5 RESULTS AND DISCUSSION

5.1 Drying characteristics of Cinnamon chips

The results of the variation of moisture content of cinnamon chips dried at different temperatures are summarized in Table 5.1.

Table 5.1: Moisture content on dry basis and drying time for different drying temperatures

	Moisture content on dry basis (kgH_2O/kg dry solid)				
Drying Temperature (°C)	30±2	35±1	40±1	45±1	50±1
Time (minutes)					
0.000	1.406	1.406	1.406	1.406	1.406
10	1.344	1.216	-	-	-
15	-	-	0.917	0.831	0.831
20	1.227	1.093	0.848	0.756	-
30	1.122	0.981	0.710	0.605	0.568
40	1.017	0.869	0.631	0.501	-
45	-	-	-	-	0.367
50	0.917	0.793	0.552	0.404	-
55	-	-	-	-	0.246
60	0.817	0.717	0.473	0.311	-
70	0.766	0.649	0.412	0.221	-
80	0.717	0.581	0.356	-	-
90	0.664	0.513	0.29	-	-
100	0.612	0.462	0.245	-	-
110	0.555	0.414	-	-	-
120	0.502	0.367	-	-	-
130	0.455	0.318	-	-	-
140	0.432	0.268	-	-	-
150	0.408	0.234	-	-	-
160	0.384	-	-	-	-
170	0.361	-	-	-	-
180	0.337	-	-	-	-
190	0.313	-	-	-	-
200	0.288	-	-	-	-
210	0.266	-	-	-	-
220	0.248	-	-	-	-

Cinnamon chips achieved the required final moisture content of 24% (w/w dry basis) within 220, 147, 100, 68 and 55 minutes for the air drying temperatures of ambient, 35 °C, 40 °C, 45 °C and 50 °C respectively. Moisture content on dry basis against the drying time and drying rate against moisture content on dry basis for different drying temperatures were plotted using MATLAB R2007b (Appendix E) and it is illustrated in Figure 5.1 and Figure 5.2 respectively.

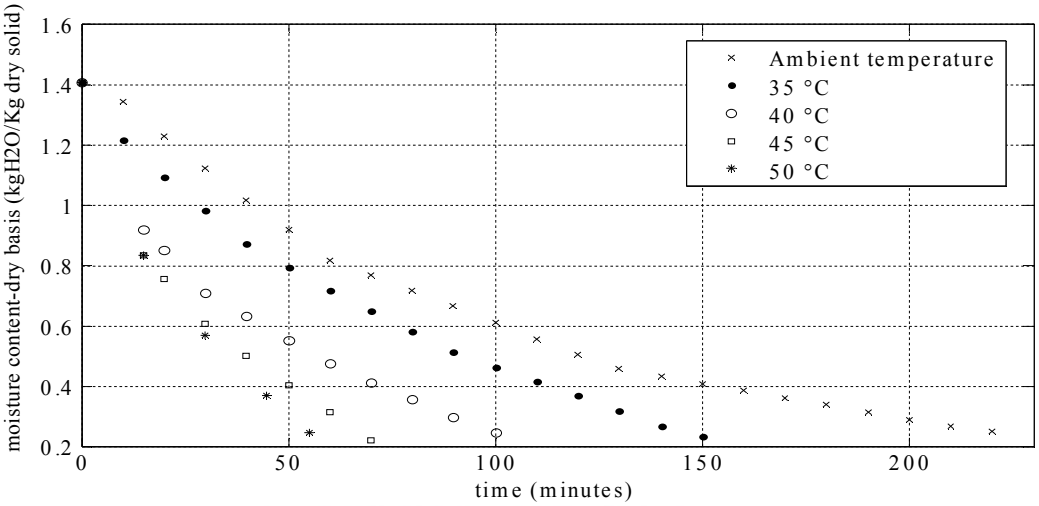

Figure 5.1: Variation of moisture content with time for different air drying temperatures

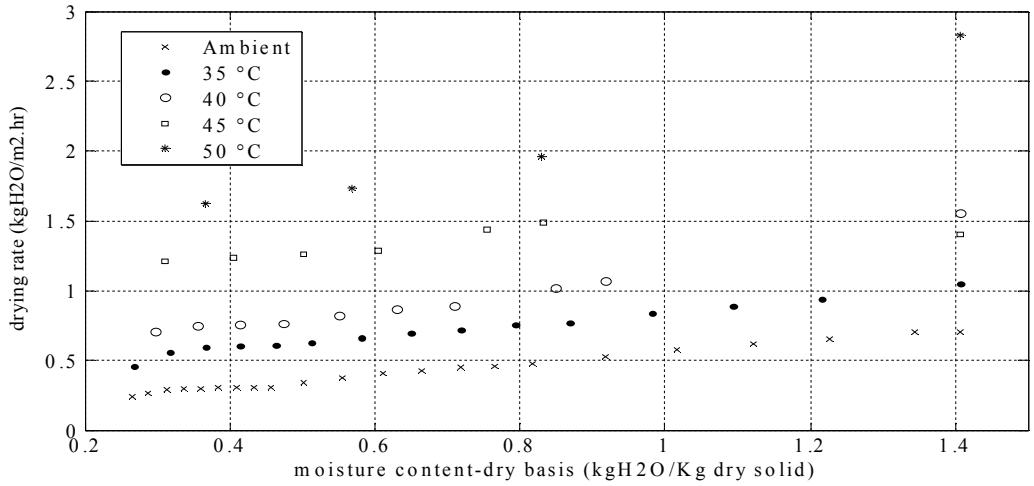

Figure 5.2: Variation of drying rate with moisture content for different air drying temperatures

The result, clearly indicates a falling rate drying period, which is corresponded to internal migration of moisture from inner layers to the surface. The reduction in drying rate may due to the shrinkage of the cell structure and the reduction in water concentration of cinnamon chips which result in a lower diffusion coefficient.

5.2 Gas Chromatography Analysis

The results of gas chromatography analysis are given in this section and it describes how the volatile organic compounds in cinnamon bark oil behaves with respect to five air drying temperatures (ambient, 35 °C, 40 °C, 45 °C and 50 °C). Relative content % for 16 identified volatile organic compounds of cinnamon bark oil at different drying temperatures are summarized in Table 5.2.

Quantitatively, cinnamaldehyde-E was the most abundant aromatic compound in cinnamon bark oil, followed by cinnamyl acetate, linalool and eugenol in all the samples. Similar results were obtained by other workers using steam distillation of cinnamon stem bark of commercial samples (Senanayake, et al., 1978) and hydro distillation of air dried cinnamon stem bark samples (Paranagama, et al., 2001) in Sri Lanka.

Table 5.2: Gas chromatography analysis for cinnamon oil dried at different temperatures

No	Volatile organic Compounds	Relative content % (in different drying temperature)																			
	Temperature (°C)	Ambient				35				40				45				50			
	No of Trials	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
1	1,4-dimethyl benzene (p-xylene)	0.972	0.957	0.948	0.927	0.827	0.897	0.871	0.886	0.795	0.813	0.848	0.823	0.871	0.903	0.859	0.894	0.656	0.679	0.671	0.652
2	styrene	0.1	0.109	0.099	0.16	0.17	0.165	0.182	0.199	0.138	0.142	0.136	0.147	0.205	0.198	0.189	0.225	0.137	0.167	0.158	0.146
3	benzene,1,2,3-trimethyl	0.202	0.184	0.172	0.218	0.132	0.147	0.168	0.175	0.204	0.21	0.215	0.208	0.215	0.195	0.204	0.174	0.275	0.223	0.204	0.249
4	α-phellandrene	0.662	0.736	0.747	0.877	0.891	0.837	0.976	1.063	0.492	0.498	0.504	0.523	0.254	0.265	0.282	0.257	0.146	0.184	0.183	0.135
5	benzene,1-methyl-4-(1-methylethyl)(p-cymene)	1.463	1.473	1.555	1.474	1.807	1.782	1.797	1.769	0.751	0.728	0.743	0.731	0.58	0.562	0.619	0.611	0.533	0.507	0.527	0.541
6	β-phellandrene	1.876	1.522	1.717	1.539	2.681	2.393	2.389	2.748	1.255	1.269	1.243	1.214	0.977	0.918	0.994	0.99	0.519	0.512	0.607	0.543
7	1,6-octadiene-3-ol,3,7-dimethyl (linalool)	4.23	4.894	4.301	4.649	5.082	5.25	5.213	5.15	4.141	4.139	4.161	4.155	4.657	4.511	4.345	4.878	3.785	3.701	3.713	3.588
8	benzenepropanal	0.332	0.326	0.32	0.358	0.441	0.459	0.482	0.485	0.46	0.475	0.473	0.456	0.426	0.418	0.491	0.45	0.399	0.343	0.375	0.371
9	3-cyclohexene-1-ol,4-methyl-1-(1-methylethyl) (terpinen-4-ol)	0.463	0.477	0.496	0.533	0.421	0.473	0.471	0.481	0.425	0.459	0.438	0.442	0.459	0.476	0.499	0.461	0.421	0.368	0.379	0.397
10	2-propenal,3-phenyl (cinnamaldehyde)	0.688	0.69	0.617	0.671	0.542	0.569	0.585	0.547	0.487	0.494	0.52	0.506	0.627	0.655	0.612	0.611	0.527	0.536	0.558	0.507
11	cinnamaldehyde-E	63.352	63.977	63.762	63.91	66.585	67.287	67.374	67.437	73.122	73.34	73.302	73.581	76.37	76.194	76.226	76.322	78.611	78.42	78.896	78.648
12	eugenol	4.216	4.546	4.477	4.169	3.807	3.688	3.699	3.635	3.349	3.33	3.334	3.325	3.42	3.444	3.599	3.572	2.221	2.168	2.291	2.271
13	caryophyllene	1.715	1.618	1.681	1.701	1.394	1.391	1.377	1.373	0.998	1.079	1.125	0.995	0.767	0.768	0.756	0.743	0.648	0.639	0.628	0.657
14	2-propen-1-ol 3-phenyl acetate (cinnamyl acetate)	14.199	14.025	14.656	14.49	10.371	10.45	10.223	9.952	8.318	7.913	8.532	8.263	5.738	6.016	5.748	6.044	8.206	8.145	7.976	7.93
15	2-propenal,3-(2-methoxyphenyl) (2-methoxy-cinnamaldehyde)	0.914	0.929	0.896	0.951	0.261	0.291	0.283	0.301	0.218	0.212	0.225	0.208	0.269	0.262	0.275	0.283	0.239	0.267	0.243	0.235
16	benzyl Benzoate	2.273	2.138	2.028	2.152	1.047	1.076	0.813	0.989	0.773	0.766	0.75	0.743	0.686	0.657	0.659	0.668	0.743	0.737	0.724	0.728

5.3 Statistical Analysis

5.3.1 Mean comparison by ANOVA

5.3.1.1 Verification for the validity of assumption

One of the assumptions of the one-way ANOVA is that the variances between the independent groups are similar (homogeneity of variances). Table 5.3 indicates the result of Levene's test of homogeneity of variance for cinnamaldehyde-E among different temperature groups.

Table 5.3: Levene's test of homogeneity of variances for cinnamaldehyde-E

Component	Significance
cinnamaldehyde-E	0.251

The significance value, greater than 0.05 means that homogeneity of variances can be achieved. For cinnamaldehyde-E, Levene's F Statistic has a significance value of 0.251. Therefore, the assumption of homogeneity of variance (similar variance) is met for cinnamaldehyde-E. By referring Appendix F.1 significance values of other volatile organic compounds of cinnamon bark oil except β-phellandrene, linalool, eugenol and caryophyllene are greater than 0.05 and their group variances are equal.

Welch test was performed to examine the statistical significance of these four components (β-phellandrene, linalool, eugenol and caryophyllene) and the results are given in Table 5.4. Results indicate that the significance values are less than 0.05 and hence the group means are statistically significant.

Table 5.4: Welch test of equality of means

Component	Significance
β-phellandrene	0.000
linalool	0.000
eugenol	0.000
caryophyllene	0.000

The assumption of normality in one-way ANOVA is used to determine whether a data set is well-modelled by a normal distribution or not. Table 5.5 represents the results of Shapiro-Wilk test (verifying the normality) for cinnamaldehyde-E at five air drying temperatures (ambient, 35 °C, 40 °C, 45 °C and 50 °C). The significance values for these temperature groups are greater than 0.05 and hence data set of cinnamaldehyde-E are normally distributed. Test of normality for other 15 volatile organic compounds of cinnamon bark oil has mentioned in Appendix F.2 and normality condition was achieved.

Table 5.5: Shapiro-Wilk tests of normality for cinnamaldehyde-E

Temperature (°C)	**Significance**
Ambient	0.318
35	0.056
40	0.827
45	0.594
50	0.828

In Figure 5.3 the normal Q-Q plot of cinnamaldehyde-E at ambient temperature indicates that the data points are close to the diagonal line. This is a clear evidence that the data is normally distributed.

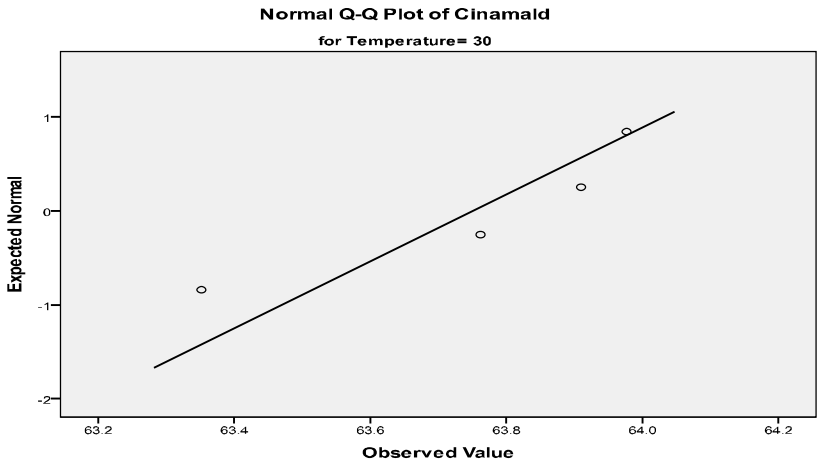

Figure 5.3: Normal Q-Q plot of cinnamaldehyde-E at ambient temperature

5.3.1.2 One way ANOVA descriptives

The results of descriptive statistics and the ANOVA analysis of cinnamaldehyde-E for the samples dried at different temperatures are given in Table 5.6 and Table 5.7 respectively.

Table 5.6: Descriptive table of cinnamaldehyde-E at different temperatures

Temperature °C	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
				Lower Bound	Upper Bound		
Ambient	63.75025	0.280284	0.140142	63.30426	64.19624	63.352	63.977
35	67.17075	.395313	.197656	66.54172	67.79978	66.585	67.437
40	73.33625	.188850	.094425	73.03575	73.63675	73.122	73.581
45	76.27800	.081976	.040988	76.14756	76.40844	76.194	76.370
50	78.64375	.195606	.097803	78.33250	78.95500	78.420	78.896
Total	71.83580	5.725439	1.280247	69.15621	74.51539	63.352	78.896

The F-value is 2464.07 and the corresponding p-value is given as <0.000. Therefore, the null hypothesis (H_0) can be safely rejected with the conclusion that the mean temperature of cinnamaldehyde-E is not the same among the five drying temperatures (ambient, 35 °C, 40 °C, 45 °C and 50 °C). Similar analysis was carried out for all the other volatile compounds and the results are summarized in Appendix F.3 and Appendix F.4 respectively.

Table 5.7: ANOVA table of cinnamaldehyde-E

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	621.886	4	155.471	2464.070	0.000
Within Groups	0.946	15	0.063		
Total	622.832	19			

The results of all the volatile organic compounds of cinnamon bark oil under investigation clearly indicate that null hypothesis (H_0) can be safely rejected.

5.3.1.3 Mean comparison using Student-Newman-Keuls (SNK) test

Table 5.8 is the mean comparison table which contains the results of Student-Newman-Keuls (SNK) test for cinnamaldehyde-E. This method, gives an idea of which groups differ from each other.

Table 5.8: Mean comparisons of cinnamaldehyde-E

Temperature	N	Subset for alpha = 0.05				
		1	2	3	4	5
Ambient	4	63.75025				
35	4		67.17075			
40	4			73.33625		
45	4				76.27800	
50	4					78.64375
Sig.		1.000	1.000	1.000	1.000	1.000

The first column contains the list of temperature groups in order from lowest to highest mean. The second column of the table identifies the number of replicate experiments in each and every temperature group. The remaining columns identify the five homogeneous subsets of temperature groups that are statistically significantly different from each other. The results of Student-Newman-Keuls (SNK) test for all the other volatile organic compounds are given in Appendix F.5. The homogeneous subsets which are formed including more than one temperature groups indicate that mean of such temperature groups are not differed significantly at the α=0.05 significance level.

The peak area of volatile organic compounds in gas chromatogram was chosen as the analytical signal for the relative content, and the identified volatile organic compounds are given in Table 5.9 with mean and relative standard deviation (RSD) values based on quadruplicated experiments carried out to find the compositions

relevant to different air drying temperatures (ambient, 35 °C, 40 °C, 45 °C and 50 °C). Table 5.9 also summarizes the results of the Student-Newman-Keuls test for comparison of mean values by using letters a, b, c, d and e.

Table 5.9: Concentration of volatile compounds (relative content %) in hydro distilled cinnamon bark

Compound	ambient temperature		35°C		40°C		45°C		50°C	
	mean (n=4)	RSD (%)	mean (n=4)	RSD (%)	mean (n=4)	RSD (%)	mean (n=4)	RSD (%)	mean (n=4)	RSD (%)
p-xylene	0.95d	1.98	0.87c	3.53	0.82b	2.70	0.88c	2.30	0.66a	1.91
styrene	0.12a	3.33	0.18c	8.45	0.14ab	3.45	0.20c	7.49	0.15b	8.68
Benzene,1,2,3-trimethyl	0.19b	10.41	0.16a	12.65	0.21bc	2.19	0.20b	8.82	0.24c	13.01
α-phellandrene	0.76d	2.60	0.94e	10.52	0.50c	2.66	0.26b	4.75	0.16a	15.58
p-cymene	1.49d	0.49	1.79e	0.93	0.74c	1.45	0.59b	4.49	0.53a	2.75
β-phellandrene	1.66d	3.45	2.55e	7.39	1.25c	1.88	0.97b	3.64	0.55a	7.93
linalool	4.52c	11.70	5.17d	1.43	4.15b	0.26	4.60c	4.92	3.70a	2.20
benzenepropanal	0.33a	15.58	0.47c	4.44	0.47c	2.02	0.45c	7.35	0.37b	6.17
terpinen-4-ol	0.49c	2.75	0.46bc	5.92	0.44b	3.18	0.47bc	3.90	0.39a	5.92
cinnamaldehyde	0.67d	7.93	0.56b	3.56	0.50a	2.89	0.63c	3.28	0.53ab	3.98
cinnamaldehyde-E	63.75a	2.20	67.17b	0.59	73.34c	0.26	76.28d	0.11	78.64e	0.25
eugenol	4.35e	6.17	3.71d	1.95	3.33b	0.31	3.51c	2.56	2.24a	2.46
caryophyllene	1.68e	5.92	1.38d	0.74	1.05c	6.08	0.76b	1.54	0.64a	1.93
cinnamyl acetate	14.34d	3.98	10.25c	2.14	8.26b	3.11	5.89a	2.82	8.06b	1.64
2-methoxy-cinnamaldehyde	0.92d	0.25	0.28c	5.99	0.22a	3.43	0.27c	3.28	0.25b	5.84
benzyl benzoate	2.15c	2.46	0.98b	12.01	0.76a	1.83	0.67a	1.98	0.73a	1.17

[a]Different letters (a,b,c,d,e) in the same row indicate statistical difference at the α=0.05 level according to the Student-Newman-Keuls test.

The RSD values for most of the volatile organic compounds were found to be less than 10% for 4 replicated experiments. This result indicates that the method of drying and hydro-distillation carried out in the present study were reasonably uniform. On the other hand, cinnamon chips used in the present study were from the same batch and hence the variations due to pre-processing (method of removal from stems), type of cinnamon chips (mas katta, wal katta etc.) and regional variations (due to acclimatization) were minimised.

Increase in air drying temperature above 35 °C resulted in the reduction of quality and yield of cinnamon bark oil (Chandra et al., 2011). Since essential oils have highly volatile aromatic compounds, they may escape during the drying operation. Increasing the temperature can damage the cell membranes of cinnamon. Rupturing of cell walls and tissues where cinnamon oil is accumulated could be the main reason for the reduction in oil yield and concentration of most of the volatile organic compounds listed in Table 5.9.

The results of Student-Newman-Keuls test indicate significant difference at α =0.05 level (as marked with letters a,b,c,d and e) among the composition of cinnamon bark oils which were extracted from cinnamon chips dried at different temperatures. Air drying at high temperatures resulted in substantial losses in concentrations of monoterpenes (α-phellandrene, β-phellandrene and p-cymene), cinnamaldehyde and cinnamaldehyde derivatives such as cinnamyl acetate, and 2-methoxy-cinnamaldehyde. Increase in air drying temperature also resulted in substantial losses in certain oxygenated terpenes (linalool, terpinen-4-ol and eugenol) and sesquiterpene (caryophyllene). The only component to have an increase in concentration with the increase in air drying temperature was found to be cinnamaldehyde-E which is also a highly volatile component. However it represents a significantly higher concentration (about 60%) than the other volatile organic compounds in cinnamon bark oil and it may probably have high affinity to the bark resulting in high internal mass transfer resistance during air drying.

5.3.2 Principal component analysis (PCA)

Principal components analysis (PCA) was carried out on the relative percentages of 16 volatile organic compounds of cinnamon bark oil to compare the possible differences among different air drying temperatures (ambient, 35 °C, 40 °C, 45 °C and 50 °C). The results are presented in Table 5.10, Figure 5.4 and Figure 5.5. Since PCA looks for groups of correlated variables along which the variance is maximized, each principal component (PC) is interpreted as a group of correlated variables. The correlated volatile organic compounds which are important to attribute a meaning to

each component are highlighted in Table 5.10 and are displayed in Figure 5.4 and Figure 5.5 at the edges of the respective PC axes.

Table 5.10: Correlations between volatile organic compounds and principal components (PC)

Compound	PC1	PC2	PC3
β-phellandrene	**0.978**	0.019	0.113
α-phellandrene	**0.941**	0.206	0.169
p-cymene	**0.906**	0.292	0.190
Benzene,1,2,3-trimethyl	**-0.789**	0.186	-0.234
linalool	**0.775**	-0.308	0.469
cinnamaldehyde-E	**-0.770**	-0.511	-0.377
caryophyllene	**0.741**	0.556	0.350
styrene	-0.030	**-0.881**	0.205
cinnamyl acetate	0.490	**0.832**	0.220
benzenepropanal	0.332	**-0.825**	-0.168
benzyl benzoate	0.296	**0.821**	0.474
2-methoxy- cinnamaldehyde	0.159	**0.790**	0.580
cinnamaldehyde	-0.001	0.282	**0.899**
terpinen-4-ol	0.387	0.019	**0.795**
p-xylene	0.517	0.109	**0.795**
eugenol	0.606	0.249	**0.694**

Correlations presented in bold are important for the attribution of a meaning to components

The explained variance % and the cumulative variance % of principal components PC1, PC2 and PC3 are given in Table 5.11. The results suggest that the components in PC1 have the highest contribution to the variance with an explained variance percentage of 39.2% while volatile organic compounds in PC2 and PC3 having explained variance percentage of 27.7% and 24.1% respectively. The volatile organic compounds selected in the principal components attribute a variance contribution ratio of 91% and only 9% of the information is lost. This indicates that the three

principal components express 91% of the all information. Hence, the three principal components can reflect the vast majority of cinnamon oil composition. All of the samples in the space of the principal components had relatively independent positions and were effectively distinguished.

Table 5.11: Correlation coefficient values for the volatile organic compounds against principal component 1 ,2 and 3

PC	volatile compound	loading	% explained variance	% cumulative variance
1	β-phellandrene	0.978	39.227	39.227
	α-phellandrene	0.941		
	p-cymene	0.906		
	benzene,1,2,3-trimethyl	-0.789		
	linalool	0.775		
	cinnamaldehyde-E	-0.770		
	caryophyllene	0.741		
2	styrene	-0.881	27.691	66.918
	cinnamyl acetate	0.832		
	benzenepropanal	-0.825		
	benzyl benzoate	0.821		
	2-methoxycinnamaldehyde	0.790		
3	cinnamaldehyde	0.899	24.070	90.988
	terpinen-4-ol	0.795		
	p-xylene	0.795		
	eugenol	0.694		

Figure 5.4 and Figure 5.5 depict the planes of principal components 1 *vs* 2 and 1 *vs* 3 respectively. PC1 is mainly separating the samples of cinnamon chips which were dried using hot air at 35 °C (loaded on the positive, right side of PC1) and 50 °C (loaded on the negative, left side of PC1). Hot air at 35 °C is characterized by high amounts of monoterpenes (α-phellandrene, β-phellandrene and p-cymene), oxygenated terpene (linalool) and sesquirtepene (caryophyllene) and 50 °C is characterized by high amounts of benzene,1,2,3-trimethyl and cinnamaldehyde-E . PC2 is mainly separating the ambient air temperature (displaced towards the positive, upper side of PC2), and hot air at 45 °C (displaced towards the negative, lower side

of PC2). Results suggest that ambient air temperature having higher amounts of cinnamyl acetate, benzyl benzoate and 2-methoxy-cinnamaldehyde, and hot air at 45 °C having higher amounts of styrene and benzenepropanal.

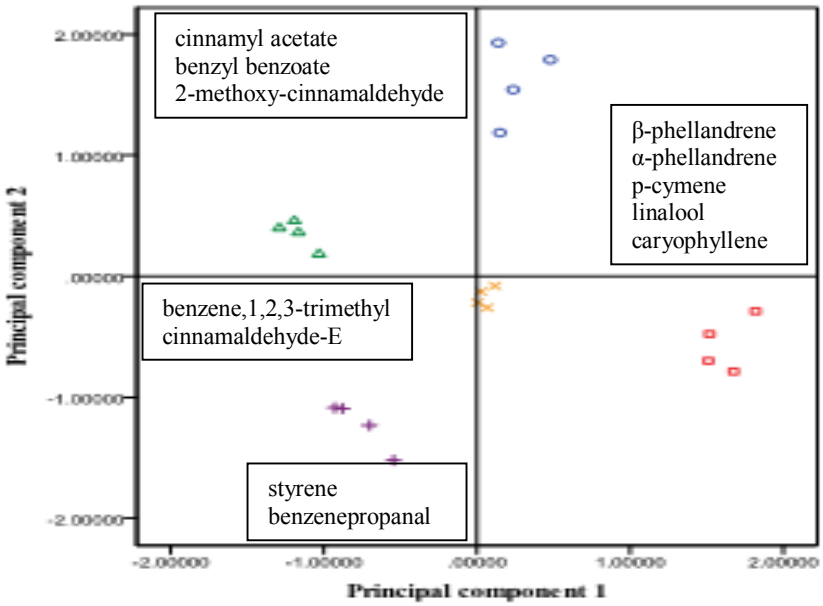

Figure 5.4: Principal component plot (PC2 vs PC1), ambient temperature dried (○), air dried at 35 °C (□), air dried at 40 °C (×), air dried at 45 °C (+), air dried at 50 °C (Δ)

PC3 separates the ambient air and hot air at 45 °C temperatures (loaded on the positive, upper side of PC3) from hot air at 40 °C (loaded on the negative, lower side of PC3) indicating higher amounts of cinnamaldehyde, terpinen-4-ol, p-xylene and eugenol in 45 °C and ambient and lower amounts of those volatile organic compounds in 40 °C.

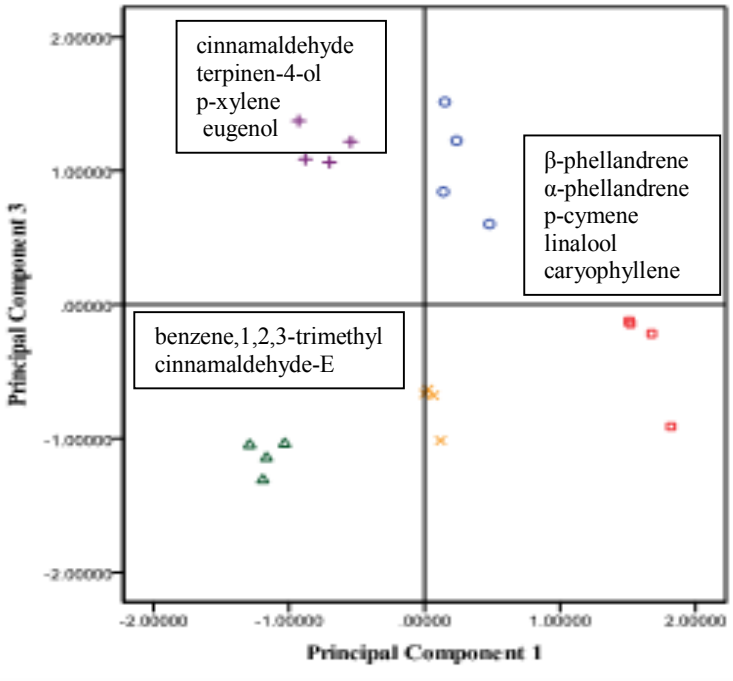

Figure 5.5: Principal component plot (PC1 vs PC3). ambient temperature dried (○), air dried at 35 °C (□), air dried at 40 °C (×), air dried at 45 °C (+), air dried at 50 °C (Δ)