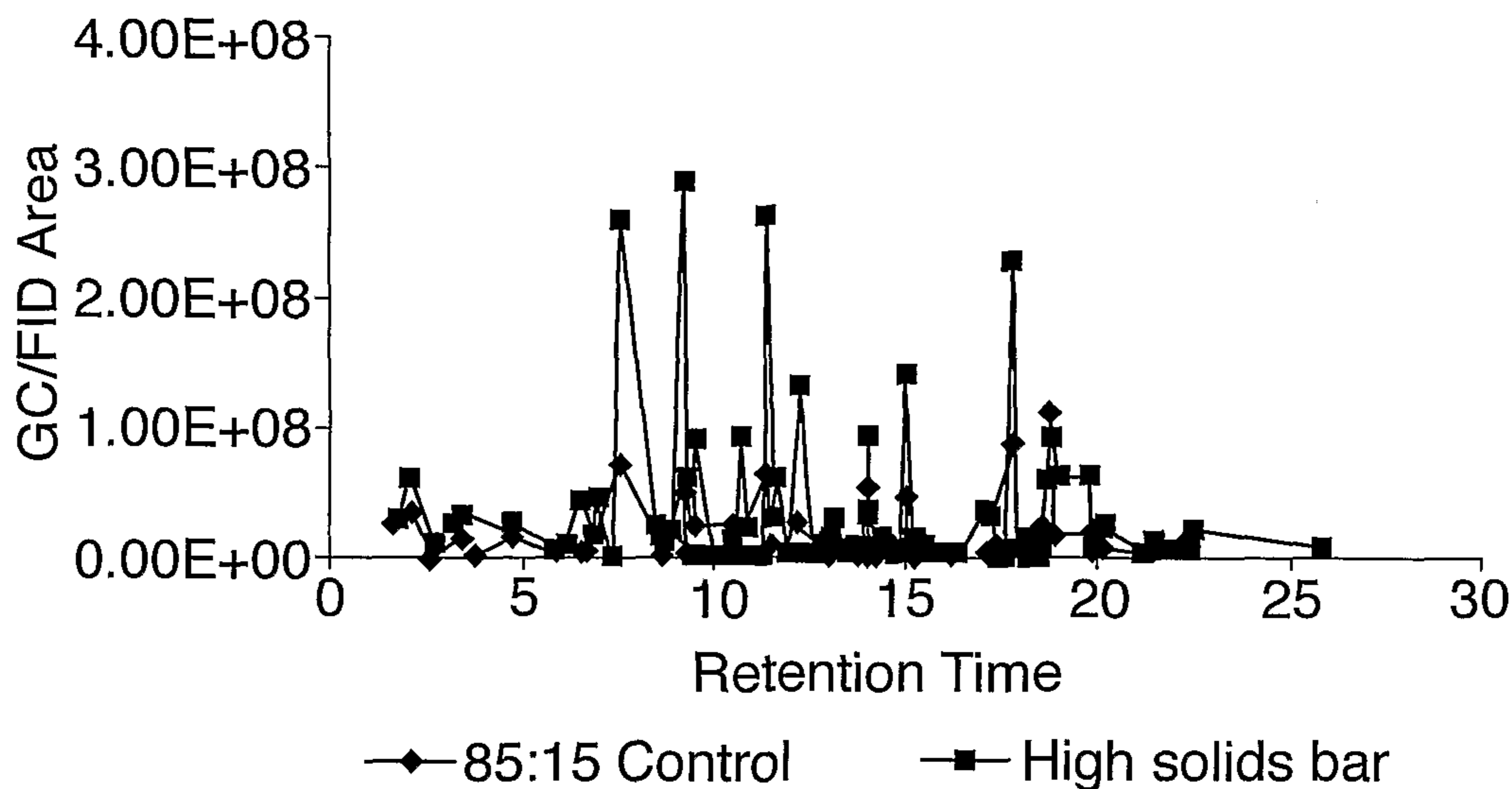


Fig.8.

SPME Data comparing arms washed with a soap bar with 1% perfume and with 4.5% perfume

