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Characterization of the Volatile Aroma Compounds from the Concrete and Jasmine Flowers Grown in India

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Jasmine is one of the important commercial traditional flower crops of India. It plays an important role in religious offerings, social and cultural activities of India. It is also used for the production of essential oils in the form of ‘concrete’ and ‘absolute’ which are used in cosmetics and perfumery industries. Fully open flowers contain maximum fragrance and needs to be collected for concrete extraction. India earns crores of foreign currency every year through export. Being an export commodity, ideal blossoming time and quality testing of jasmine flowers are extremely crucial matters in exportation of flowers and concrete. The quality evaluation is human dependent and their sensory organs may give different results at different points of time, as well as the result may vary from the one evaluator to another since no two person can perceive a thing identically. The results may also vary based on the physiological climatic and many other allied conditions. In a nutshell, the evaluation methodology is highly subjective and lacks the precision of an automated machine.
Hence, there is a need for an automated, portable, low-power, easy-to use and reliable machine, which can evaluate quality objectively and repetitively, so that it can assist the Floriculture Industry, research laboratories and flower exporters for final evaluation of jasmine flower and its concrete quality. A handheld Electronic Nose system has been developed which can be used to monitor the volatile emission pattern of jasmine flower and concrete on the basis of sensor outputs.
This paper presents a study where, first, the selection of appropriate sensors was carried out based on sensitivity with the major aroma-producing chemicals of jasmine flower and concrete. Then, this sensor array was exposed to flowers at its different stage of maturity that were collected from the farmer’s field at Sathyamangalam, Erode district, Tamil Nadu in India and to concrete of different species. The experimentation was conducted on the three species of Jasmine namely, Jasminum sambac, Jasminum auriculatum and Jasminum grandiflorum at the Tamil Nadu Agricultural University (TNAU), Coimbatore. The computational model has been developed based on statistical correlation methods to correlate the measurements with the human expert’s views. With unknown jasmine samples and concrete of different species of jasmine flowers, encouraging results have been obtained with more than 90% classification rate.

1. Introduction

Indian Jasmine (L.) Aiton (Family: Oleaceae), flowers was picked at June, the peak time of flowering season was studied using GC-MS and the developed new technology “Handheld Electronic Nose (HEN)” to describe and discriminate the jasmine fragrance. Concrete of jasmine is one of the most expensive substances that was used in cosmetics, the pharmaceutical industry, perfumery and aromatherapy. A Handheld Electronic Nose system has been developed to monitor the volatile emission pattern of jasmine flower and concrete on the basis of sensor outputs.
In India, the flowering period of Jasminum Sambac started in April, reaches its maximum in June and then declines in September. The flowering period of Jasminum Grandiflorum started in July, reaches its maximum in September and then declines in November. The immature buds are having no smell but it

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develops odour during its blossoming. The optimum blossoming time is found at night and the flowers are developing its characteristic odour. Jasmine Blossoms at the mid night - early morning. It needs to be harvested at its optimum blossoming state & need to be marketed immediately. Market price depends on the fragrance and appearance. The world production of jasmine concrete is around 20 tonnes per annum out of which India is producing and exporting about 2 tonnes.

The fully blossomed flower is used to extract its oil and concrete. A non-polar solvent such as Hexane is used to "wash" the aromatic compounds out of the flowers. After the hexane is evaporated a waxy, semisolid substance known as a "concrete" is left. The concrete then undergoes a series of "washings" with a polar solvent such as ethanol. The polarity of the ethanol will allow extraction of the volatile aromatics from the concrete while leaving behind the non-polar plant waxes which do not dissolved in the ethanol. Finally, the ethanol is evaporated to leave behind the ABSOLUTE which will typically have 1-5% ethanol remaining in it and sometimes a trace of hexane.

The volatile emission pattern varies widely in different climatic conditions and agricultural resources. The chemical composition of the odour were analysed and studied. Optimum blossoming of Jasmine Flower depends on Seasonal Variation. The quantum emission of fragrance compounds present in the harvested flowers shows increasing trend from morning to evening. Presence of all the volatile compounds in the flowers only will give good quality concrete. All the volatile compounds exhausted from the flowers will give only inferior quality concrete/absolute. In nature all the volatile compounds are fixed in the flowers with fibrous materials. Concrete is extracted from the freshly harvested flower or when the fragrance emission is slow. All the fragrance compounds are not easily released from the fibrous materials of the flowers. It is advisable to do the extraction of concrete when the major fragrance compounds are started released vigorously i.e. when sudden increase in fragrance takes place from the harvested flower.

2. Materials and methods

2.1 Plant Material

Three species of jasmine, *Jasminum sambac*, *Jasminum auriculatum*, *Jasminum grandiflorum* were of our interest for experimentation. Matured buds, semi-blossomed buds and fully blossomed flowers were collected from different parts of Tamil Nadu. The concrete of jasmine were collected from M/s Cigma Essence & Aromatics Pvt. Ltd, Karamadai, Coimbatore, Tamil Nadu. The absolute was analysed using Gas Chromatography & Mass Spectrophotometry instrument (GC-MS).

2.2 Handheld E-Nose System

The Electronic nose used in the study was a handheld, battery operated, low weight system equipped with an array of five (5) metal oxide sensors (MOS), a touch screen based user interface, integrated odour delivery unit, both battery and ac adapter operated. The volatile response pattern can be stored in the SD memory card and the results are displayed in the Graphics Display unit. The sample needs to be placed in a glass sample holder in the e-nose set-up.

2.3 Odour delivery

The entire process of sampling the volatiles is divided into three processes, namely-

a. Headspace time- Building adequate air pressure inside the sample chamber to generate aroma volatiles by blowing fresh air from outside.
b. Sampling time- Generated aroma are allowed to expose to the sensor array to produces an output voltage in mV range.
c. Purging time- To re-establish the sensor array to its baseline, the sensors are exposed to clean air for at least three (3) minutes.

Figure 1: Experimental Set-up

2.4 Data Acquisition and Processing
The sensors output are captured to the 16-bit embedded processor through an in-built ADC after proper signal conditioning. The processor runs a statistical algorithm namely Singular Value Decomposition (SVD) and generates an index, called Aroma Index, which has a direct relationship of the aroma of the sample. The captured data is stored in the SD card and as well as the result is displayed on the Display. A 16-bit Serial Flash is in built to the processor for storing calibration data.

2.5 Power supply
The device can be operated by a 12 V battery and ac adapter. Power supply has the capability to generate +12 Volt, +10Volt, +9Volt, +5Volt and +3.3 Volt. The separate heater supply is generated using a DC-DC converter.

2.6 Firmware developed
The system software for HEN is an application firmware developed on a 16-bit embedded platform to serve the purpose of the following functions-
Data acquisition and analysis
Quality assessment of bud, flower, concrete.
Determination of optimum blossoming time of jasmine flower from bud to flowering.
Graphical user interface on a touch screen based display.
Data storage in FAT file format in SD card memory.

3. Sensors selection

The sensors considered for jasmine classification were TGS-822, TGS 880, TGS 2444, TGS 2620, TGS 816, TGS 823, TGS 832, TGS 2600, TGS 826, TGS 825, TGS 2442, TGS 2610 C00, TGS 2611 C00, TGS 2611 E00, TGS 2610 D00,TGS 2612, TGS 830 and TGS 2602 of Figaro Engineering Inc. Though sensor selection is based on sensitivity analysis with a handful of major aroma determinants, there will be contribution of other volatiles on the sensor responses when exposed to smell of flower. But our specific objective in this study was to track the overall effect of these volatiles on the sensor array and investigate the correlation of the multi-sensor output data with sensory evaluation. Further, only fresh jasmine flower has been used for all our experiments. So, effect of humidity is negligible on the sensor responses.
From the response of individual sensors to the *Jasminum sambac*, *Jasminum auriculatum*, *Jasminum grandiflorum*, it is observed that the responses of the sensors – TGS 2610 C00, and TGS 2611 D00 are same as of TGS 2610 D00 and TGS 2611 E00 and hence have not been considered for inclusion in the sensor array in our experimental electronic nose for jasmine's classification. After various experimentation using these sensors finally the following sensors were selected for jasmine and the sensors that were considered for jasmine classification were TGS 823, TGS 825, TGS 2620, TGS 2602 and TGS 832 of Figaro Engineering Inc. and used in the electronic nose set-up.

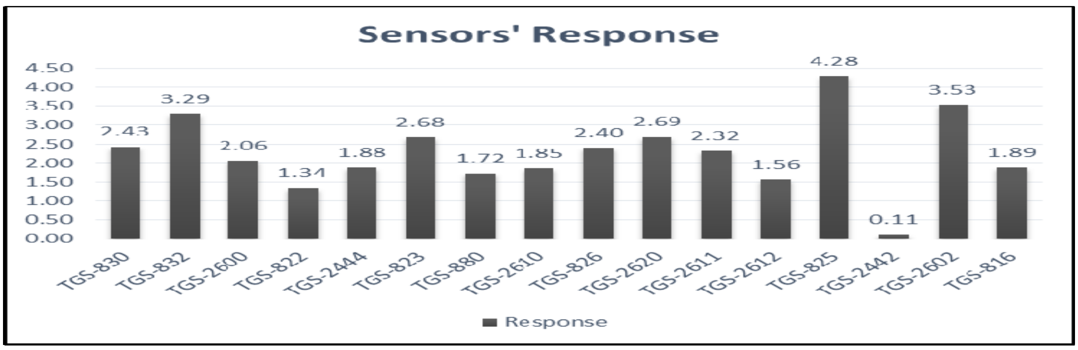

Figure 2: Response of MOS sensors

4. Results and Discussion

Gas Chromatography-Mass Spectrometry (GC-MS)
The concretes were made from jasmine flowers at three different intervals i.e. 10AM, 6PM, and 10PM and then from it 1µg volume of sample were taken and tested in GC-MS for 37.5 min at a base

temperature 200° C with a split ratio 1:10. Constituents were identified by comparison of both mass spectra and retention indices, strictly measured on the same instrument (GC-MS) with those of authentic Jasmine samples.

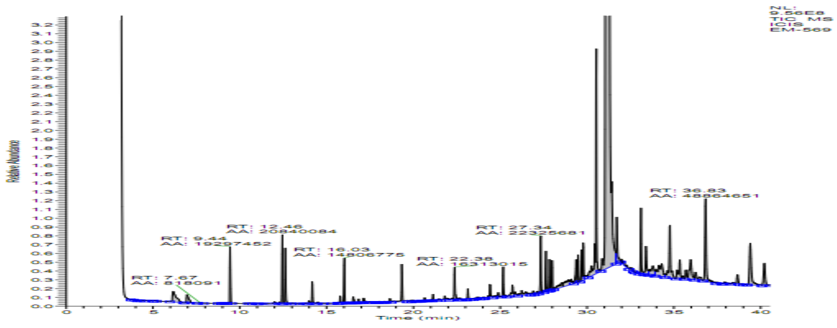

Figure 3: GC analysis data-concrete extraction time -10 AM

In decreasing order of important compounds, they are: 1, 2-Benzenedicarboxylic acid, bis (2-ethylhexyl) ester (0.94%), Cyclohexasiloxane and Cycloheptasiloxane, tetradecamethyl (0.23%), Hexadeca methyl cyclo octasiloxane (0.17%), Cyclodecasiloxane, eicosamethyl (0.15%) and Linalool (0.13%). It is noteworthy that high molecular weight esters were observed under the chromatographic conditions.

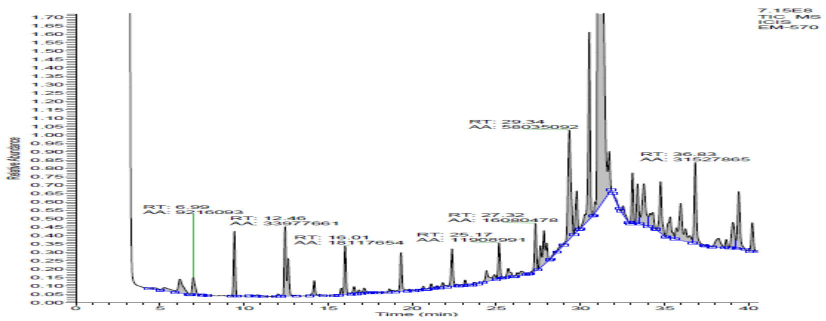

Figure 4: GC analysis data-concrete extraction time -6 PM

The important active plant principles in essential oil of jasmine extracted at 6 pm was reported to be of twenty chemical constituents, they are: 1, 2-Benzenedicarboxylic acid, bis (2-ethylhexyl) ester (0.82%), Hentriacontane (0.71%), Cycloheptasiloxane, tetradecamethyl- (0.29%), Cyclohexasiloxane, dodecamethyl-(0.26%) and Linalool (0.09%). These jasmine volatile compounds are responsible for its unique fragrance started to release during this time.

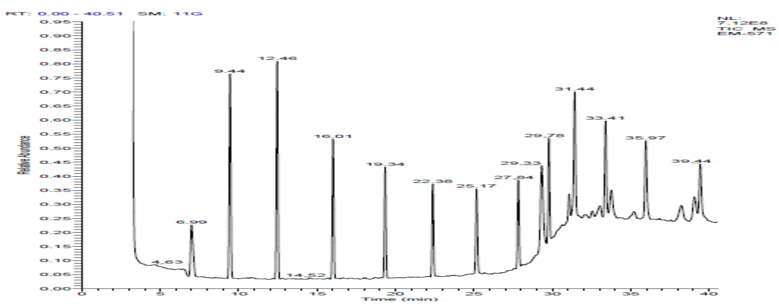

Figure 5: GC analysis data-concrete extraction time -10 PM

The jasmine flower possesses maximum composition during this time. They are Cycloheptasiloxane, tetradecamethyl (7.93%), Cyclohexasiloxane, dodecamethyl (7.22%), Cyclodecasiloxane, eicosamethyl (5.44%) and Heneicosane, 11-(1-ethylpropyl) (5.05%).

Table1: Comparison Table

Sl. No.	*Compound Name*	*Molecular Weight*	*Timing*	*Retention Area %*
1	Cyclohexasiloxane, dodecamethyl-	444	10 AM	0.23
			6 PM	0.26
			10 PM	7.22
2	Cycloheptasiloxane, tetradecamethyl-	518	10 AM	0.23
			6 PM	0.29
			10 PM	7.93
3	Hexadecamethylcyclooctasiloxane	592	10 AM	0.17
			6 PM	0.19
			10 PM	4.94
4	Cyclohexasiloxane, eicosamethyl-	740	10 AM	0.15
			6 PM	0.17
			10 PM	3.24

Handheld Electronics Nose

Samples, made from same jasmine flowers, of volume 15gm were tested under handheld e-Nose system, which produce a fragrance index of tested samples. This test was occurred at Micro Analytical Laboratory, Tamil Nadu Agriculture University, Coimbatore at ambient temperature (23^{o} C). Flowers were collected from different parts of Coimbatore like auction market, Sathyamangalam, Botanical garden, TNAU, local vendors, Coimbatore etc. Fully matured unpen buds were taken as sample, and spread on ground and allowed them to open. During these stages the fragrance of flowers was tested using handheld e-Nose system, which produced the graphs.

Table 2: Aroma index w.r.t. time

Sl. No.	*Time*	*Opening Index*	*Batch ID*	*Aroma Index*
1	12:00	0	SB1	6.94
2	12:45	0	SB2	4.98
3	14:17	0	SB3	8.58
4	15:14	0	SB4	6.83
5	16:07	0	SB5	8.73
6	16:44	1	SB6	11.03
7	17:27	1	SB7	10.72
8	17:43	1	SB8	14.07
9	18:03	1	SB9	14.47
10	18:18	1	SB10	14.57
11	19:10	2	SB11	22.33
12	19:29	2	SB12	21.75
13	23:14	3	SB13	23.24

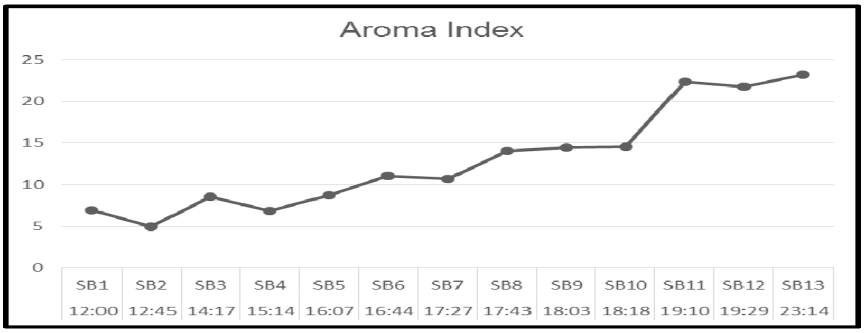

Figure 7: Fragrance profile of Jasmine flowers

Inference:

Equal amount of the concrete was injected into GC–MS with a split ratio 1:10. The mean area percentages of the individual peaks were calculated for the analyses of Jasmine samples taken at three different intervals Viz., 10am, 6pm and 10pm. The study also revealed that, the preliminary indication about the composition of some major volatile components. However, here its quantitative composition of these compounds differs considerably from the other samples. The jasmine flower possesses maximum composition during this time. They are Cyclohexasiloxane dodecamethyl-, Cycloheptasiloxane tetradecamethyl-, Hexadecamethy lcyclooctasiloxane, Cyclohexasiloxane, eicosamethyl- . The volatile compounds were identified according to their mass spectra and their retention indices were used to confirm the major components involved in fragrance emission. The result clearly indicates that there was a sharp increase in these volatile compounds as the time progresses.

Aroma index (or alternatively, Norm Aroma Index) is the HEN generated aroma value of the given sample based on the responses obtained from the sensors of the HEN sensor array. Fragrance profile of jasmine flowers clearly illustrates that aroma gradually increase as time progresses.

5. Conclusions

The quantum emission of fragrance compounds present in the harvested flowers shows increasing trend from morning to evening. The fragrance emission is slow and steady between 11 am to 6 pm, thereafter sudden increase has observed in harvested flower. From 6.30pm – 7 pm onwards major increase in fragrance observed in jasmine flowers. The handheld Electronic Nose system gives the similar kind of output from the volatile emission pattern of jasmine flower and concrete on the basis of sensor outputs. While the results obtained are quite encouraging in terms of nucleation of new methodology for quality estimation which is fast, non-invasive and user-friendly, the point to be noted is, no attempt has been made to make any universal model. The result definitely opens up a new horizon of future research based on electronic nose for quality assessment of flower and concrete.

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