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# Tea lovers' alternative approach to analyze dynamic changes of aromatic components of Chinese tea

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Abstract

Analyses of aromatic components of Chinese teas have been done by various scholars and researchers in connection with its manufacturing process, quality control, storage and distribution. Consequently, a number of volatile chemicals related to Chinese tea have been identified by conventional GC and GC-MS analyses. As Chinese tea lovers, we are intrigued by dynamic changes of aromatic fragrance at the time we prepare and taste tea rather than identifying aromatic chemicals of tea. What happens on the invisible and intangible world of tea aroma at the time we take a sip and savor a small tasting cup of Chinese tea? Why does a different grade tea taste different even though the manufacturing process is identical? Why is the tea of the first infusion different from that of the second one? Why is the tea brewed in a Yixing teapot different from that brewed in a Gaiwan (covered bowl)? Out of curiosity, we brewed Wenshan Pouchong tea in various ways - a tasting mug, a Yixing teapot and a Gaiwan, and tested the aroma of its beverage with a newly developed electronic nose called zNose™ which could analyze the concentration of aroma in real time with picogram sensibility.

## Introduction

Since Emperor Shen Nung, the Divine Cultivator, was charmed by the aroma of Camellia sinensis and took a sip of its beverage 5000 years ago, the invisible and intangible world of tea aroma has fascinated mankind. Our predecessors spent an enormous time and effort to express an ever-changing tea aroma in art, music, and literature.

Scientific analyses of aroma components of Chinese teas have been done by various scholars and researchers in connection with its manufacturing process, quality control, storage and distribution. Consequently, a number of volatile chemicals related to Chinese tea have been identified by conventional GC and GC-MS analyses.

But as Chinese tea lovers, our interest is mainly the changing faces of tea aroma at the time we take a sip and savor a small tasting cup of Chinese tea. In order to observe this, we use a newly developed electronic nose called zNose™ which can measure aroma in real time and display the results in chromatogram and olfactory image called VaporPrint™.

## Instrumentation

The zNose™, EST Model 4100, is a portable ultra-fast GC/SAW tester (gas chromatography combined with a single non-polymer-coated 500MHz surface acoustic wave sensor), developed by Electronic Sensor Technology (USA). It can detect and quantify the concentration of headspace vapors of hydrocarbons (C4-C25) in real time with picogram sensitivity. The built-in helium bottle contains enough helium carrier gas to perform more than 300 consecutive measurements. The outcomes are displayed on a notebook PC screen in the form of sensor frequency vs retention time graph as well as a traditional gas chromatogram format. Moreover, the zNose™ can transform these graphs into two-dimentional olfactory images in a polar format called VaporPrint.

## System Setting

For this test, a 1 meter db5 GC column was used. The temperatures of the sampling inlet and the SAW sensor were set to 150$^{o}$C and 30$^{o}$C respectively. The sampling time was set to 20 seconds to sample 10cc of the headspace tea aroma. The data acquisition time (retention time range) was defined 20 seconds. The column was ramped linearly from 40$^{o}$C to 140$^{o}$C at 5$^{o}$C/sec. step throughout 20 seconds of data acquisition, so that the obtained unknown components can be estimated by their retention times relative to the n-alkanes Kovats linear retention indices.

## Sample Preparation

Prior to the test, a C6-C14 n-alkane standard solution in methanol was measured in order to create the retention time scale for Kovats Indices.

Three grades (high, middle and low) of Wenshan Pouchong tea leaves were used for the test. Each sample tea was prepared in the manners described below. Water temperature at the time of infusion was about 95$^{o}$C.

(1) A tasting mug: A tasting mug was used to compare three grades of Wenshan Pouchong tea. 3 grams of each grade was placed in a mug and then 150cc of the boiling water was poured into it. After five minute infusion, its beverage was poured into a vial for zNose test.

(2) A gaiwan (covered bowl) with an optimal infusion time: A gaiwan was used to prepare the traditional gongfu tea. 6.7 grams of the middle grade Wenshan Pouchong tea leaves was place in a gaiwan, and then the boiling water was poured into it. After 39 seconds of the initial infusion, the tea was poured into a tea jug and then served in a vial for zNose test as well as small tasting cups for our personal evaluation. The tea leaves were re-steeped two more times. The 2nd and 3rd infusions were 47 and 43 seconds respectively. Each infusion time was determined based on our past experience.

(3) A gaiwan with different steeping times: A gaiwan was used to prepare the traditional gongfu tea in the same manner as the (2). But this time the longer and shorter infusion times (78 and 20 seconds) were selected.

(4) A Yixing teapot with an optimal infusion time: A Yixing teapot was used to prepare the traditional gongfu tea in the same manner as the (2). The 1st, 2nd and 3rd infusion times were 42, 39 and 39 seconds respectively. Each infusion time was determined based on our past experience.

## Sampling & Testing

In order to perform tea test, 10cc of a sample beverage was poured into a 40ml septa sealed vial. After a sparging and a sampling needles were inserted through the septa (see Appendix 1), 10cc of the headspace sample was collected and analyzed by the zNose™. The test was conducted three cycles to verify its repeatability accuracy, and the outcome of the first cycle was used for evaluation. Before testing a next sample, three blank runs were conducted to clean up inside the zNose™. The entire process of testing each sample, including tea preparation, vial setting, three cycles of chromatograms and three blank runs, took less than 10 minutes. Since the testing time is very short, the zNose™ and we were able to TASTE every infusion at the same time.

## Data Acquisition

By measuring the C6-C14 n-alkane solution by the zNose, the hydrocarbon retention time scales relative to alkane number were created. These scales were used to interpolate Kovats Retention Indices (KI) of the peaks found in each zNose chromatogram.

A chromatogram table in each Appendix shows retention times (average of three tests), estimated KI values and frequency values (concentration) of the chromatogram peaks. It will be possible to relate these KI values to those of the compounds listed in the database such as the Flavornet of Cornell University. As shown on Appendix 2, among 22 aromatic chemicals of Pouchong Tea listed in the paper of Mr. Takeo, 17 chemicals were found in the Flavornet db5 Kovats Retention Indices list.

## Findings

Appendix 3 - 6 show chromatograms, their VaporPrint™ image (olfactory images) and tables of chromatogram peaks of each sample analysis.

1. Appendix 3 (Three grades of Pouchong tea): The chemical components of three grades were very similar each other, but the VaporPrint™ images indicated that there were striking differences in the density distribution of the components among three grades. In addition, the overall concentration of the components of the low grade tea seemed smaller than the other two grades.
2. Appendix 4 (Three infusions of the Gaiwan gongfu tea): The chromatograms and their VaporPrint™ images indicated that some components in the first infusion were found in much higher concentration than those in the second infusion (e.g. RT(Retention Time)= 17.49sec.), but some other components were found on the contrary (e.g. RT=13.29). It seemed that the change of aromatic expression of tea was caused by the change of the density distribution of their chemical components.
3. Appendix 5 (The Gaiwan gongfu tea with three different infusion times): The optimal infusion time (39 seconds) had the highest concentration for the components of RT=1.87, 5.43, 10.37, 15.05, and 18.17 and the lowest concentration for the components of RT=12.25 and RT=16.25 among three infusion times.
4. Appendix 6 (Three infusions of the Yixing gongfu tea): The result was similar to three infusion of the Gaiwan gongfu tea.
5. Appendix 7 (Comparison between the Gaiwn and Yixing gongfu tea): The initial infusions of two gongfu tea were compared. Two samples showed a very similar concentration pattern for the components below RT=11, but the density distribution of the components above RT=11 was significantly different from each other.

## Conclusion

In this paper, neither identifying chemicals of Chinese tea nor searching for a new chemical was our major topic, even though the zNose™ is capable to speciate and quanitfy aromatic components of tea. We would like to yield this painful effort to well-informed professional researchers and experts.

However, it will be possible for a layman like us to identify indirectly an aromatic component by calculating a Kovats retention index of a chemical whose peak is found at the zNose™ chromatogram based on the retention time scale of C6-C14 n-alkanes and locating it in the library of the Kovats Indices which is available in public through the Internet.

Our predecessors of Chinese tea have left a plenty of profound and imaginative words and phrases to express a subtle but dynamic shift of tea aroma. In this paper, we, because of a lack of vocabulary and expressive phases, do not dare to make any comments on the teas we tasted. Instead, let the zNose™ itself express the dynamic shift of aroma and aromatic components by means of chromatogram and its olfactory image.

When we brewed tea with the optimal infusion time which we learned by our past experience, some components had maximum density and some others minimum density among three infusion times. It is a self-evident truth that infusion time is one of the vital elements to brew tea. The data seems to show the meaning of this statement.

Also, we found that there is a significant difference on the concentration of the relatively lower volatile components between a Yixing teapot and a gaiwan.

The chromatogram and its olfactory image show us the dynamic movement of aromatic components as if we listen to the fugues of J.S.Bach. After the first infusion some components suddenly disappeared, and some others were emerged through the leaves. Some stayed without change as if they insisted their existence. Some became fainter and fainter. On the other hand, some became powerful than ever.

Aromatic components of Chinese tea are intricately intertwined and make tea aroma rich and colorful. As a result, Chinese tea becomes more fascinating and attractive.

## Reference

Takeo, T., "Characteristic Properties of Oolong Teas Made in Different Areas of China," Chagyo Kenkyu Hokoku, Vol. 60, p.50-53. (1984)

http://www.nysaes.cornell.edu/flavornet/

http://chemfinder.cambridgesoft.com/

http://www.estcal.com/ (zNose Web site)

http://www.beehive.co.jp/est/ (zNose Web site in Japanese language)

# Appendix 1. Test Method

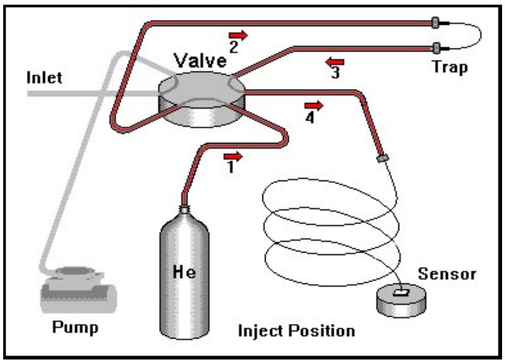
## Tea Preparation

10cc of tea beverage
in 40ml vial

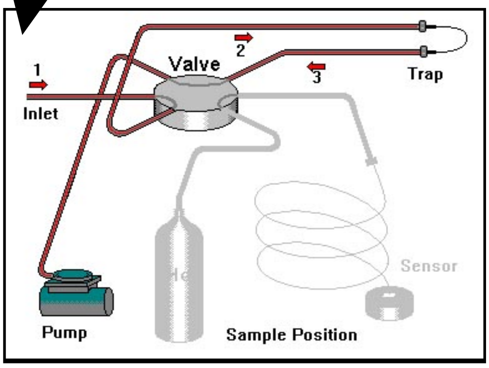
## Vial Setting

zNose™ with the vial

## Testing




The valve turns to the inject position, and the trap is fired and helium is injected. The components, being desorbed from the trap, pass through the column and reach the sensor surface.

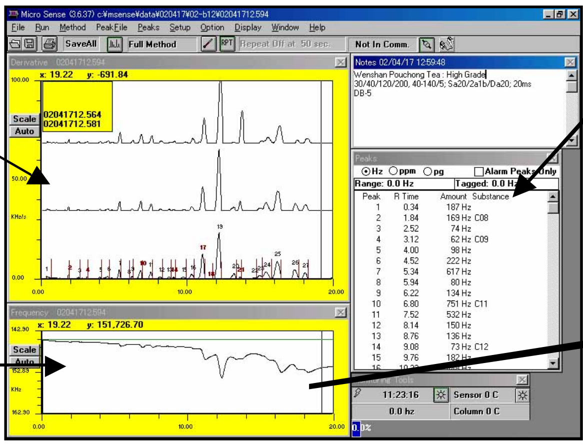



The valve turns to the sample position, and the headspace is absorbed by the vacuum pump. Consequently, aroma components are caught in the trap.

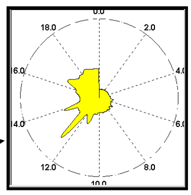
## Result Display

Chromatogram

Frequency Graph

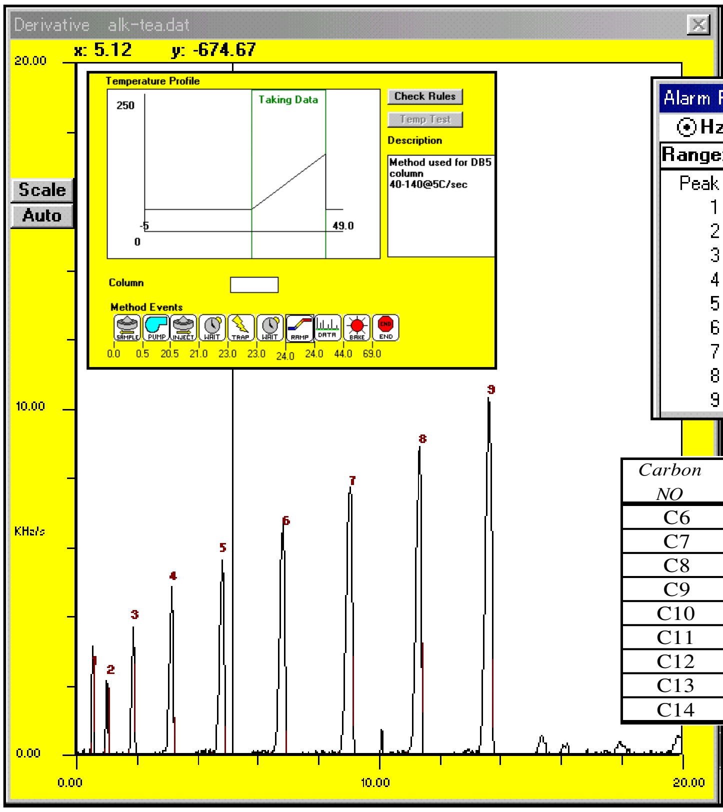


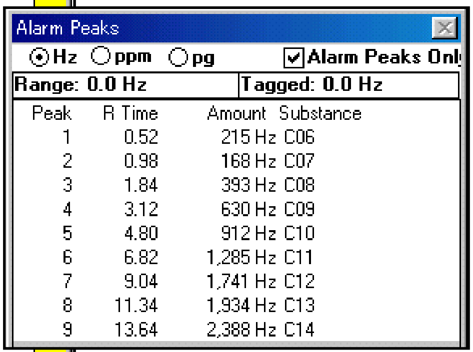

Peaks Window
1. Retention time
2. Amount (Total frequency change due to the material adsorbing on the sensor.)



VaporPrint™
Olfactory Image

# Appendix 2. Alkane solution (C6-C14) in methanol and Kovats Indices List of aromatic components related to Chinese tea



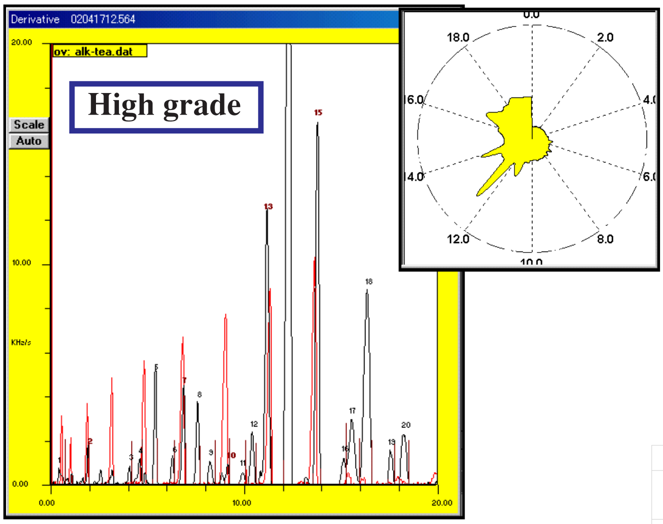

| Carbon NO | Component | Retention Time | Kovats Indices |
|---|---|---|---|
| C6 | n-Hexane | 0.52 | 600 |
| C7 | n-Heptane | 0.98 | 700 |
| C8 | n-Octane | 1.84 | 800 |
| C9 | n-Nonane | 3.12 | 900 |
| C10 | n-Decane | 4.80 | 1000 |
| C11 | n-Hendecane | 6.82 | 1100 |
| C12 | n-Dodecane | 9.04 | 1200 |
| C13 | n-Tridecane | 11.34 | 1300 |
| C14 | n-Tetradecane | 13.64 | 1400 |

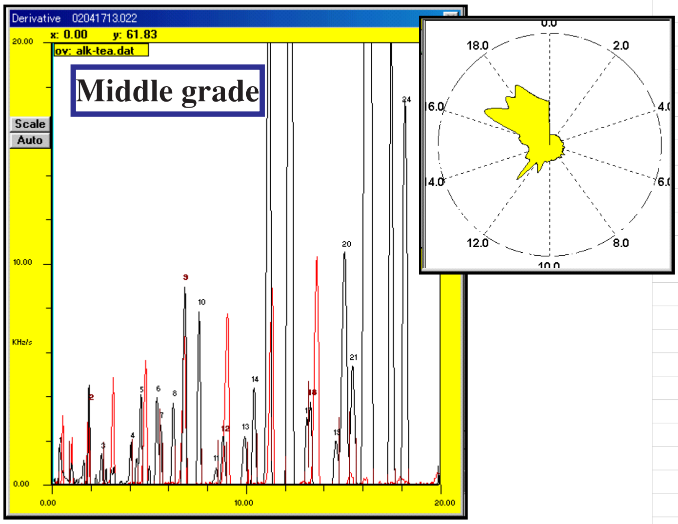
**Note: Among 22 aromatic components of Pouchong Tea listed in the paper of Mr. Takeo, 17 components were found in the db5 Kovats Retention Indices list of the Flavornet.**

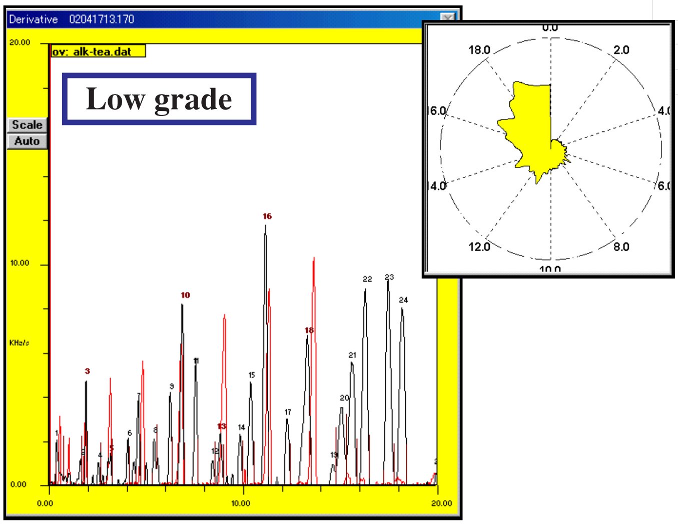
| | Component | db5 Kovats Indices | Odor |
|---|---|---|---|
| 1 | n-Amyl alcohol | 764 | balsamic |
| 2 | 1-Penten-3-ol | 809 | butter |
| 3 | n-Hexanol | 851 | resinous |
| 4 | cis-3-Hexenol | 853 | green grass |
| 5 | benzaldehyde | 968 | almond |
| 6 | E,E-2,4-Heptadienal | 1011 | nutty |
| 7 | Hexenoic Acid | 1019 | sweaty |
| 8 | Benzyl alcohol | 1039 | sweet |
| 9 | Linalool | 1100 | lemon |
| 10 | 2-Phenylethanol | 1118 | honey |
| 11 | a-Terpineol | 1195 | pine-oil |
| 12 | Linalool oxide (Z-furanoid) | 1212 | woody |
| 13 | Methyl salicylate | 1234 | peppermint |
| 14 | Geraniol | 1275 | rose |
| 15 | Indole | 1292 | mothballs |
| 16 | b-ionone | 1493 | nori, dry grass (hay) |
| 17 | Nerolidol | 1581 | woody |
| 18 | 1-Ethylpyrol-2-aldehyde | Not listed | |
| 19 | Benzyl cyanide | Not listed | |
| 20 | cis-Jasmone | Not listed | |
| 21 | Jasmine lactone | Not listed | creamy jasmine peach |
| 22 | Z-2-Penten-1-ol | Not listed | cherry |

*Not listed: Not listed in the Kovats Indices of the Flavornet
(http://www.nysaes.cornell.edu/flavornet/)

# Appendix 3. Three grade of Wenshan Pouchong Tea



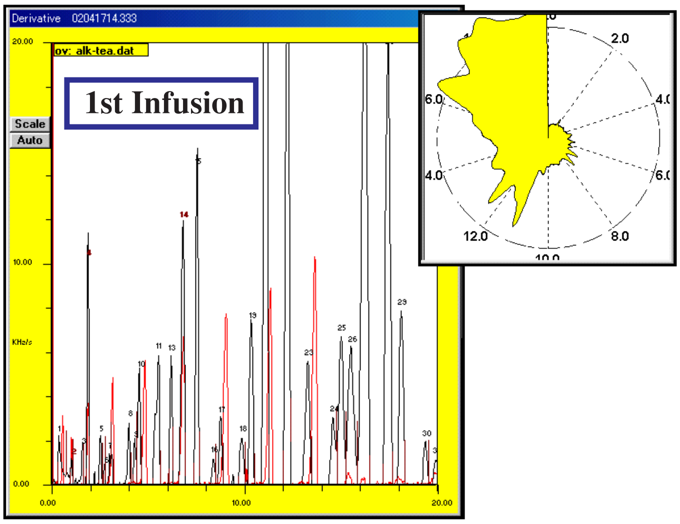



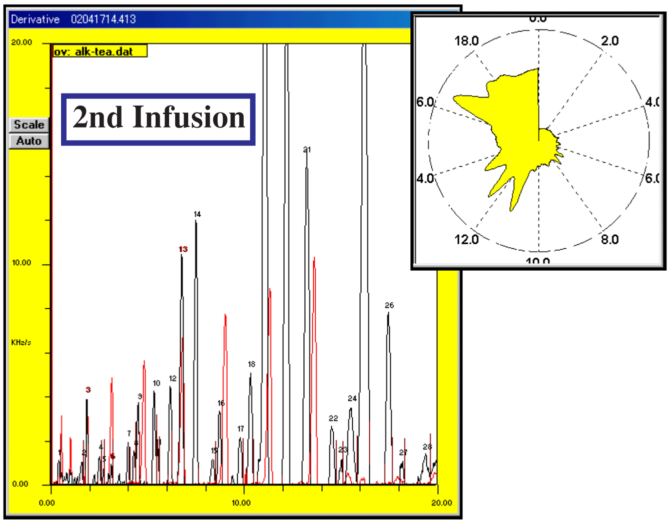

Tasting cup: Wenshan Pouchong

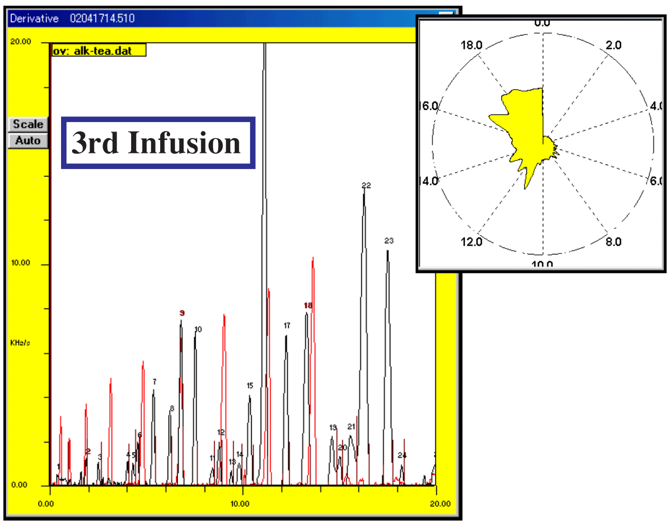
| | Retention Time (s) | Kovats Indices | High Grade (Hz) | Mid. Grade (Hz) | Low Grade (Hz) |
|---|---|---|---|---|---|
| 1 | 0.36 | 565 | 127 | 352 | 311 |
| 2 | 1.58 | 770 | | | 128 |
| 3 | 1.87 | 803 | 161 | 396 | 415 |
| 4 | 2.52 | 853 | | 170 | 119 |
| 5 | 3.14 | 901 | | | 263 |
| 6 | 4.04 | 955 | 118 | 246 | 254 |
| 7 | 4.57 | 987 | 217 | 468 | 477 |
| 8 | 5.39 | 1029 | 800 | 434 | 231 |
| 9 | 5.58 | 1039 | | 166 | |
| 10 | 6.24 | 1071 | 188 | 507 | 565 |
| 11 | 6.84 | 1101 | 807 | 1656 | 1509 |
| 12 | 7.57 | 1134 | 597 | 1200 | 903 |
| 13 | 8.22 | 1163 | 211 | | |
| 14 | 8.42 | 1172 | | 120 | 168 |
| 15 | 8.82 | 1190 | | 404 | 434 |
| 16 | 9.14 | 1204 | 129 | | |
| 17 | 9.89 | 1237 | 116 | 471 | 400 |
| 18 | 10.39 | 1259 | 472 | 799 | 938 |
| 19 | 11.16 | 1292 | 2888 | 5857 | 2404 |
| 20 | 12.29 | 1341 | 8577 | 11090 | 588 |
| 21 | 13.14 | 1378 | | 252 | |
| 22 | 13.32 | 1386 | | 274 | 2229 |
| 23 | 13.80 | 1407 | 3456 | | |
| 24 | 14.64 | 1443 | | 289 | 108 |
| 25 | 15.11 | 1464 | 130 | 2407 | 699 |
| 26 | 15.56 | 1483 | 709 | 1024 | 1495 |
| 27 | 16.30 | 1516 | 2921 | 18946 | 2463 |
| 28 | 17.53 | 1569 | 322 | 4173 | 2628 |
| 29 | 18.23 | 1600 | 685 | 4057 | 2432 |
| 30 | 20.04 | 1678 | | | 159 |

**Note: A chromatogram of each sample is overlaid by that of C6-C14 n-alkane solution.**

# Appendix 4. Gaiwan Tea Preparation (Wenshan Pouchong Tea)



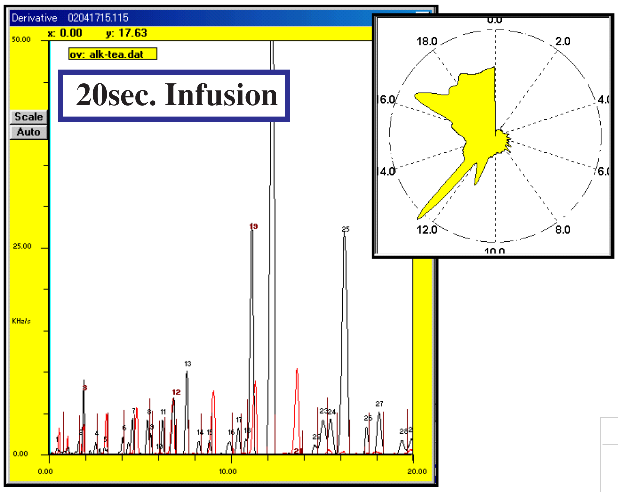



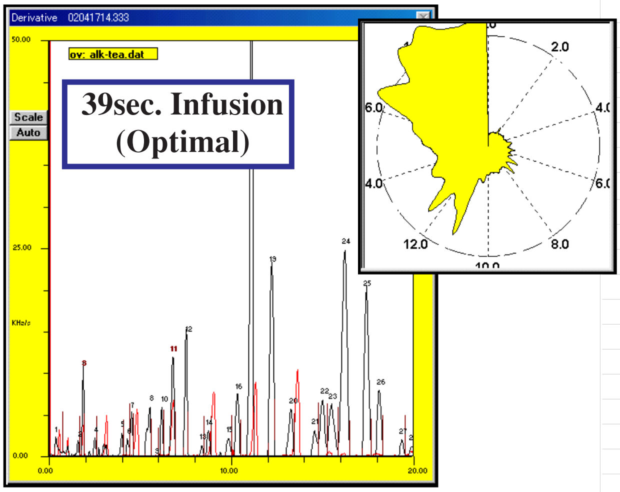

Gaiwan tea preparation

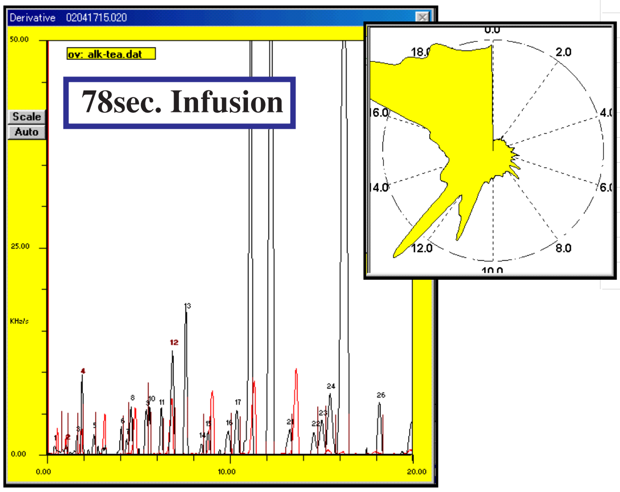
| | Retention Time (s) | Kovats Indices | 1st Infu. (Hz) | 2nd Infu. (Hz) | 3rd Infu. (Hz) |
|---|---|---|---|---|---|
| 1 | 0.35 | 564 | 317 | 105 | 154 |
| 2 | 1.56 | 767 | 192 | 125 | |
| 3 | 1.83 | 799 | 1071 | 350 | 114 |
| 4 | 2.48 | 850 | 264 | 160 | 111 |
| 5 | 3.97 | 951 | 349 | 197 | 112 |
| 6 | 4.28 | 969 | 151 | 111 | |
| 7 | 4.51 | 983 | 590 | 420 | 198 |
| 8 | 5.39 | 1029 | 1260 | 481 | 649 |
| 9 | 5.86 | 1052 | 371 | | |
| 10 | 6.17 | 1068 | 775 | 623 | 482 |
| 11 | 6.77 | 1098 | 2233 | 1848 | 1324 |
| 12 | 7.51 | 1131 | 2314 | 1909 | 1043 |
| 13 | 8.39 | 1171 | 171 | 211 | 137 |
| 14 | 8.74 | 1186 | 504 | 575 | 306 |
| 15 | 9.81 | 1234 | 471 | 404 | 191 |
| 16 | 10.33 | 1256 | 1493 | 1002 | 848 |
| 17 | 11.11 | 1290 | 11048 | 8319 | 5152 |
| 18 | 11.54 | 1309 | 3418 | | |
| 19 | 12.23 | 1339 | 5316 | 5581 | 1421 |
| 20 | 13.29 | 1385 | 1417 | 3649 | 2017 |
| 21 | 14.59 | 1441 | 456 | 601 | 418 |
| 22 | 15.04 | 1461 | 1121 | 159 | 173 |
| 23 | 15.55 | 1483 | 1428 | 1074 | 512 |
| 24 | 16.27 | 1514 | 7699 | 8309 | 4191 |
| 25 | 17.49 | 1567 | 5411 | 1899 | 3103 |
| 26 | 18.20 | 1598 | 1900 | 175 | 137 |
| 27 | 19.42 | 1651 | 387 | 290 | |
| 28 | 20.06 | 1679 | 203 | 157 | 195 |

**Note: A chromatogram of each sample is overlaid by that of C6-C14 n-alkane solution.**

# Appendix 5. Gaiwan Tea Preparation (Wenshan Pouchong Tea) with different infusion time



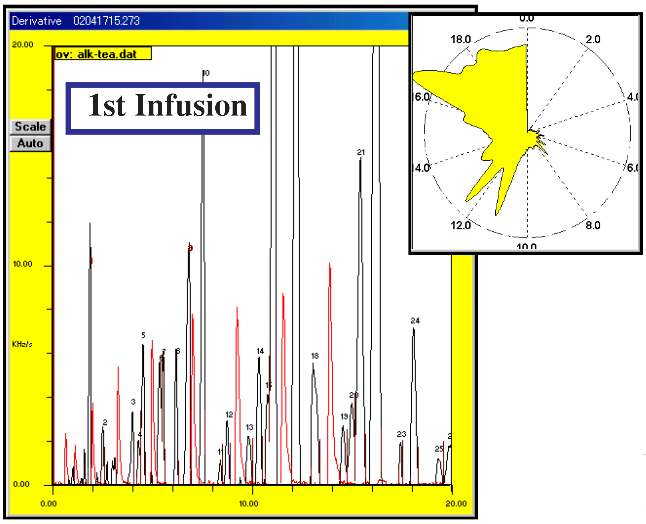

Gaiwan tea preparation: Different infusion time

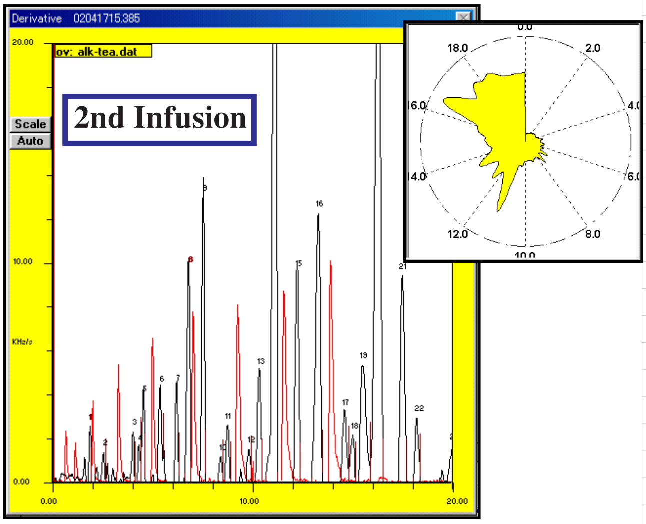
| | *Retention Time(s)* | *Kovats Indices* | *20sec. (Hz)* | *39sec. (Hz)* | *78sec. (Hz)* |
|---|---|---|---|---|---|
| 1 | 0.36 | 565 | 117 | 317 | 148 |
| 2 | 1.00 | 702 | | | 107 |
| 3 | 1.58 | 770 | 142 | 192 | 170 |
| 4 | 1.87 | 802 | 809 | 1071 | 887 |
| 5 | 2.51 | 852 | 166 | 264 | 303 |
| 6 | 3.02 | 892 | 127 | | |
| 7 | 4.01 | 953 | 283 | 349 | 436 |
| 8 | 4.31 | 971 | | 151 | 126 |
| 9 | 4.54 | 985 | 485 | 590 | 652 |
| 10 | 5.43 | 1031 | 430 | 1260 | 464 |
| 11 | 5.67 | 1043 | 124 | 371 | 340 |
| 12 | 5.92 | 1055 | 274 | | |
| 13 | 6.21 | 1070 | 553 | 775 | 749 |
| 14 | 6.82 | 1100 | 1219 | 2233 | 2231 |
| 15 | 7.55 | 1133 | 1569 | 2314 | 2750 |
| 16 | 8.22 | 1163 | 263 | | |
| 17 | 8.40 | 1171 | | 171 | 176 |
| 18 | 8.78 | 1188 | 235 | 504 | 428 |
| 19 | 9.89 | 1237 | 363 | 471 | 603 |
| 20 | 10.37 | 1258 | 611 | 1493 | 974 |
| 21 | 10.82 | 1277 | 129 | | |
| 22 | 11.13 | 1291 | 5362 | 11048 | 11681 |
| 23 | 11.54 | 1309 | | 3418 | 5125 |
| 24 | 12.25 | 1340 | 15065 | 5316 | 16308 |
| 25 | 13.29 | 1385 | | 1417 | 668 |
| 26 | 13.66 | 1401 | 155 | | |
| 27 | 14.60 | 1442 | 140 | 456 | 451 |
| 28 | 15.05 | 1461 | 702 | 1121 | 685 |
| 29 | 15.51 | 1481 | 638 | 1428 | 1748 |
| 30 | 16.25 | 1514 | 8515 | 7699 | 21098 |
| 31 | 17.46 | 1566 | 628 | 5411 | |
| 32 | 18.17 | 1597 | 1319 | 1900 | 1282 |
| 33 | 19.41 | 1651 | 359 | 387 | |
| 34 | 19.97 | 1675 | 637 | 203 | 1551 |

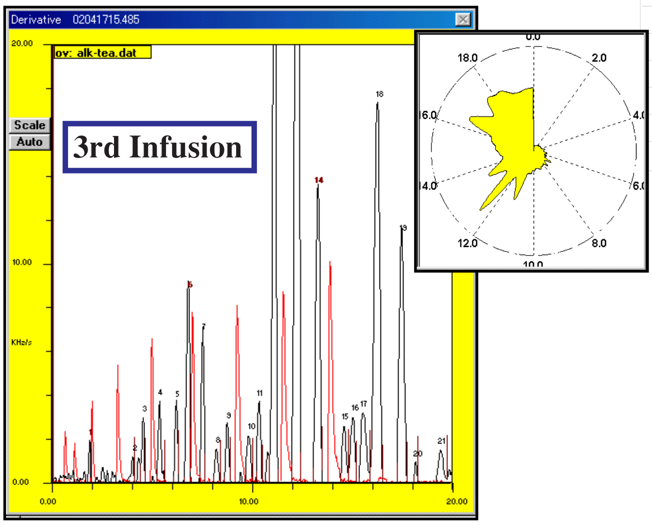
**39sec. Infusion**
**(Optimal infusion time)**

**Note: A chromatogram of each sample is overlaid by that of C6-C14 n-alkane solution.**
**The Y-axis scale range of the above is 50kHz.**

# Appendix 6. Yixing teapot Tea Preparation (Wenshan Pouchong Tea)




Yixing teapot tea preparation

| | *Retention Time (s)* | *Kovats Indices* | *1st Infu. (Hz)* | *2nd Infu. (Hz)* | *3rd Infu. (Hz)* |
|---|---|---|---|---|---|
| 1 | 1.83 | 799 | 1085 | 222 | 170 |
| 2 | 2.49 | 851 | 320 | 187 | |
| 3 | 3.98 | 951 | 453 | 276 | 179 |
| 4 | 4.28 | 969 | 140 | 126 | |
| 5 | 4.51 | 983 | 781 | 486 | 330 |
| 6 | 5.34 | 1027 | 493 | 550 | 606 |
| 7 | 5.52 | 1036 | 329 | | |
| 8 | 6.19 | 1069 | 772 | 663 | 578 |
| 9 | 6.80 | 1099 | 2094 | 1713 | 1644 |
| 10 | 7.52 | 1132 | 3126 | 2119 | 1103 |
| 11 | 8.20 | 1162 | | | 290 |
| 12 | 8.39 | 1171 | 133 | 177 | |
| 13 | 8.74 | 1186 | 468 | 449 | 471 |
| 14 | 9.81 | 1234 | 499 | 271 | 483 |
| 15 | 10.33 | 1256 | 1197 | 1000 | 689 |
| 16 | 10.78 | 1276 | 287 | | |
| 17 | 11.11 | 1290 | 10965 | 9612 | 5152 |
| 18 | 12.24 | 1339 | 9351 | 2035 | 9110 |
| 19 | 13.06 | 1375 | 1661 | | |
| 20 | 13.29 | 1385 | | 3359 | 3352 |
| 21 | 14.59 | 1441 | 487 | 661 | 506 |
| 22 | 15.03 | 1461 | 459 | 366 | 664 |
| 23 | 15.49 | 1481 | 3600 | 1553 | 900 |
| 24 | 16.28 | 1515 | 12433 | 7837 | 5361 |
| 25 | 17.49 | 1567 | 257 | 2277 | 3171 |
| 26 | 18.18 | 1597 | 1717 | 577 | 126 |
| 27 | 19.40 | 1650 | 279 | | 375 |
| 28 | 20.02 | 1677 | 866 | 790 | |

**Note: A chromatogram of each sample is overlaid by that of C6-C14 n-alkane solution.**

## Appendix 7. Comparison between Gaiwan and Yinxing teapot (Wenshan Pouchong Tea)