# FIT OR UNFIT - ELIMINATE THE UNCERTAINTY

Julie Arthur, Chemist Rachel Sanderoff, Chemist Janet M. Scalese, Chief Nonbeverage Products Laboratory

## **OVERVIEW**

- Eliminating Uncertainty and Subjectivity
  - Fitness Guidelines
    - Additions
    - Fenaroli's Use Levels
      - Worksheet
- Current Method Development
- Formulas Online

# FITNESS GUIDELINES

## GUIDELINES

- Additions to Guidelines:
  - Anise Oil
  - Fennel Oil
  - Tartaric Acid
  - Triacetin
  - Washed Extracts
  - 2% Total Flavor Chemicals
  - Citric Acid
  - Propylene Glycol

With mitigating ingredients

- Randomly selected tasted samples back to 1991
- Collected and compiled formula information
  - Normalized to 15% abv
- Compared to published use rate in Fenaroli's Handbook of Flavor Ingredients

#### • Determined:

- Any product containing at least one ingredient present at 5X or greater than the max use level is unfit for beverage purposes
- Guideline can be used with products containing mitigating ingredients

- Created an excel database
  - FEMA GRAS chemicals
  - Max Use Rate
    - Highest value (alcohol and nonalcoholic beverages)

#### BENZYL ACETOACETATE

Synonyms: Benzyl acetyl acetate; Benzyl  $\beta$ -ketobutyrate; Benzyl 3-oxobutanoate; Acetoacetic acid, benzyl ester (8CI); Benzyl acetylacetate; Benzyl 3-oxobutanoate; Butanoic acid, 3-oxo-, phenylmethyl ester (9CI); Phenylmethyl 3-oxobutanoate

CAS No.:	5396-89-4	FL No.:	09.406	FEMA No.:	2136	NAS No.:	2136
CoE No.:	244	EINECS No.:	226-416-4	JECFA No.:	848		

Description: Benzyl acetoaceate has a sweet, floral, fresh, balsamic, fruity odor similar to that of ethyl acetate.

Consumption: Annual: <1.00 lb Individual: 0.00000149 mg/kg/day

Regulatory Status:

CoE: Used provisionally. Bev.: 3 ppm; Food: 10 ppm

FDA: 21 CFR 172.515 FDA (other): n/a

JECFA: ADI: Acceptable; No safety concern at current levels of intake when used as a fla-

voring agent (2001).

Trade association guidelines: FEMA PADI: 4.791 mg

IOFI: n/a

Empirical Formula/MW:

$$C_{11}H_{12}O_3/192.22$$

Specifications: (Burdock, 1997)

Appearance	Oily liquid
Melting point	Approx. 240°C (162-164°C at 16 mmHg)

Solubility	Soluble in alkali solutions at room
Solubility	temperature

Reported uses (ppm): (FEMA, 1994)

Food Category	Usual	Max.
Alcoholic beverages	2.00	5.00
Baked goods	27.09	43.49
Chewing gum	19.00	37.45
Frozen dairy	11.02	22.21

Food Category	Usual	Max.
Gelatins, puddings	16.00	27.56
Nonalcoholic beverages	3.00	5.81
Soft candy	14.60	22.33

Synthesis: By heating ethyl acetoacetate and benzyl alcohol to 160°C.

Aroma threshold values: n/a Taste threshold values: n/a

Natural occurrence: Reported found in litchi (Litchi sinensis Sonn.).

### Calculation Spreadsheet

- Enter total weight
- Total Alcohol (box #10)
- FEMA #
- Weight of ingredient

#### Flavor Unfitness Worksheet

Formula Information:	
Total Weight	
Alcohol content (high end of box #10)	

Don't know how to use this worksheet? See the instructions below!

FEMA #	Ingredient	Weight of ingredient	ppm in flavor	ppm @ 15% ABV	MAX Use Level	Factor higher MAX Use Level	Fit or Unfit?	Remarks
	-		-	) <del>-</del> .	-	-	-	-
	-		-	-	-	-	-	-
	÷		-	Ε	-	-	-	-
	-		-	-	-	-	-	-
	-		-	-	-	-	-	-
	-		-	-	-	-	-	-
	-		-	-	-	-	-	-
	-		-	-	-	-	-	-
	-		-	) <b>=</b> .	-	-	-	-
	-		-	-	-	-	-	-
	÷		-	-	-	-	-	
	-		-	-	-	-	-	-
	-		-	-	-	-	-	-
			-	-	-	-	-	-
	-		-	-	-	-	-	-
	-		-	-	-	-	-	•
	-		-	-	-	-	-	•
	-		-	-	-	-	-	-
	-		-	-	-	-	-	-
	-		-	-	-	-	-	-

#### Flavor Unfitness Worksheet

Formula Information:	
Total Weight	100
Alcohol content (high end of box #10)	33.4

Don't know how to use this worksheet? See the instructions below!

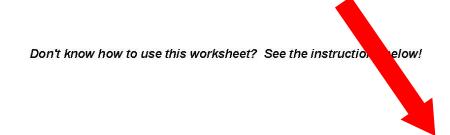
FEMA#	Ingredient	Weight of ingredient	ppm in flavor	ppm @ 15% ABV	MAX Use Level	Factor higher MAX Use Level	Fit or Unfit?	Remarks
2427	ETHYL BUTYRATE	0.04	400.0	179.6	37.88	4.7	FIT	*
2560	2-HEXENAL	0.01	100.0	44.9	6.7	6.7	UNFIT	-
	÷		0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	-	•
	-		0.0	0.0	-	-	-	•
	-		0.0	0.0	-	-	-	•
	_		0.0	0.0	-	-	-	•
	-		0.0	0.0	-	-	-	•
	-		0.0	0.0	-	-	-	•
	-		0.0	0.0	-	-	-	•
	-		0.0	0.0	-	-	-	•
	_		0.0	0.0	-	-	_	-
			0.0	0.0	-	: <del>-</del> :	-	-
	_		0.0	0.0	-	-	-	-
			0.0	0.0	-	-	-	•
	-		0.0	0.0	-	-	-	-
			0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	-	*

'FIT' or 'UNFIT' will display after values are entered.

# 'FIT (Max Use Level is higher)' appears in the Remarks column when the Max Use Level is higher than the ppm of the ingredient at 15% ABV.

#### Flavor Unfitness Worksheet

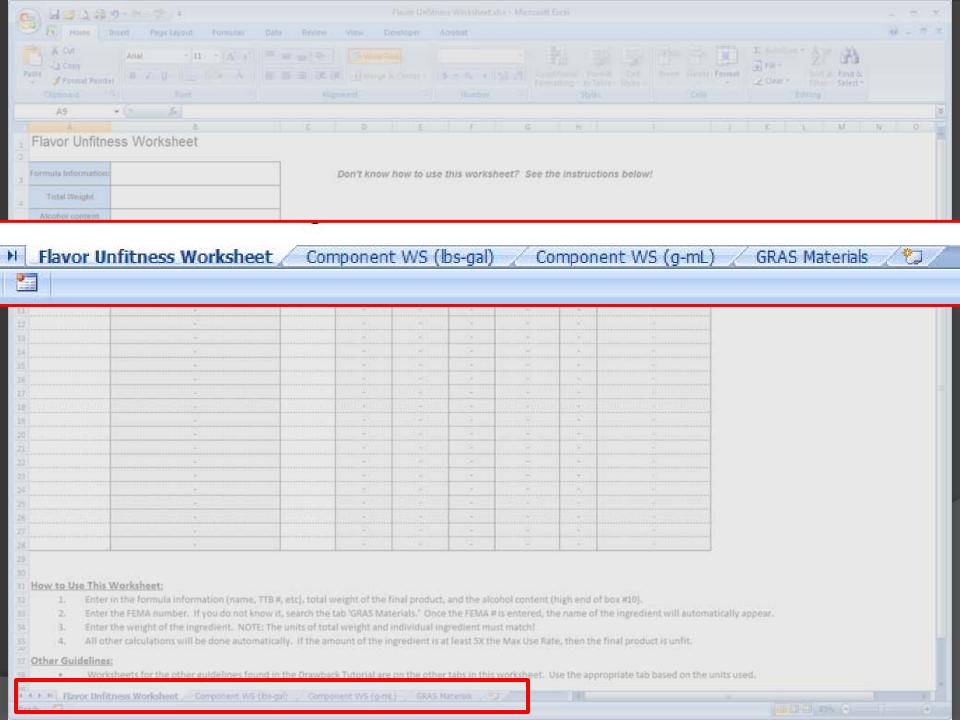
Formula Information:	
Total Weight	100
Alcohol content (high end of box #10)	45.9



FEMA #	Ingredient	Weight of ingredient	ppm in flavor	ppm @ 15% ABV	MAX Use Level	Factor higher MAX Use Level	Fit or Unfit?	Remarks
2127	BENZALDEHYDE	0.01	100.0	32.7	57.55	-	_	FIT (Max Use Level is higher)
	-		0.0	0.0	-	-	-	
	2		0.0	0.0	-	-	-	-
	<del>-</del>		0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	-	-
	4		0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	-	-
	<u>-</u>		0.0	0.0	-	-	-	_
	-		0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	-	-
	¥		0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	-	-
	<u> </u>		0.0	0.0	-	_	_	-
	-		0.0	0.0	-	-	-	-
	2		0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	_	-
	-		0.0	0.0	-	-	-	•
			0.0	0.0	-	-	-	-
	-		0.0	0.0	-	-	-	
	-		0.0	0.0	-	-	-	-

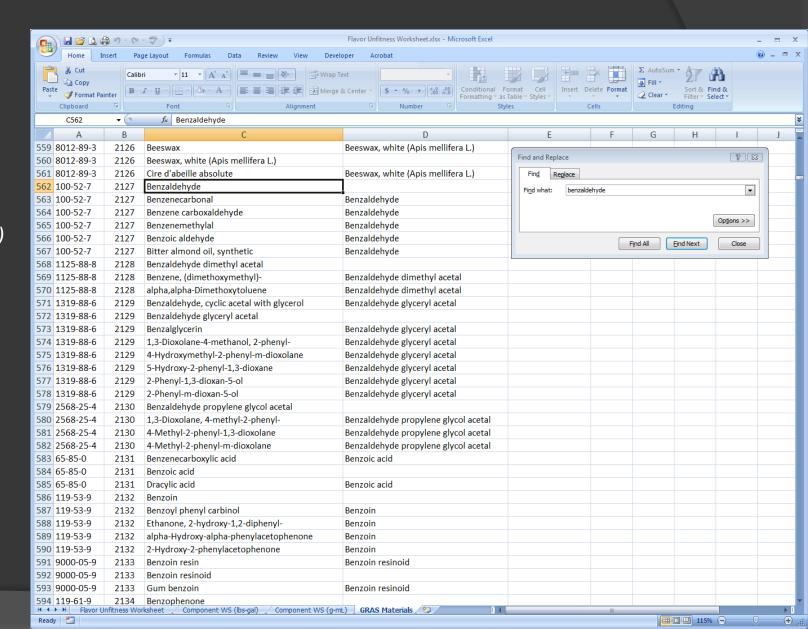
- Materials excluded from this guideline:
  - Ingredients with established guidelines
    - Ex: PG, ethyl acetate, etc...
  - Materials found to be fit at 1% or 0.1%
    - Ex: isoamyl acetate, limonene
  - TTB and FDA limited ingredients

FEMA#	Ingredient	Weight of ingredient	ppm in flavor	ppm @ 15% ABV	MAX Use Level	Factor higher MAX Use Level	Fit or Unfit?
2414	ETHYL ACETATE		0.0	0.0	REMOVED	: <del>-</del>	-
2656	MALTOL		0.0	0.0	REMOVED	-	-
2633	LIMONENE (d,l-, and dl-)		0.0	0.0	REMOVED	-	-
2489	FURFURAL		0.0	0.0	REMOVED	-	-
2940	PROPYLENE GLYCOL		0.0	0.0	REMOVED	-	-



#### GRAS MATERIALS TAB

<u>Hint:</u>
Use ctrl-f
(find function)
to quickly
search the
list.



### COMPONENT WS TAB

available for lbs/gal and g/mL

		ABC:				Flance	Unfitness Workshee	t ulau - N.C.	wasaft F.	1								_	
								LXISX - IVIIC	TOSOTE EXCE	31									`
	Home Insert	Page Layout		Data		iew Developer	r Acrobat						1		Α.	2.2	<b>0</b> –		
	Copy	Arial 🔻	10 - A A	= =		Wrap Text		+	≦\$					∑ AutoSui	m Z	<i>a</i>			
Pas	te Format Painter	B / <u>U</u> -	- A -			Merge & Center	\$ - % ,	00. 00. 00. ⇒.0	Conditio	nal Format C ng = as Table = Sty	ell Ins	ert Delete	Format	② Clear ▼	Sort &	Find & Select *			
	Clipboard	Font	Fa.		Alignme	nt	Number	G.	Tormuttin	Styles		Cells			Editing	Sciecc			
	B114 <b>▼</b>	f <sub>x</sub>																	¥
	А	В	С	D	E	F	G	Н	1	J	K	L	M	N	0	Р	Q		_
																			П
103	Vanillin	2.0 (	-4 OFW/44	1															П
104	vannin	_	Minimum Value	ianoi															П
105		(upper end of range in item 10)	Needed to Make Product Unfit		Amount of Vanillin (pounds)	Volume of Final Product (gallons)	av.oz. / gal of Vanillin	Unfit?											ı
103		,	0.000				_	_											П
106			0.500																
107																			
107	Washed Extracts	6 33% by weigh	nht at 95% v/v	ethar	nol														
108	Washed Extracts	_	Minimum Value	elliai	101	144-1-14 - <b>F</b> F11													П
		(upper end of range in item	Needed to Make Product		Amount of Oil (pounds)	Weight of Final Product	% by weight of Oil	Unfit?											П
109		10)	Unfit (wt%)		(pounds)	(pounds)	01011												
110			0.00				-	-											
111																			
112	Flavor Chemicals unfit at 1%	1% by weight	at 95% v/v eth	anol															
112	allitat 1/0		Minimum Value		Amount of Flavor	Weight of Final	0/ humaight -f												
		(upper end of range in item	Needed to Make Product		Chemical (pounds)	Product (pounds)	% by weight of Flavor Chemical	Unfit?											
113		10)	Unfit		(pourido)	(poundo)													
114		<u> </u>	0.158				-	-											
		(cannot be scale	ed below 15% alco	hol)															
115	Total Flavor																		
116	Chemicals		at 95% v/v eth	anol	(chemicals n	nust be listed on t	the 1% list)												
		Alcohol Content (upper end of	Minimum Value Needed to		Amount of Flavor	Weight of Final	% by weight of												
117		range in item	Make Product Unfit		Chemicals (pounds)	Product (pounds)	Flavor Chemicals	Unfit?											
		,	0.316				-	_											
118		(cannot be scale	ed below 15% alco	hol)															
119 120				/															
121																			
122 123																			_
		Worksheet	Component WS	(lbs-ga	al) Component	WS (g-mL) / (	GRAS Materials	<b>2</b> /					III					<b> </b>	
Read	ly 🛅													<b>=</b> 0	90%	9-	-0-	<b>—</b> (+)	.::

Formula approval: OMB No. 1512-0095 (09/30/98) DEPARTMENT OF THE TREASURY 1. FORMULA NUMBER **BUREAU OF ALCOHOL, TOBACCO AND FIREARMS** 15 FORMULA AND PROCESS FOR NONBEVERAGE PRODUCT KIND (e.g. Alcohol, Rum) (See instructions attached-Prepare in triplicate, except if manufactured abroad) PROOF OF SPIRITS ON WHICH 3. NAME OF PRODUCT. 4. CHECK IF SAMPLE 5. NUMBER OF DAYS TO DRAWBACK WILL BE CLAIMED. WILL BE SUBMITTED COMPLETE PROCESS Alcohol 190 proof **Natural Raspberry Flavor WONF** CHECK KIND OF PRODUCT: FORMULAS SUPERSEDED. NAME OF THE MANUFACTURER & ADDRESS WHERE PRODUCTS WILL BE PRODUCED (if multiple production sites, list other addresses on reverse). ■ MEDICINE/ MEDICINAL PREPARATION FLAVOR/ FLAVORING EXTRACT Company A 6000 Ammendale Rd ☐ FOOD PRODUCT PERFUME Beltsville, MD 20705 9. ELIGIBLE ABSOLUTE ALCOHOL 10. ALCOHOL CONTENT BY VOLUME OF FINISHED PRODUCT. VOLUME USED. (See instructions) 42.6% 42.6 +/- 2.0% 11. IF MADE WITH RECOVERED SPIRITS: 12. IF FINISHED PRODUCT IS TO BE USED IN ALCOHOLIC BEVERAGES: ELIGIBLE PLUS RECOVERED ABSOLUTE ALCOHOL A DOES PRODUCT CONTAIN NATURAL FLAVORING? (YES OR NO) BY VOLUME USED. (See instructions). B. DOES PRODUCT CONTAIN GREATER THAN 0.1% ARTIFICIAL FLAVORING(Excluding Vanillin, Ethyl Vanillin, Maltol, Ethyl Maltol)? C. STATE PARTS PER MILLION IN PRODUCT OF: VANILLIN ETHYL VANILLIN SYNTHETIC MALTOL ETHYL MALT OL D. DOES PRODUCT CONTAIN A COLOR ADDITIVE? E. ARE ALL INGREDIENTS APPROVED BY FDA FOR USE WITHOUT LIMITATION OR RESTRICTION? (YES OR NO) 13. FORMULA AND PROCESS (Use Additional Space on Reverse if Necessary). Ethanol 190 proof 35 lbs (5.15 gal) **25 lbs Glycerine** Citric Acid 9.4 lbs Raspberry Essence (purchased 3% abv) 1 lb (.13 gal) **Natural Acetic Acid** 0.5 lbs Nat Ethyl Butyrate (0.04 lbs) and other natural esters 0.1 lbs

Water **29 lbs** 

Theoretical Yield 100 lbs (11.5 gal)

Simple Mixture

Citric Acid

Ethanol ≤ 30% v/v – acid must be ≥ [(0.1 × ethanol %) + 0.5] (g/100 mL)

Ethanol > 30% v/v – acid must be  $\geq$  [0.1 × ethanol %] (g/100 mL)

	Alcohol Content (upper end of range in item 10)	Needed to Make
Ethanol ≤ 30% ∨/∨		0.500

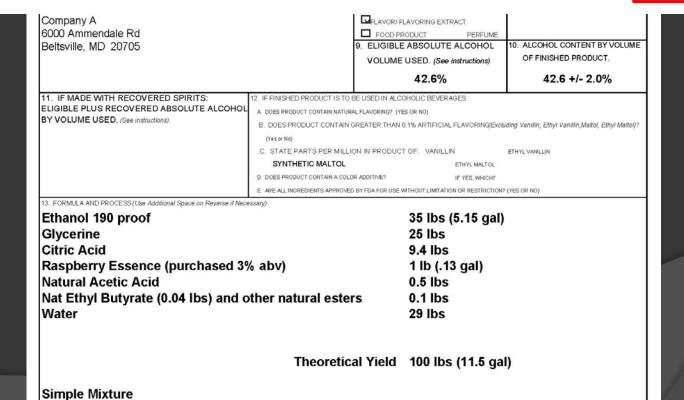
Amount of Citric Acid (pounds)	Volume of Final Product (gallons)	g / 100 mL of Citric Acid	Unfit?
		2	•

Needed (if product contains mitigating ingredients)	Unfit?
1.000	•

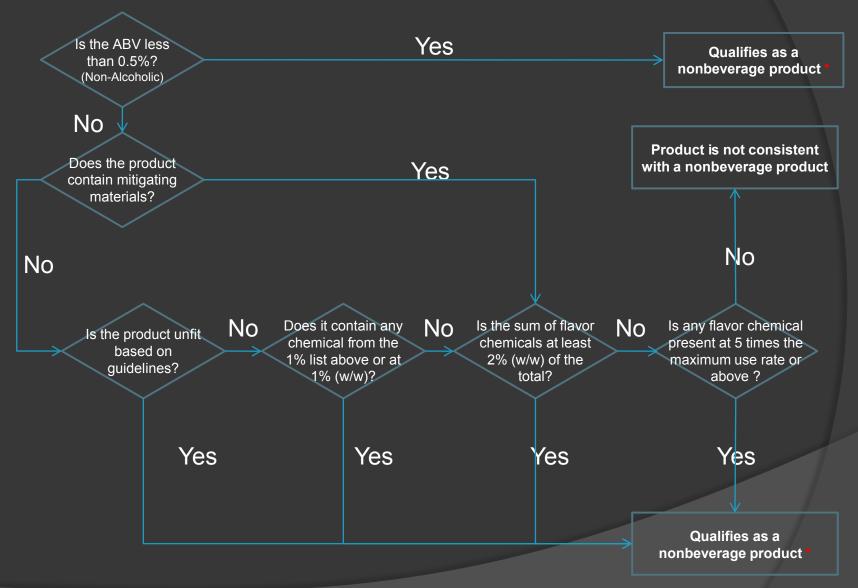
	Alcohol Content (upper end of range in item 10)	Needed to Make
Ethanol > 30% ∨/∨	44.6	4.460

Amount of Citric Acid (pounds)	Volume of Final Product (gallons)	g / 100 mL of Citric Acid	Unfit?
9.4	11.5	9.794720235	YES

Needed (if product contains mitigating ingredients)	Unfit?
8.920	YES



# NONBEVERAGE FITNESS DETERMINATION PROCESS



# CURRENT METHOD DEVELOPMENT

# CURRENT METHOD DEVELOPMENT

- Vanillin/ Ethyl Vanillin/ Maltol / Ethyl Maltol
- Vanilla Extracts
- Caffeine
- Ethyl Isobutyrate
   2-Methyl Butyrate
   Ethyl Butyrate
   Myrcene
   Limonene
   cis-3-Hexenol
   Cinnamyl Alcohol

Linalool Menthol Ethyl Benzoate Benzyl Alcohol Thymol Anisyl Alcohol

# CURRENT METHOD DEVELOPMENT

- Multi-lab method validation
- 13 commonly used flavor chemicals
- Analysis for compliance and fitness determination

- Contact: Ed Limowski
  - •

# INSTRUMENTATION AND EXPERIMENTAL CONDITIONS

Gas chromatograph

Autosampler

Autosampler mode

Injection volume

Inlet

Oven profile

Post run

Backflush inlet flow

Backflush pressure splitter

Column

Column dimensions

Presssure at splitter

Restrictor 1 (to FID)

Restrictor 2 (to MSD)

Mode

**MSD** Detector

FID Temperature

FID Detector flows

Solvent delay-(MSD)

Scan-(MSD)

Agilent 6890

Gerstel MPS 2

Liquid

1 µL

250 °C; 5:1 split

40 °C 2'; 3 °C/min 240 °C; 1.0'

240 °C for 5 min

0.1 mL/min

60 PSI

Phenomenex ZB-WAXplus

 $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ } \mu\text{m}$ 

**20 PSI** 

0.18 µm ID; 2.128 m

0.18 µm ID; 2.886 m

Constant flow 1 mL/min

Agilent MSD 5975 Inert

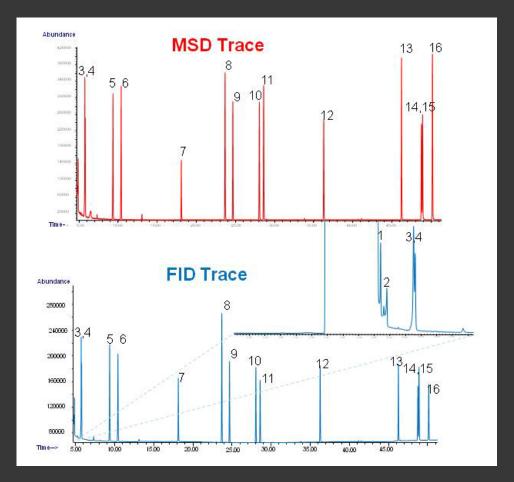
300 °C

H<sub>2</sub> 30 mL/min, air 400 mL/min

4.67 min

30-300 amu

### SAMPLE CHROMATOGRAMS



Total Ion Chromatogram (TIC, red trace) and chromatogram (FID, blue trace) for 125 ppm standard, 1 µl single injection.

1 Ethyl Isobutyrate; 2 2-Methyl Butyrate; 3 Deuterated Ethyl Butyrate (IS); 4 Ethyl Butyrate; 5 Myrcene; 6 Limonene, 7 cis-3-Hexenol; 8 2-Nonanol (IS); 9 Linalool; 10 Menthol; 11 Ethyl Benzoate 12 Benzyl Alcohol; 13 Thymol; 14 Anisyl Alcohol; 15 Cinnamyl Alcohol, 16 3',4'-(Methylenedioxy)-acetophenone (IS)

## FUTURE WORK

More method development of flavor chemicals

Borneol cis/trans isoeugenol

1-decanol cis-6-nonen-1-ol

1-dodecanol 1-nonanol

Geraniol 1-octanol

1-heptanol 2-octanol

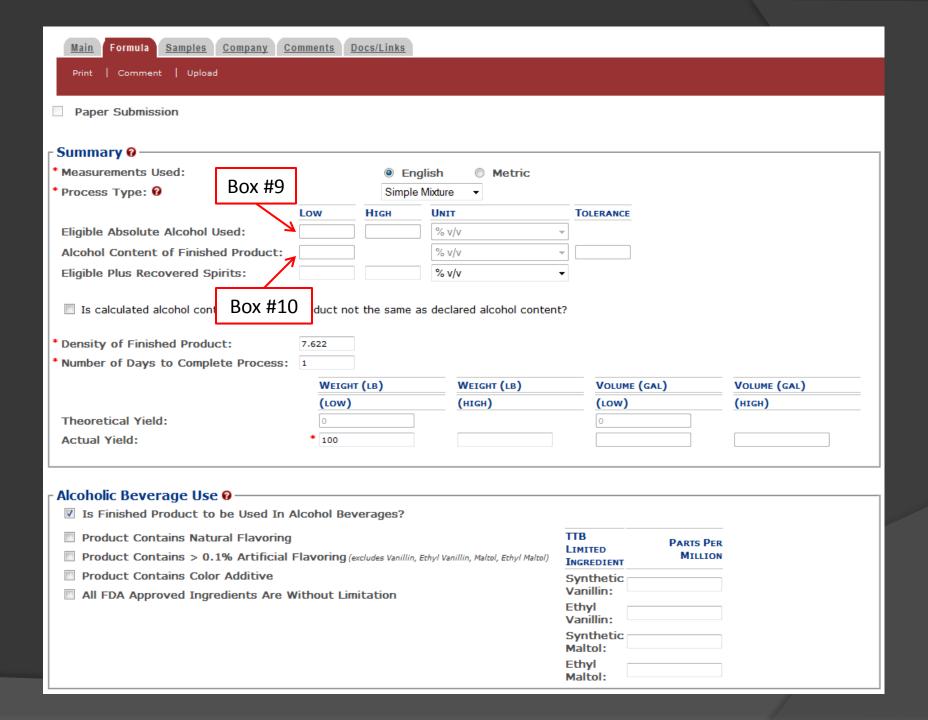
1-hexanol 1-octen-3-ol

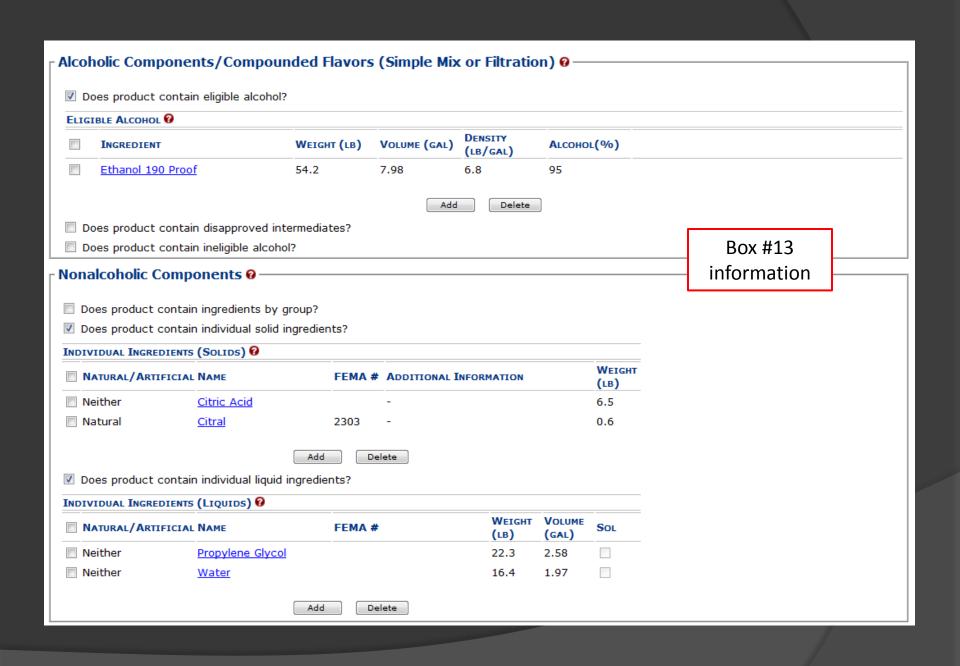
- May also be included in multi-lab validation
- Materials found in both Drawback and SDA products
- Stability of Flavor Chemicals

- Online submission of Drawback and SDA formulas
- Automatic calculations of eligible and total alcohol
- Status tracking through system
  - In Progress
  - Needs Correction
  - Complete
- Automatic notification of completed formula
- Contact chemist assigned formula in system

- Various formula types
  - Simple Mixture
  - Filtration
  - Washed Extract
  - Dietary Supplement
  - Other no automatic calculations

Alcohol Calculations
Automatic





- 1.0 release ('uniform' and user registration)
  - Winter 2011
- 1.1 release (drawback and SDA)
  - Summer 2011
- User Testing
  - Volunteers needed for external/submitter user testing
  - Winter/Spring 2011
  - Contact Rachel Sanderoff

# QUESTIONS?