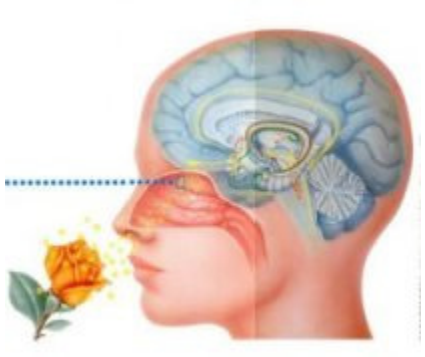

"Odour Profiling (of Essential Oils) and Subjectivity."

by Tony Burfield.

- Being a synopsis of the talk given at the RQA's 12th Annual Conference Saturday, 9th March 2002 Regent's College Conference Centre, London.

N.B. The lecture was profusely illustrated by passing round genuine essential oils and their key odour components on perfumers strips!

Introduction.

Extracting "Aroma" from the term "Aromatherapy" and examining the subject more closely reminds us that many lay people have poor and largely undeveloped odour memories, odour vocabularies and odour recognition abilities. There is good evidence however that the majority of us can improve these skills with proper training, and these lecture notes reflect on a session involving over 200 aromatherapists, who had some opportunity to verbalise about some of the oils they were smelling and the odour chemicals that they contained. Although it is obviously not possible to reconstruct the practical session, the first half of the lecture (the theory session) and notes from the smelling exercise are set out below.

Definitions:

An odour profile is a written description of the olfactory sensations evoked during the smelling of an essential oil or other natural raw material. Perfumers assess the odour profile by dipping the essential oil/absolute/resinoid etc. onto a perfumers' strip in order to appraise top, middle and bottom notes. A "smelling strip" is made of carefully selected paper which has a certain degree of absorbency which enables a smooth evaporation profile of all contained individual components.

Certain powerfully-odoured materials (such as tagete oil, blackcurrant absolute etc.) are diluted in inert solvents prior to smelling on a strip. Some absolutes are assessed after dissolution and "maturing" in 96% ethanol for a given period (up

to a month). Routine assessment of some fragrance odour chemicals (e.g. hydroxycitronellal) are carried out by dispersing in water prior to sniffing – it is felt that this technique is more likely to show up impurities. Powdered or solid materials are freshly ground and placed on a clean filter paper just prior to smelling.

- **Top note**: the odour impression of a freshly sampled aromatic material has been classically regarded as consisting of the most volatile elements. It is incorrect to assume the top-note profile *entirely* consists of very volatile elements, although it is strongly weighted in this direction.
- **Middle note**: smelled after several hours (varies with essential oil studied, might for example be one hour with lemon oil, eight hours for sandalwood oil), reveals heart of compound after some of the more volatile substances have departed.
- **End-note**: (dry-down) at 24 hours: bears the least volatile, longer-lasting component materials.

Odour has three aspects: character, intensity, tenacity Ref: Sell C. (2000). Important aspects of odour perception include the measurement of detection or recognition threshold values, scaling of the olfactive quality or odour-similarity rating of the odourants, intensity rating over various concentrations, hedonic preference rating: very unpleasant to pleasant.

The ideal specific requirements for carrying out an odour appraisal include an odour-free environment, constant humidity, avoiding adaptation/cross-adaptation effects.

There are several problems associated with odour profiling: persons trained in the art of odour assessment should ideally carry out the description. These people are rare, and may use vocabulary terms which are not understood by the layman. Points of reference and classification used by those trained in the art may differ from another differently trained. Thus we might be relying on the commonality of language rather than a precise definition of the terms.

Primary information from a trained nose may be detailed insightful and sophisticated, it is also affected by the limitations of an individual response. Specific anosmia and parasomia are widespread phenomena even amongst perfumers. There are differences in odour discriminatory abilities between the sexes and the fall-off of powers of perception with increasing age. Other difficulties arise as the quality of information obtained is subject to critical examination, especially since descriptions of odour are subjective. There may also be confusion of terms and meaning, as an hedonistic appraisal, like or dislike, and judgments of intensity of specific odour characters, can be influenced by previous events and other factors.

The act of smelling an essential oil in itself evokes a complex intellectual response involving sensations, mental images and memory associations which all contribute to the identification and characterisation process.

Benefits of odour profiling.
There are many benefits to establishing odour profiles. These include the classification of odour type (if the oil is unknown or rarely met) and assessment of oil quality. An evaluation of its usefulness and issues of integrity may also be raised

An odour profile can be used to:

- help establish accords
- predict how they might perform in application
- provide information on how they dry down (this latter procedure may reveal impurities, or characteristics not evident in the top-note, substantivity, nature of long-lasting components, likely performance on skin, oxidative changes etc.)
- establish similarities and differences with aroma compounds
- explore the possible influence of individual character components.

But there may be some difficulties with odour terms. There is, for example, no agreed vocabulary (unless "in-house" agreement between colleagues) and botanical descriptors have been criticised as they may be composed of several aspects, rather than one reference compound; there is confusion of inherent terminology in botanical classifications e.g. eugenol in clove oil is spicy in clove oil, but is floral in carnation, smoky in sandalwood, and fruity in banana.

Major groups of compounds:
The major groups of compounds are:

- *Monoterpenes*: have weak odour impact , but are important to impart lift and freshness aspects to essential oils. Little character impact. Have good solubility in hydrocarbons, but poor solubility in alcohol. Volatility is low and they tend to resinify.

- *Sesquiterpenes*: have weak odour impact with some exceptions; often not vital to the character of the essential oil. Have good solubility in hydrocarbons, but poor solubility in alcohol. Volatility is low, and they tend to resinify.

- *Oxygenated compounds:* have strong odour impact and high character impact. They have relatively good keeping qualities and good solubility in alcohol and hydrocarbons. They are of moderately low volatility. Some are reactive: eg aldehydes, and some can be hydrolysed by water eg esters.

Mans Boelens (1997) describes four classes of substances occurring in essential oils:

- Character compounds which he notes are recognised by experts as possessing the olfactory quality of the oil

- Essential compounds necessary to complete the normal odour profile but not characteristic of odour quality
- Balance compounds "neither characteristic nor essential"
- Artefacts

Other factors:

Modifiers. The character component of an essential oil/absolute is subject to modification by minor and trace components (which may number hundreds).

Accords. An accord is a blend of (a few) odourants to produce a distinctive note. The search for accords can occupy much of a senior perfumers' time. Odour descriptions of essential oils are often attempts to describe important accords perceived in the very nature of essential oils. Accords are a harmonious blend of two or three fragrance notes in a perfume. They are the building blocks of perfume composition and can represent the character-forming odour aspects of a fragrance. Example: a mix of β-pinene, γ-terpinene, thymol, perilla aldehyde and citral can give the impression of tangerine oil.

Working examples.
Samples of some of the following oils, and pure single aroma chemical isolates from them, were distributed amongst the audience for appraisal & comment.

Cardamom oil India (*Elletaria cardamomum*) India. Described as penetrating, camphoraceous (i.e. cineolic!), spicy and warm, with a woody element and almost glowing aldehydic heart. The top-note is woodier than the Guatemalan oil. Dry-down is fresh, lemon-like, but not unduly spicy (Burfield T. 2000).

Under controlled conditions perfumers' classified the ***top notes*** as follows:

1. cineolic i.e. similar to odour impression of 1,8-cineole
2. spicy
3. peppery
4. warm
5. fresh
6. aromatic

citrus lime notes (authors observation: fresh seeds only)

***Middle note*:** Loses the cineole & peppery impact now:

1. spicy
2. fresh
3. warm, aromatic
4. with a distinct terpinyl acetate note

End-note: becomes disappointingly woody-soapy and musty

Compare the odour of: α -terpinyl acetate

1,8-cineole

Gas Chromatographic (GC) Analysis of Indian Cardamom oil *miniscula* type (T. Burfield unpublished data):

α-pinene 2.06%; camphene tr; sabinene 3.45%; myrcene 2.03%; α-terpinene 0.42%; 3-methyl butanol tr; limonene 2.51%; 1,8-cineole 34.57%; *cis*-β-ocimene 0.02%; γ-terpinene 0.73%; *tr*-β-ocimene 0.11%; *p*-cymene 0.20%; terpinolene 0.20%; n-octanal 0.07%; methyl allyl benzene?: 0.05%; methyl heptenone 0.02%; citronellal 0.03%; *tr*-2-decenal <0.01%, *E*-5-decenal <0.01%, n-nonanal <0.01%, *tr*-sabinene hydrate 0.49%; n-decanal 0.02%; camphor <0.01%, linalol 2.89%; linalyl acetate 3.51%; terpinen-4-ol 1.21%; neral 0.13%; α-terpineol 3.42%; borneol < 0.01%; α-terpinyl acetate 39.00%; neryl acetate 0.18%; geranyl acetate 0.70%; nerol 0.05%; geraniol 1.13%; geranyl propionate < 0.01% *Z*-nerolidol 0.02%; *E*-nerolidol 0.56%; carvacrol 0.03%; ascaridole 0.03%.

Rose oil (*Rosa* spp.)

The composition of rose oil varies with species, cultivar etc. The odour is powerful, heady, rounded fruity-rose odour, more floral and rosaceous than other rose oils (e.g. from Morocco, India, Russia etc.).

Top notes for Bulgarian rose oil (*R. damascena*) were established as follows:

1. Floral: rose alcohols nerol, geraniol, linalol, b -phenylethyl alcohol
2. Fruity: has been ascribed to damascones
3. Spicy: methyl eugenol
4. Honeyed: benzyl tiglate, phenylethyl isobutyrate etc.
5. Fresh citrus: perillene, rose furan, tetrathydro-rose furan, p-menth-1-en-9-al.
6. Green dewey: rose oxide

The basic rose note is provided by β -ionone, modified by damascenone, α - and β -damascones.

Odour unit: (the relative value of an odour in a mixture) is the concentration of a constituent divided by its odour threshold; the higher the value the greater the importance of the perceived odour. In the case of rose oil, the relative percentage of odour units gives the following picture:

70.0 % β –damascone

19.2% β –ionone

4.3% *laevo*-citronellol

4.1% *laevo* -rose oxide

1.0% *laevo* - linalol

0.8% geraniol (Ref: Ohloff G. 1994).

However odour units are an approximation: they do not take into account physiological and additive effects, or synergistic factors.

Clove Oils

Clove oils from *Syzygium aromaticum* can be divided into bud, leaf and stem oils. The leaf oil contains 12% (-)-β-caryophyllene and 90% eugenol as major components. No anosmia for eugenol is known. (Gilbert A. & Wysocki C. 1987).

Clove oil notes: The unrectified Madagascan oil has a sharp slightly crude medicinal (eugenol), often phenolic odour without any of the sweet smoothness of the rectified material.

Leaf oil. This is how perfumers have categorised odour aspects in the ***top note*** of clove leaf oil (Burfield T 2000):

1. Spicy (eugenol, b -caryophyllene)
2. Warming (a property common to most spices)
3. Fruity (methyl N-amyl ketone, benzaldehyde)
4. buttery (bud oil)
5. sweet (eugenyl acetate)
6. smoky
7. woody
8. phenolic
9. unpleasant (sulphides)
10. castoreum (bud only)

The ***middle note*** of the leaf oil gives the following profile:

1. much spicier
2. warm
3. more medicinal (methyl salicylate) and
4. has lost some of the etherial fruitiness
5. Also often woodier.

The ***end-note*** is somewhat smoky, phenolic and spicy.

Stem oil: Clove Stem oil (Zanzibar) analysed by the author (Tony Burfield: unpublished data) was found to contain:

α-pinene 0.02%, limonene <0.01%, *p*-cymene <0.01%, methyl N-amyl ketone 0.04%, methyl heptenone <0.01%, 2-heptanol 0.02%, furfural 0.08%, α-cubebene 0.07%, α-copaene 0.15%, linalol <0.01%, linalyl acetate <0.01%, β-caryophyllene 10.50%, *E*-α-bergamotene 0.03%, methyl benzoate 0.03%, methyl salicylate 0.13%, terpinen-4-ol 0.02%, α-humulene 1.13%, 5-methyl furfural 0.05%, benzaldehyde 0.02%, α-ylangene 0.03%, α-terpinyl acetate <0.01%, β-caryophyllene oxide 0.19%, methyl eugenol 0.13%, chavicol 0.11%, anisaldehyde <0.01%, farnesol 0.30%, *E*-calamnene 0.03%, eugenol 73.50%,

eugenyl acetate 11.98%, *E*-isoeugenol 0.16%, *Z*-isoeugenol 0.02%, benzyl benzoate 0.05%, humuladione 0.01%.

Bud oil: Clove bud oil gives the following profile:

Top note**:** The superior bud oil is warm spicy with a caramellic impression, etherial wine-like notes and fruity (banana) like aspects are also often present (eugenol compounds & derivatives are present in banana volatiles). The ***top-note*** has the following characters:

1. spicy (eugenol, b -caryophyllene)
2. warm
3. creamy/buttery caramelic (vanilla-like to some assessors)
4. fruity (methyl N-amyl ketone)

The ***middle note*** of the bud oil is

1. warm
2. smooth-spicy whereas the top note is quite jagged
3. distinct castoreum-animal note impression
4. also fruity.

The ***end note*** is spicy and still creamy/vanillic.

The dominant odour components of clove oil are:

Eugenol, eugenyl acetate, vanillin plus and unknown substance with a green odour. Additionally contributions are made by cresol, guaiacol, *p*-methyl guaiacol, (phenolic musty) linalol, damascenone, γ-decalactone, methyl salicylate (spicy peppery), 2 unknown trace compounds, β-caryophyllene and caryophyllene oxide. (Kollmannsberger & Nitz 1994)

Rosemary oil Tunisia
Rosmarinus officinalis (Tunisian oil), described as very toppy, very camphoraceous, more cineolic than Rosemary oil Spanish (camphor type) herbaceous, colder and fresher than the oil sold as the borneol type, but also thinner by comparison. Dry-out is delicate clean, sweet herbaceous, pleasant.

Top notes*:*

1. Cineolic: 1,8-cineole
2. Fresh herbaceous
3. Camphoraceous : camphor (minty)
4. Sweet
5. Woody

Also: Piney, Floral (methyl jasmonate; viridiflorol (green floral)

Middle note is:

1. herbaceous

2. resinous
3. sweet

Lost the cineole note, any wood note.

***End note**:* woody, herbaceous, soapy.

Figures for headspace analysis of the essential oil vs. herb B.D. Mookerjee et al: (1989).are very revealing:

Constituent	Living Herb	Picked herb	Essential oil
α-pinene	1.1	0.7	16.3
β-pinene	0.3	0.1	7.0
myrcene	9.5	11.1	1.7
limonene	14.1	14.3	1.0
1,8-cineole	2.0	0.7	44.8
p-cymene	19.8	13.7	1.7

From the same article, the living herb was found to contain methyl chavicol, *cis*-carveol, citronellol, α-campholenic alcohol and acetate – not necessarily compounds thought of as characteristic of the oil.

Rosemary Oil Tunis analysis (Burfield T. unpublished data):

α-thujene 0.11%, α-pinene 11.86%, tricyclene <0.01%, camphene 1.16%, β-pinene 6.93%, β-phellandrene 0.20%, α-phellandrene 0.21%, myrcene 0.65%, limonene 1.53%, fenchene <0.01%, α-terpinene 1.53%, 1,8-cineole 47.45%, *Z*-β -ocimene 0.07%, γ-terpinene 0.31%, *E*-β-ocimene 0.02%, *p*-cymene 1.14%, terpinolene 0.31%, isoborneol 0.02%, n-nonanol 0.59%, α-ylangene <0.01%, α-cubebene 0.01%, γ-muurolene 0.23%, methyl heptenone <0.01%, α-pinene oxide <0.01%, fenchone 0.01%, *tr*-sabinene hydrate 0.01%, α-*para*-dimethyl styrene <0.01%, *tr*-thujan-4-ol 0.08%, isopinocamphone <0.01%, camphor 9.46%, α-copaene 0.20%, aromadendrene 0.02%, α-cubebene <0.01%, linalol 0.61%, bornyl acetate 0.60%, β-caryophyllene 3.92%, α-isobornyl acetate 0.01%, α-fenchol 0.03%, terpinen-4-ol 0.82%, α-humulene, methyl chavicol < 0.01%, verbenone 0.01%, β-bisabolene <0.01%, α-terpinyl acetate <0.01%, α-muurolene 0.02%, α-terpineol 1.73%, borneol 2.75%, geraniol <0.01%, δ-cadinene 0.35%, γ-cadinene 0.20%, piperitone <0.01%, caryophyllene oxide 0.12%, viridiflorol 0.18%, methyl eugenol < 0.01%, thymol <0.002%.

Vetiver Bourbon oil
(*Vetiveria zizanoides*): Powerful woody earthy smoky with a nutty aspect and hint of grapefruit, thus:

1. Earthy (rooty)
2. Woody
3. Vegetable
4. Smoky
5. Nutty

6. Grapefruit

Others: dry, musty, smoky bacon.

Middle note is

1. woody-earthy
2. smoky
3. nutty
4. grapefruit
5. dry

Vegetable character has gone

End-note: earthy, woody, smoky.

The analysis of vetiver is quite complex and over 150 sesquiterpene compounds are known. α- and β- vetivones are characteristic of vetiver oil (except those from N. India), but not characteristic of the overall odour. (+)-α-vetivone is said to have a grapefruit character as well as a woody balsamic profile.

Cedarwood Oil Chinese
As a contrast, the oil of *Chamaecyparis funebris* syn. *Cupressus funebris* is considered. It is imported into the US on a large scale to adulterate home-produced Cedarwood oils (Virginian, Texan etc), and for use in cheap toiletries etc. The oil top-note is described as invariably smoky, woody, bordering on crude, with almost cresylic character. In comparison the Virginian oil is seen as smooth woody, slightly oily pencil-sharpenings, and somewhat slightly sweet in comparison. The Chinese oil is however, more powerful (Burfield T. 2000).

The following odour characters were established for Cedarwood Oil Chinese:

1. Woody
2. Smoky
3. Burnt
4. Green, unpleasant (guaiacol)

α- and β-cedrenes together with thujopsene are considered weak smelling woody odourants. Specific anosmia is high for woody notes in the general population. (+)-cedrol is considered the character compound for Cedarwood Oil Virginian.

Cedarwood Chinese; major components (Burfield T., unpublished data):

α-cedrene 27.1%, α-cedrene 8.8%, thujopsene 30.0%, α-himalchene 0.5%, β-himalchene 0.5%, *ar*-curcmene 0.4%, α-selinene 3.0%, cuparene 3.3%, cedrol 12.0%, widdrol 4.9%, methyl carvacrol 0.6%.

GC Sniffing.

If separation is adequate this allows individual compounds to be smelled in pure state at the exit of the GC column "sniff port". Interesting fractions or compounds may be isolated by preparative GC techniques for further investigation.

Odours are often perceived by sniffing where no GC peak exists, which shows the vast superiority of the human nose as a detector over electronic detection (absolute traces of powerful materials for example can change an odour profile completely).

The problems with GC sniffing (GC-O or GC-Olefactometry) include:

- individual assessors have different responses
- aromagrams differ from GC traces: eluted odours do not coincide with peaks
- absolute concentration and freedom from interruption is required during the GC run.
- odours may linger "round the ports" giving cross-contamination
- analysts can suffer fatiguing and adaptation effects from continuous smelling tasking.

AEDA (Aroma extract Dilution Analysis)
Methodology: serially dilute the substance being studied and examine each consecutive by GC-O. As the dilution progresses eventually fewer and fewer odorants are detected and the most powerful substances are eventually determined. For example P. Schieberle et al. (1990) looked at cucumbers (*Curcumis sativis*) by AEDA and found that *E/Z*-2,6-nonadienal and *E*-2-nonadenal were the most potent odourants of cucumber.

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