Turkish Rose Oil Research: Recent Results

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Rose oil was produced by hydrodistillation from fresh flowers of *Rosa damascena* Miller. (Turkey and Bulgaria are the two main producers of this precious material.) Results of the analysis of Turkish rose oil produced by the Gülbirlik Cooperative in the past 16 years are provided in this article. Additionally, the main odorous components characterizing Turkish rose oil are indicated. Results of phytosol and SFE experiments, and headspace and headspace-SPME (Solid Phase Micro Extraction) techniques on living rose plants and freshly picked rose flowers are presented.

Background and History

Rose oil is produced in Turkey and Bulgaria by water distillation of fresh flowers of *R. damascena* Miller (damask rose). It is a cultivated hybrid of *R. gallica* L. and *R. phoenicia* Boiss. The cultivated variety is called "trigintipetala," meaning "having 30 petals." The characteristic scent given off by these flowers is highly regarded by perfumers.

Rose distillation for the production of rose oil and rose water probably originated in Iran. By the 17th century, rose cultivation had spread from Iran to India and Turkey. There is evidence of rose cultivation for the production of rose water in European Turkey dating to the 17th century. Towards the end of that period, rose cultivation was introduced by a Turkish merchant to Bulgaria, which was then a province of the Ottoman Empire. By the middle of the 18th century, Bulgaria had already become a world center for the cultivation of roses and the production of rose oil.

A variety of fragrant rose species was used for oil production until, finally, *R. damascena* established itself as the singularly desirable source. In late 19th century, rose oil cultivation was initiated in several provinces of Turkey through a royal decree. Over time, however, the Isparta and Burdur provinces in southwest Anatolia have become the only cultivation and production sites.

Since 1934, a cottage industry of rose oil production has been replaced by modern factories. At present, there are seven large and several small companies producing rose oil and rose water in Turkey. Five companies also produce rose concrete.

Rose oil is produced by water distillation of the freshly picked flowers. Oil is generally obtained in 0.02 percent yield; the aqueous distillate, which is left out of distillation, is sold as rose water. Rose concrete is produced by n-hexane extraction of fresh rose flowers.

Annually, an average of 7,000 tons of roses are processed to produce about 1,600 kg of rose oil and about 2,400 kg of rose concrete. To produce 1 kg of rose oil via distillation, 3,500-4,000 kg of fresh roses are needed. One kg of rose concrete may be solvent extracted from 400 kg of fresh roses. Rose absolute is not produced in Turkey at commercial scale — it is usually obtained by ethanol-extraction of the rose concrete (1-5).

Rose oil and rose concrete production figures covering 1998 to 2000 are shown in T-1. A slight downward trend in production is evident.

In 2000, the sale price of Turkish rose oil and rose concrete were $3,300 to $3,500 and $475 to $500, respectively. That year, the New York spot market price of Turkish rose oil was $4,200/kg, while the Bulgarian rose oil was selling at $3,900/kg (Chemical Market Reporter, July 17, 2000). The marketable rose products are: rose oil, rose concrete, rose absolute, rose water, rose jam and dried rose flowers.

Rose oil and rose concrete production in Turkey **T-1**

	1998	1999	2000
rose oil	1.800 kg	1.600 kg	1.400 kg
rose concrete*	2.500 kg	2.200 kg	2.300 kg
rose flowers*	9.200 tons	8.600 tons	6.200 tons

*estimated

The authors carried out several studies involving new techniques such as phytosol extraction, supercritical fluid extraction, solid phase micro extraction (SPME) and conventional headspace trapping to analyze the odor of roses.

Distillation

The current industrial rose oil distillation in Turkey is as follows:

The process is a batch operation. Fresh rose flowers (400-500 kg) and water (1,500-2,000 L) are charged into 3,000-L jacketed stainless steel or copper stills. Distillation lasts for 1.5 h. Condenser temperature is kept at 35°C to avoid solidification of the oil due to paraffins. The distillate is collected in stainless steel separators called Florentin flasks. Rose oil starts separating in the distillate only after the third or fourth batch. When enough oil separates, it is decanted and kept separately. This greenish yellow oil is called "crude oil," "first oil" or "direct oil." Distillation waters are accumulated in 5,000-L stainless steel tanks and redistilled in 3,000-L stills to yield "second oil"— also called "indirect oil" or "cooked oil." The distillate of this second distillation, after removal of oil, is diluted with distilled water and sold as rose water. The first and second oils are mixed to produce Turkish rose oil.[6-8]

Percentage values of major and minor components in the Gülbirlik rose oil over 16 years (1986 to 2001) are given in T-2 and T-3, respectively. T-4 indicates the percentage ratios of the groups of compounds and shows the terpenoid character of the rose oil. Finally, olfactory features of rose oil components are summarized in T-5.

Sixteen years of Gülbirlik rose oil **T-2**

Compound	Main components (%) Min.	Max.
citronellol	30.9	43.9
geraniol	9.3	14.1
nonadecane	8.3	14.7
nerol	5.2	7.6
1-nonadecene	2.6	4.9
methyl eugenol	2.7	4.0
heneicosane	2.5	4.2
geranyl acetate	1.0	2.2
linalool	0.6	2.1
2-phenylethyl alcohol	1.2	1.9
β-caryophyllene	0.7	1.6
citronellyl acetate	0.7	1.4
germacrene D	0.7	1.4
(2E,6E)-farnesol	0.6	1.4

Sixteen years of Gülbirlik rose oil — other interesting contributors to rose odor **T-3**

	%	No. Samples (year)
(E)-β-damascenone	0.03	1 (2000)
cis-rose oxide	0.3-1.0	16
trans-rose oxide	0.1-0.5	16
rosefuran	<0.1-0.1	9
nerol oxide	<0.1-0.2	15
isonerol oxide	0.01-0.02	6
rosefuran epoxide	0.02-0.04	3
(E)-3,7-dimethyl-5-octene-1,7-diol	0.1-0.4	8
(2Z,5E)-3,7-dimethyl-2,5-octadiene-1,7-diol	0.02-0.1	3
(2E,5E)-3,7-dimethyl-2,5-octadiene-1,7-diol	0.02	1

Sixteen years of Gülbirlik rose oil — compound groups (%) **T-4**

Compound groups	Compound groups (%) Min.	Max.	Exception (year)
terpenoids	61.9	77.4	-
OMT	64.0	71.3	56.7 (1991)
STHC	2.9	5.3	-
OST	0.5	2.0	-
MTHC	0.3	1.9	2.3 (2000)
hydrocarbons	17.8	22.8	30.5 (1991)
phenylpropanoids	3.1	4.8	5.4 (1990)
others	0.5	1.8	-

Rose oil is produced in Turkey by water distillation of fresh flowers of R. damascena Miller (damask rose), a cultivated hybrid of R. gallica L. and R. phoenicia Boiss; the characteristic scent given off by these flowers is highly regarded by perfumers.

As a foundation, we have carried out several studies involving new techniques such as phytosol extraction, supercritical fluid extraction, solid phase micro extraction (SPME) and conventional headspace trapping to analyze the odour of roses.[5,8]

Phytosol Extraction

Using a hand-held phytosol extraction unit, fresh *R. damascena* flowers were extracted with phytosol D [1,1,1,2-tetrafluoroethane (90 percent) + dimethylether (10 percent)] for 45 min, 5 h, 8 h and 24 h, separately. The results are listed in T-6 and F-1. The results indicated that phenylethyl alcohol was the main component in almost all the periods, the best yield (69.6 percent) being at 45 min. As T-7 and F-2 indicate, the total terpenoid content decreased during prolonged extraction while that of the paraffins increased, as expected. Since phytosol is an extraction procedure, a concrete is obtained with 2-phenylethyl alcohol as the main constituent.

A similar study was reported from Bulgaria; however, due to the lack of quantitative data a comparison was not possible.[9]

SFE Extraction

Using an ISCO bench top extractor, dynamic CO_2 extraction was carried out with ca.5 g *R. damascena*

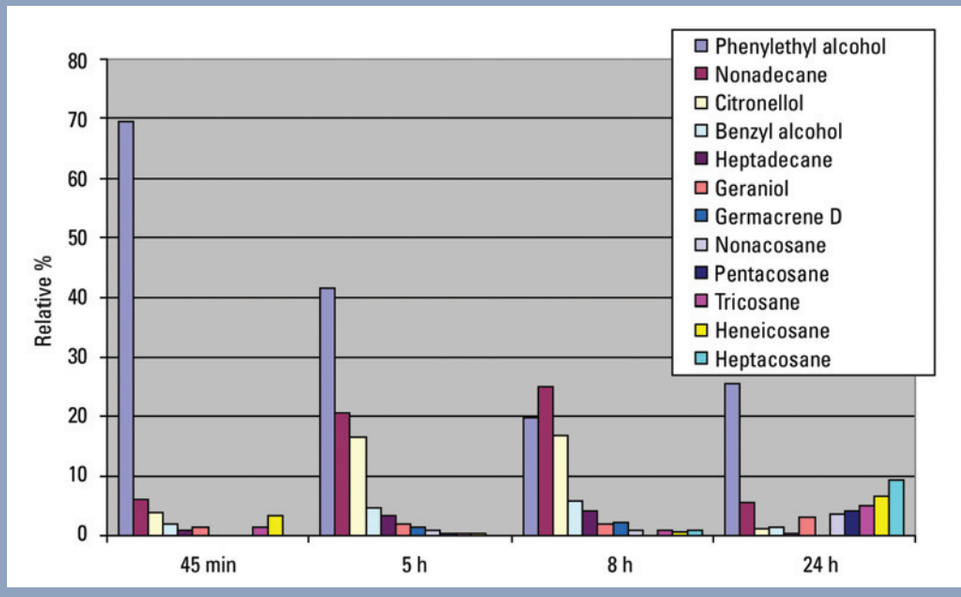
Olfactory evaluation of rose oil components **T-5**

Component	Effect
citronellol	Basic rosaceous character; higher citronellol content leads to increased sweetness.
geraniol	Leads to strength and fortification of the body note. When geraniol content is comparatively low, the sweetness of the body note is maintained, but strength diminishes.
nerol	Adds to the rosaceous character and freshness.
2-phenylethyl alcohol	Enhances the floral character.
cis-rose oxide	Leads to a stronger top note.
methyl eugenol	Improves the body note.
linalool	Strengthens the top note and adds to the floral character.
citronelly acetate	Strengthens the sweetness and typical rosaceous character.
citronellol + geraniol + nerol + farnesol	Establish the basic character of rose oil.
paraffins (stearoptenes)	Dilute the body note.

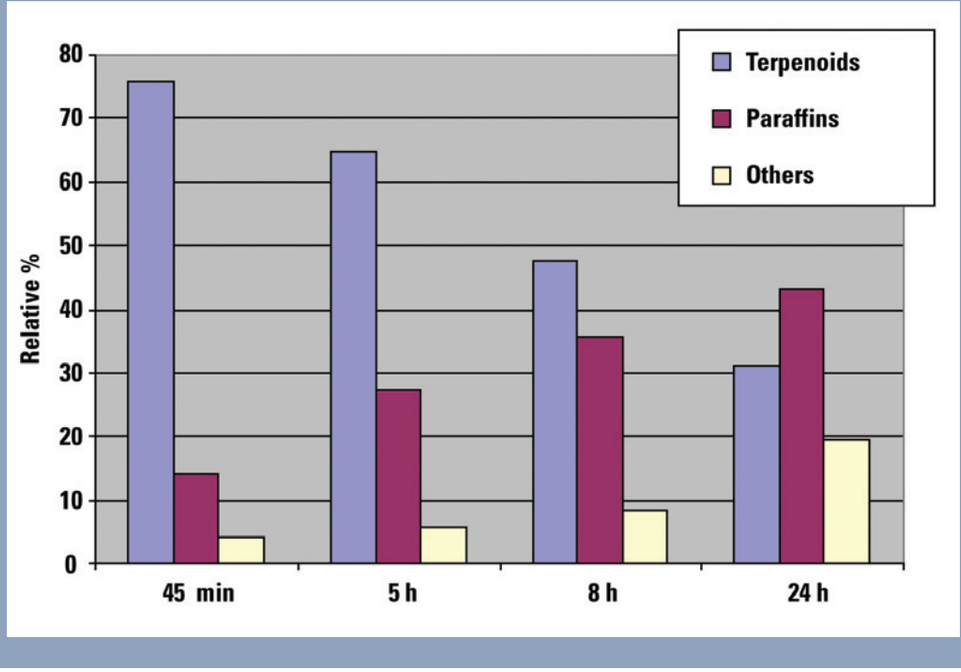
Phytosol extraction of fresh rose flowers (individual components) **T-6**

Main components (percentage)	45 min	5 h	8 h	24 h
2-phenylethyl alcohol	69.6	41.4	19.8	25.6
nonadecane	6.1	20.5	25.1	5.5
citronellol	3.8	16.5	16.8	1.1
benzyl alcohol	1.9	4.7	5.7	1.5
heptadecane	0.8	3.3	4.0	0.3
geraniol	1.5	1.8	1.8	2.9
germacrene D	<0.01	1.4	2.2	0.03
nonacosane	-	0.7	0.9	3.5
nonacosene	-	0.6	1.1	1.1
pentacosane	-	0.3	-	4.2
tricosane	1.3	0.3	0.8	5.0
heneicosane	3.4	0.2	0.6	6.7
heptacosane	-	-	0.8	9.3

Phytosol extraction of fresh rose flowers (individual components) F-1



Phytosol extraction of fresh rose flowers (groups of components) F-2



Phytosol extraction of fresh rose flowers (groups of components) T-7

Main groups (%)	45 min	5 h	8 h	24 h
terpenoids	75.9	64.6	47.5	31.3
paraffins	14.1	27.4	35.7	43.2
others	4.1	5.7	8.3	19.6

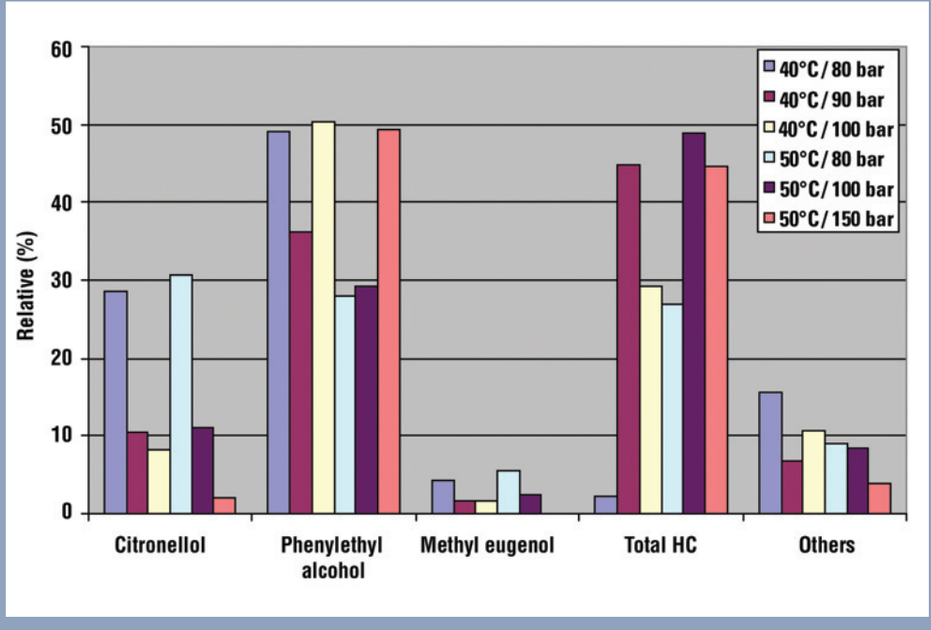
R. damascena **T-8**

Live flowers — Procedure time: 2 h (10:00 AM to 12:00 PM)

Compound	Porapak Q	Compound	Porapak Q
2-phenylethyl alcohol	59.2	geranyl acetate	0.9
citronellol	18.1	methyl eugenol	0.9
nonadecane	3.2	2-phenylethyl acetate	0.7
α-pinene	2.8	pentadecane	0.7
geraniol*	2.1	nerol	0.5
benzyl alcohol	2.0	(E,E)-α-farnesene	0.3
heptadecane	1.2	heneicosane	0.3
citronelly acetate	1.1		

*impure

SFE extraction of fresh roses (components) **F-3**



fresh flowers at 40°C and 50°C with 80, 90, 100 and 150 bar extraction pressure. Fluid flow rate was ca. 1.5 mL/min, and the trap solvent was n-hexane.

The results of supercritical CO_2 extraction of rose flowers (*R. damascena*) at different temperature and pressure conditions showed that 2-phenylethyl alcohol was always the main component. Citronellol content was high at low temperature and pressure conditions only. However, increasing pressure at the same temperature gave a low citronellol content. Meanwhile, increasing pressure increased the hydrocarbon (paraffin) content. This was the case even at low temperatures (F-3 and F-4).

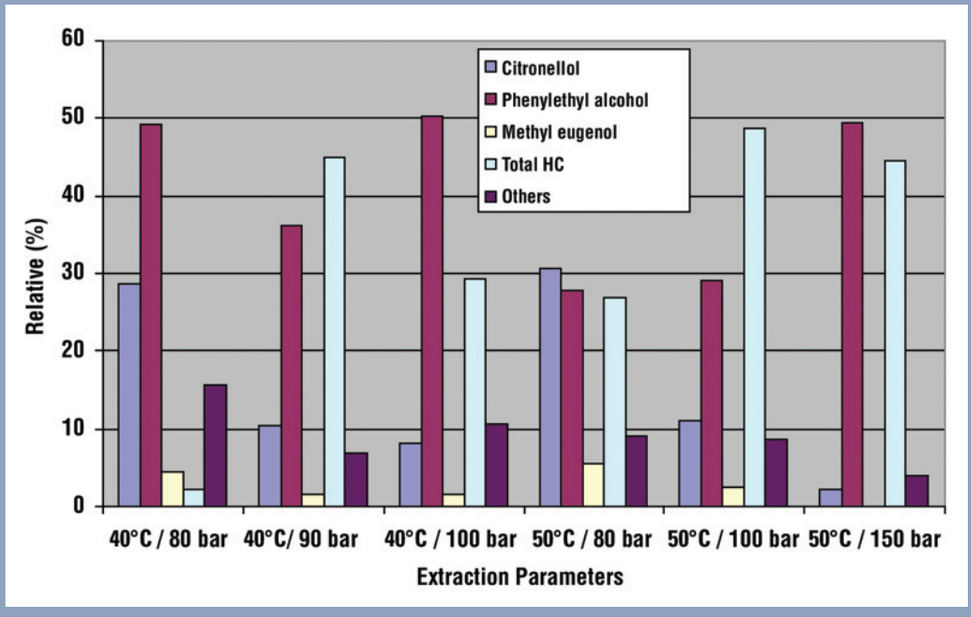
To obtain an extract with a high citronellol and 2-phenylethyl alcohol content, the operation temperature and pressure must be kept low.

Supercritical CO_2 extraction of rose at 40°C and 80 bar condition can be considered optimum for acceptable citronellol and phenylethyl alcohol contents.

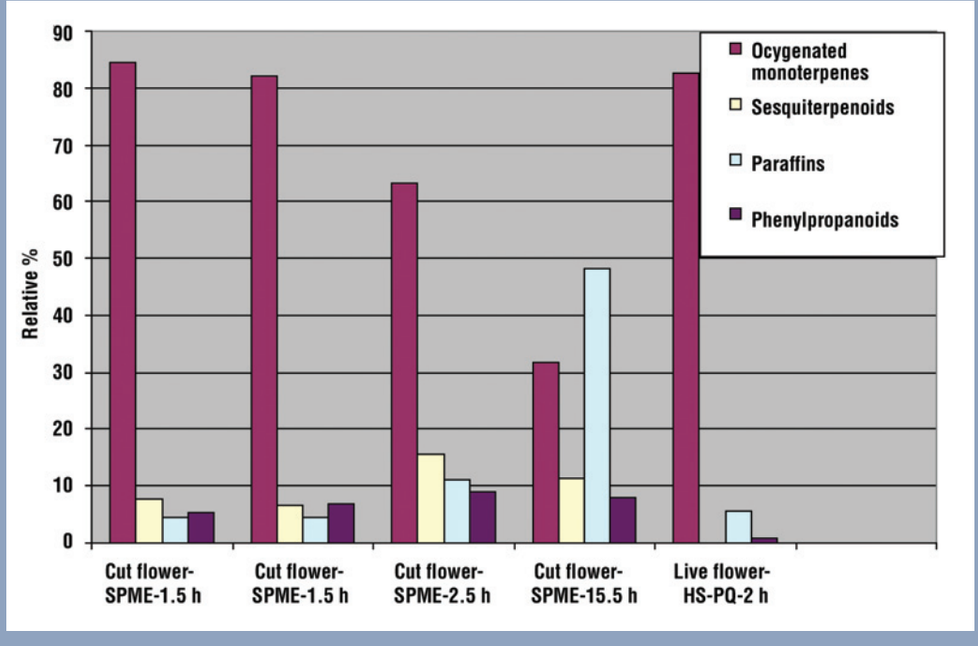
Headspace Trapping

Direct sampling headspace analysis of living rose flowers, using Porapak Q as the trap for 2 h (10:00 AM to 12:00 PM), gave the results shown in T-8. Hexane was used as the eluting solvent. 2-Phenylethyl alcohol (59.2 percent) and citronellol (18.1 percent) were the main components, quite akin to that of a concrete.

SFE extraction of fresh roses (conditions) **F-4**



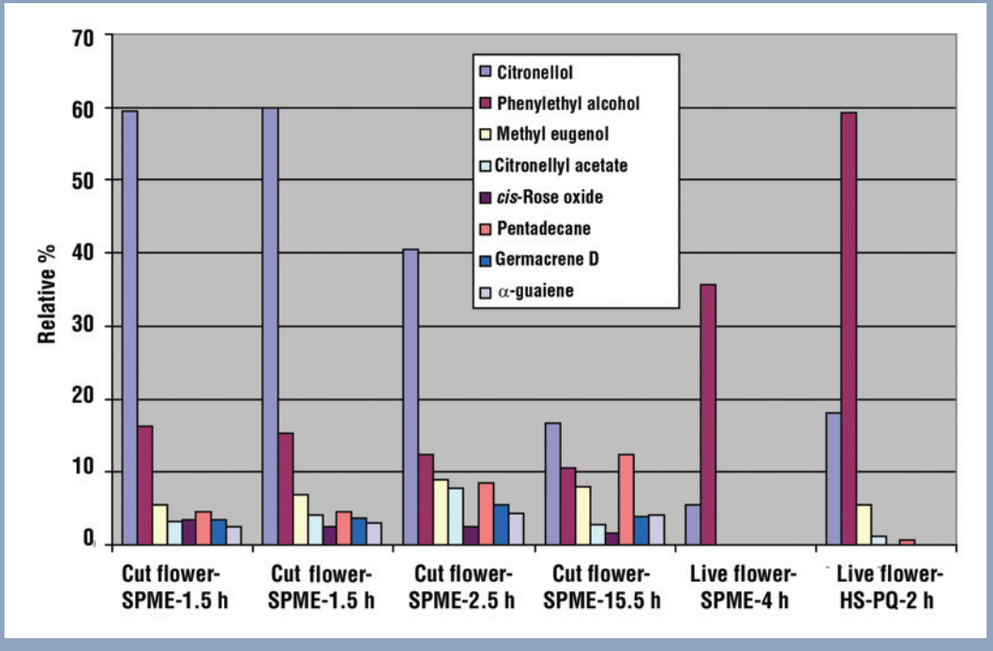
Headspace trapping of live and cut rose flowers (groups of compounds) **F-5**



Solid Phase Micro Extraction

Solid phase micro extraction (SPME) is a solvent-free sample preparation technique that can be used to analyze the vapor space above a liquid or solid sample (headspace SPME), or aqueous solutions (immersion SPME) directly. Due to the high efficiency of extracting organic molecules (less time consumption and low cost of operation), it represents an excellent alternative to conventional extraction techniques, and has found wide application in the flavor and fragrance industries. The simplicity of the technique is that analytes from a liquid or from the headspace of a sample are trapped on a polymer

Headspace trapping of live and cut rose flowers (individual compounds) **F-6**



film coated on a fused silica fiber. After an equilibrium of analytes is reached between the sample phase and the SPME film, the fiber can be directly inserted into the injector port of GC or HPLC equipment for analysis after thermal desorption.

Polar polymer films coated on fused silica fiber are as follows:

- PDMS/DVB — poly (dimethylsiloxane)/ divinylbenzene (65 µm)
- CW/DVB — Carbowax/divinylbenzene (65 µm)
- PDMS — poly(dimethylsiloxane) (7 µm, 30 µm, 100 µm)
- PA — polyacrylate (85 µm)
- CW — Carbowax (50 µm)
- Carboxen/PDMS — Carboxen/poly (dimethylsiloxane) (75 µm)

The fiber is used with a special holder designed to conceal or expose it inside an injector needle, whichever is desired. This assembly is used both for adsorption and desorption steps. There is no need to remove the fiber during the entire operation. The same fiber can be used over and over again if handled properly.[10-18]

Experiments with cut flowers: Experiments were carried out indepently with cut flowers for 1.5 h, 2.5 h and 15.5 h. Citronellol was the main constituent of cut flowers. 2-Phenylethyl alcohol ranked second in abundance. Contents of these two main components decreased during prolonged extraction period while those of less volatile compounds such as paraffins (pentadecane) and sesquiterpenes (α-guaiene) increased (F-5 and F-6).

Experiments with live flowers: Headspace-SPME was carried out on living rose plants for 4 h. SPME-trapping with live rose flowers showed the occurrence of 2-phenylethyl alcohol as the main constituent. Citronellol was the second most abundant constituent (F-5 and F-6).

It was interesting to note that live rose flowers emitted 2-phenylethyl alcohol, while in cut flowers the main component emitted was citronellol.

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