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Optimization of hydrodistillation and microwave assisted hydro distillation extraction of essential oil from Kinnow (*Citrus reticulate* Blanco) peel: Response surface methodology.

Optimización de la extracción por hidrodestilación y hidrodestilación asistida por microondas de aceite esencial de cáscara de Kinnow (*Citrus reticulate* Blanco): Metodología de superficie de respuesta.

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ABSTRACT

This study was planned to extract the essential oil from kinoow fruit peel. Peel collected from local vendor was dried and ground to powder. Further powder (100g) was dissolved in stipulated volume of water. A Box-Behnken design using response surface methodology (RSM) model was effectively used to optimize both processes (hydrodistillation and Microwave assisted extraction). The effects of material/solvent ratios (600-800mL), extraction time (4-6 h), extraction temperature (70-90 ^{o}C) and microwave power (200-600W) on the yield of *Citrus reticulata* Blanco Peel extraction of essential oils were studied. The result showed that the hydro-distillation technique showed minimum yield of 0.7% and maximum of 2.1%, whereas the microwave-aided extraction process produced minimum yield of 0.8% and maximum of 2.6% of essential oil. The best extraction conditions for kinnow essential oil were 70.69^{o} C, solvent/ material ratio of 769.16 mL, extraction duration of 4.41 h for hydro distillation 324.52^{o} C extraction power, 644.48 mL solvent ratio, and 12.20 min extraction duration for microwave assisted extraction.

Keywords- Citrus peel, extraction techniques, essential oil, characterization, design expert.

RESUMEN

Este estudio se planificó para extraer el aceite esencial de la cáscara del fruto del kinoow. La cáscara recogida del proveedor local se secó y se molió hasta convertirla en polvo. Se disolvió más polvo (100 g) en un volumen estipulado de agua. Se utilizó eficazmente un diseño de Box-Behnken utilizando el modelo de metodología de superficie de respuesta (RSM) para optimizar ambos procesos (hidrodestilación y extracción asistida por microondas). Los efectos de las proporciones material/disolvente (600-800 ml), tiempo de extracción (4-6 h), temperatura de extracción (70-90 oC) y potencia de microondas (200-600 W) sobre el rendimiento de la extracción de aceites esenciales con cáscara de *Citrus reticulata* Blanco. fueron estudiados. El resultado mostró que la técnica de hidrodestilación presentó un rendimiento mínimo de 0,7% y máximo de 2,1%, mientras que el proceso de extracción asistido por microondas produjo un rendimiento mínimo de 0,8%

y máximo de 2,6% de aceite esencial. Las mejores condiciones de extracción para el aceite esencial de Kinnow fueron 70,69 o C, relación disolvente/material de 769,16 ml, duración de extracción de 4,41 h para hidrodestilación, potencia de extracción de 324,52 o C, relación disolvente de 644,48 ml y duración de extracción de 12,20 min para extracción asistida por microondas.

Palabras clave- Cáscara de cítricos, técnicas de extracción, aceite esencial, caracterización, experto en diseño.

INTRODUCTION

The Rutaceae family's popular citrus variety, Citrus reticulata Blanco, is one of the most important horticultural commodities grown and marketed globally. It has considerable economic and gastronomic value. By-products of citrus include pulp, rind and seeds, the rind mainly yielding about 0.05–3 kg oil/tonne fruit (Pathak et al., 2017).

Citrus peel contains carbohydrates, lipids, volatile compounds, pigments, lavonoids, essential oils (up to 95% d-limonene), acids, enzymes, mineral elements, and vitamins (Jeong et al. 2021, Elkhatim et al. 2018, Satari and Karimi 2018). Citrus plant peels are said to contain several physiologically active chemicals that are widely used for flavouring drinks, meals, perfumes, cosmetics, and so on (Mohanapriya et al. 2013, Zaker et al. 2016). Flavonoids are the primary ingredients of both dried citrus fruits and citrus peels (Jamil et al. 2015).
The volatile constituents of the essential oils extracted from citrus peels are composed of a mixture of monoterpene, sesquiterpene, and their oxygenated derivatives, which are 85%-99%, while the non-volatile components are composed of hydrocarbons, flavonoids, sterols, fatty acids, coumarins, waxes, and carotenoids which are 1%-15% (Javed et al. 2014, Hojjati and Barzegar 2017). The use of essential oils is widely known, with uses ranging from flavours, aromatic agents in cosmetics and food preservatives to medicinal agents used in biomedical research (Tran et al. 2019, Dao et al. 2019).

Traditional or advanced methods can be used to extract essential oil. The benefits of employing an improved technology for essential oil extraction over traditional methods include shorter extraction times, lower energy usage, less Solvent utilized and lower carbon dioxide emissions (Aziz et al. 2018).Response surface methodology (RSM) with Box Behnken design (BBD) was applied to examine the impact of such factors and optimize the procedure. RSM is an analytical method that enables the assessment of the impacts of various action and their relations on certain responses (Tran et al. 2017, Tran et al. 2017a, Bach et al. 2018, Hien et al. 2018).

When optimizing an experiment procedure, this method is frequently used to produce second degree polynomial models. The approach has the added benefit of requiring the least amount of experimental runs possible, which cuts down on both experiment time and expense. The objective of the current research was to extract essential oil (EO) constituents from *C. reticulate Blanco* peels by applying the hydro distillation and microwave-assisted hydro-distillation (MAHD) method in consideration of the increasing interest in the extraction of essential oils. The current study optimizes the following variables for the highest oil output from Citrus reticulate Blanco peels: material/solvent ratios, extraction temperature, extraction time, and extraction

power by hydro distillation and Microwave assisted hydro distillation processes and characterization of extracted oil by FT-IR.

MATERIALS AND METHODS

Material: Kinnow peel used in this study was collected from juice vendor of Hisar and Sirsa market. Collected peel sample were subjected to washing under running tap water to remove the adherent dirt, dust and microbial load, after separating the damaged and unhealthy peel portion.

Drying of peel: All collected peel was dried in hot air oven (MSW-211, MAC) at 30-40 ^{o} C depending upon the quantity during loading. Dried peel thus obtained with 5% moisture content was grounded to powder by using a commercial grinder (Sujata). Powder was filled in LDPE pouches and stored at 4 ± 0.2 °C.

Hydro distillation extraction (HD): Conventional hydro distillation was performed with a Clevenger apparatus. 100 g dried kinnow peel powder was dissolved in distilled water in 1000ml flask. Flask was placed on heating element, followed by attachments of Clevenger apparatus and water supply pipes. By heating the flask the vapor generated were condensed by circulation of water in condenser.

When the oil is extracted, then turns open the knob and condensed material was collected in eppendof tube. The weight of essential oil was measured and the percentage yield of oil was calculated. The yield was expressed as follows:

$$\text{Yield (\%)} = \frac{\text{Volume of essential oil extracted}}{\text{Initial weight of dried peel powder taken}} \times 100$$

Extracted essential oil was stored at 4 ± 0.2 °C.

Microwave assisted hydro distillation (MAHD): The IFB 20PG4S domestic microwave oven was used for microwave aided hydro-distillation. The maximum output power of the power source was 800W, and frequency 2450MHz. 100 g dried kinnow peel powder was dissolved in stipulated amount of distilled water in 1000ml beaker. Put the flask on microwave oven and turn on the switch. After providing the microwave treatment with stipulated time, power and solvent, the solution was transferred into the conical flask, placed into the heating mental and hydro distillated the microwave treated sample solution at 80^{o}C for 5hour.

Experimental Design: The RSM design examined the effects of the material-to-water ratio, extraction temperature, extraction time for hydro distillation and MAHD on the yields of essential oil. Table 1, 3 contains a list of relevant parameters and their accompanying coding. The early experimental findings were used to set the initial parameter settings. Design Expert version 7.0.0 software has been used for the ANOVA analysis, coefficient calculations, and plotting. To assess the model's applicability to the data, anticipated yields and actual yields were also analyzed.

RESULTS AND DISCUSSION

Hydro distillation: By Hydro distillation process minimum and maximum yield of essential oil obtained is 0.7%, 2.10%. According to Aruna et al (2022), the oil recovery was 2 mL/100 g for dried shad orange peel, mosambi peel and1.5 mL/100 g for lemon peel. Zeleke et al (2022) showed average amount of essential oils

extracted from lemon and orange peels were 1.56% and 3.55%, respectively. Geographical differences in EO yield were observed (Le et al. 2020). As an example, Aripin et al (2015) extracted EO from materials gathered from Caringin Central Market, Bandung, and West Java, Indonesia, was conducted for eight hours with an extraction efficiency of 2.26%. On the other hand, Chanthaphon et al (2008) extracted 2.56% of the content from Kaffir lime cultivated in Songkhla (Thailand) using hydro-distillation.

Tran et al (2021) showed the similar results as compared to the present study. The essential oil composition of citrus varies based on particular characteristics of the components, conditions for growth, soil, and stage of harvesting. Toan et al (2020) extracted C. aurantifolia peel essential oil in the laboratory with a 2.1% efficiency. Meanwhile, Atti-Santos and his colleagues employed a Clevenger apparatus in the laboratory to distil essential oils from C. latifolia peels, yielding 5.45% essential oil content (Atti-Santos et al. 2000). Bourgou et al (2012) showed a similar yield as compared to the present study, 0.46 to 2.70% from Citrus species which included mandarin (2.7%) and orange (0.74%) . Citrus peel crushing level, hydrodistillation period, and added salts all had an effect on the peel of Citrus reticulata Blanco stated from China (Hou et al. 2019).

The result was accomplished by using Box Benken's method. Tables 1 display experimental findings and predictions made by Design Expert version 7.0.0. ANOVA was used to explore the results. To find out the factor effects in the model are statically significant, the p- values less than 0.05% shows that model term are significant, however the lack of fit (LOF) was insignificant. Table 2 shows the (ANOVA) findings for the quadratic model of essential oil yield, which includes three independent varibles: solvent/material (A), extraction temperature (B), extraction time (C), the term of interaction (AB, AC, BC), and the second-order term (A2, B2, C2).

For validation of the model, Figures 1(a) and (b) show the oil yields and residuals from 15 runs, respectively. Figure 1(a) demonstrated that experimental yield residuals perfectly followed a random pattern, demonstrating that the assumptions about the independence of the factors and uniform variance were not disturbed. Figure 1(b), which compared predicated and actual values, also displayed how near certain scattered data points were to the 45-degree line. Both the actual and predicted values are on the same 45 degree line, confirming the significance of values, as well as the quadratic model, in the context of the experiment.

Influence of factor on yield: Figures 2 (a), 2 (b), 2(c) and 3 (a), 3 (b), 3 (c) illustrated the influence of variable on extraction of essential oil from kinnow peel by hydro distillation. First, as shown in fig 2(b) and 3 (c), investigate the effect of temperature on the quantity of extracted essential oil. The yield seems to increase as the temperature rises from 70°C to 80°C. When the process temperature is less than 85°C, the yield is maximum. The effectiveness of the process increases as the process temperature rises; yet, above 85° C, the effectiveness begins to fall. The reason for this may be because the quantity of heat applied originally heated the water rather than the sample. Yield progressively grows to the center value, and then begins to drop. This may have been related to heat degradation when the volatile content of the essential oil becomes altered by high temperatures or extended heat exposure (Dao et al. 2021). Then comparable to temperature, the solvent/material ratio correlates directly with efficiency of oil; as the solvent quantity rises, the efficiency of

extracted essential oils progressively increases. According to the fig (3a), essential oil yield estimated to attain its maximum when the solvent amount is 700ml, but after 700ml, increasing the solvent quantity, the yield of essential oil begins to decrease continuously. Fig 2(c) showed interaction of solvent and temperature, it's likely that when the water content is too high, the water absorbs more heat, which reduces the performance's value in this range (Dao et al 2021). Fig (2a) showed the interaction between solvent and time examine the material/water ratio, the extraction process will suffer if there is inadequate or too much water. The apparatus will burn or lose heat to the water during the heating phase rather than the samples if there is insufficient water present to dissolve the adhesive in the essential oil sac. As a result, a sufficient volume of water required in both the experimental design and the process experiment to prevent the challenge. There are the extraction temperature as well as time factors, which describe the heat amount affecting the container carrying the raw materials/water mixture as depicated in fig 3(b). If the ideal conditions are identified, these two elements allow extracting more essential oil, boosting process yield. The most significant effect of the method is that a high level of heat supply and prolonged heat exposure might denature the volatile elements of the essential oil (Ferhat et al. 2006).

Dao et al (2021) observed similar patterns as the components that positively correlate with process yield, such as time-ratio, ratio-time, and temperature-ratio. The quantity of pixie mandarin essential oil grew as the value of these three pairs of parameters increased. Simultaneously, when the value of the remaining elements rises, so the process efficiency tends to decrease. Tran et al (2021) further discovered that when all three parameters were altered individually, the yield appeared to be overly susceptible to change.

Validation of model: Based on the similarity of the data presented above, optimization was performed using the surface response graphs. The best extraction conditions for kinnow essential oil are 70.69^{o} C, solvent/ material ratio of 769.16 mL, and extraction duration of 4.41 h (Cube graph in box benken matrix, Fig. 7). Predicated oil yield under these optimum conditions was 1.078% with desirability of 1.00.

Microwave assisted hydro distillation: Microwave assisted hydro distillation process shows maximum and minimum yield was 2.50% and 0.9% from dried kinnow peel powder. Tran et al (2019a) also showed yield, 2.4% from citrus aurantifolia peel (Lemon Fruit) which are comparable to our results but show minimum yield 1.6% which is quite higher as compared to the present study. A study by Golmakani and Moayyedi 2015) observed MAHD extraction yield 1.18% from citrus limon peel which is quite lower as compared to present study.

The result was accomplished by using Box Benken's method. Tables 3 display experimental findings and predictions made by Design Expert version 7.0.0. ANOVA analysis for the quadratic model of essential oil extraction was shown in table 4. Extraction power (A), extraction time (B), solvent (C), term of interaction (AB, AC, BC), and second order (A2, B2, C2) terms are three independent variable in the ANOVA table. The Model F-value of 30.73 indicates that the model is significant. Figures 4(a) and (b) show residuals from 15 runs and oil yields for validating the final model. As observed in Figure 4(a), the experimental yield residuals exhibit a random pattern. This demonstrated that the assumptions of variable independence and constant variance were not violated. Figure 4(b), which contrasted anticipated values with actual values, also demonstrated a

close accessibility of scattered data points to the 45-degree line, demonstrating the model's accepted predictability.

Influence of factor on yield: Figures 5 (a), 5 (b), 5 (c) and 6 (a), 6 (b), 6 (c) indicated the connection between essential oil yield and three process factor variables. The overall trend of the components were similar; as the power supply, extraction time, and material/ water ratio steadily grow, so the yield of extracted peels oil also increased up to the centre value and after that the yield eventually starts decreasing. The extraction yield steadily increases as the material and water ratios increase, but at a certain point, the yield begins to decrease as the solvent quantity increases. When the microwave power increases from 200W to 450W, yield of oil increases constantly, but after 450W, the yield starts to decrease. Microwave irradiation improves extraction yield by accelerating the destruction of plant cells, which was accompanied by a rapid diffusion rate of intercellular components into the liquid solution (Akhhbari et al. 2018). Decrease in essential oil extraction output was due to rapid variation in temperature was result of excessive microwave irradiation. This subsequently resulted in partial thermal decomposition of essential oil, which reduced extraction yields (Chen et al. 2016, Liu et al. 2018).

Extraction duration was another factor being observed to improve the efficiency of EO extraction. As shown in Figure 5 (b), increasing the extraction time from 5 to 23 minutes enhanced the extraction yield of EO, shows maximum yield at 23 minutes. But the extraction yield declined as the irradiation period increased. One probable explanation is EO emulsification after lengthy irradiation times. Golmakani and Moayyedi (2016) reported a similar pattern when they discovered that prolonging the extraction time by MAHD did not result in a substantial increase in essential oil yields from lemon peels. Fig 6(a) showed the interaction between power and time, as power and time increase continuously there was negative impact were observed on yield %. Martinez-Abad et al (2020) proposed that utilizing a microwave results in more efficient heating of the inner section of the tissue, creating a rapid rupture of the glandular walls and boosting the extraction efficiency of the essential oil from the food matrix at shorter time period.

As observed in fig 5(c) when solvent amount increase from 600ml to 700ml, yield % increase with increasing the solvent amount. Because the water inside the peel matrix absorbs microwave power, internal superheating ruptures cells, allowing chemicals to diffuse from the matrix and so boosting EO recovery (Golmakani, & Moayyedi 2015, Tran et al. 2019a). However, after raising the solvent level from 700ml, a decrease in yield is seen because too much water dissolves or emulsifies the essential oil (Tran et al. 2019a).

A rapid rise in volume was noted during the initial stage of extraction. The amount of oil distillation, however, slowed as the extraction process progressed. This was most likely due to the fact that in the later stages of the process, EO tends to dispense steadily from the remaining oil sacs internal the plant particles to their surface (Milojevic et al. 2008). Rosemerry (Cassel et al. 2009) and aniseed (Romdhane and Tizaoui 2005, Yu et al. 2021) have both shown a similar trend in the literature.

Validation of model: Based on the uniformity of the data presented above, optimization was performed using the surface response graph. The best extraction parameters for kinnow essential oil are 324.52 W extraction power, 644.48 mL solvent ratio, and 12.20 min extraction duration (Cube chart in box benken matrix, Fig. 8). The anticipated oil yield under these optimum circumstances was 2.046 % with a desirability of 1.00.

Fourier Transform Infrared Spectroscopy (FTIR): Fourier transform infrared spectroscopy is the most extensively used procedure for identifying functional groups. Figures 9 and 10 depicted the infrared spectra and distinctive bands observed in citrus oils extracted by HD and MAHD in the 4000-400 cm-1 region. The FTIR study spectra for both samples revealed identical results in terms of the various functional groups present. These findings reveal that microwave pre-treatment has no major effect on the constituents of the essential oil. Conjugation influences the reported carbonyl frequency for a double-bonded functionality (Manaila et al. 2016). This comprises joining an aromatic ring or conjugating to a C=C or another C=O (Kondo et al. 2000). Finally, the presence of limonene was demonstrated by absorption at around 887 cm-1. Elzey et al (2016) showed the FTIR spectra of pure essential oil of Lemon (from the same family as Mandarin) shows the predicted terpenoid components C-H stretch (2900 cm-1), C=O stretch (1700 cm-1), broad O-H stretch (3400 cm-1), and C-O stretch (1100 cm-1). The compositions and constituents of essential oils vary and are heavily influenced by the geochemistry of the soil in which they are grown. Solubility, partition coefficient, stereochemistry, and inherent acid-base characteristics may all be significantly impacted by the presence of distinctive functional groups that are responsible for specific therapeutic qualities (Knittel and Zavod 2008).

Conclusion: Throughout the research, the surface response technique was viewed for optimizing the conditions for the extraction of essential oils from kinnow peel. RSM was used with a Box benken to quantify and optimize variable parameters - water/material ratio, extraction time, extraction temperature on the extraction yield. MAHD provided significant improvements over traditional HD. When MAHD was used instead of HD, a comparable extraction yield was produced in a much quicker extraction time. As a result, in terms of operation expense, MAHD might be carried out for half the expanse of HD. FT-IR findings showed that there was no significant difference between essential oil extracted by HD proposing MAHD as best alternative for HD with no adverse effects on the constituents of the extracted essential oil.

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REFERENCES

Akhbari, M. Masoum, S. Aghababaei, F. Hamedi, S. 2018. Optimization of microwave assisted extraction of essential oils from Iranian Rosmarinus officinalis L. using RSM. *Journal of Food Science and Technology*, 55(6), 1–11. 10.1007/s13197-018-3137-7. doi: 10.1007/s13197-018-3137-7

Aripin, D. Julaeha, E. Dardjan, M. Cahyanto, A. 2015. Padjadjaran J. Dent. 27 1–11. DOI. 10.24198/pjd.vol27no1.26751

Aruna, T. Hemalatha, G. Vellaikumar, S. Kanchana, S. Kumutha, K. 2022. Hydrodistillation and Soxhlet Method of Extraction and Analyses of Chemical Composition of Citrus Peel Essential Oil. *Madras Agricultural Journal*, 1.

Atti-Santos, A. C. Cassel, E. Atti-Serafini, L. 2000. Supercritical carbon dioxide extraction of essential oils from mandarin (Citrus deliciosa Tenore) from South Brazil. Perfumer and Flavorist, 25, 26-36

Aziz, Z. A. Ahmad, A. Setapar, S. H. M. Karakucuk, A. Azim, M. M. Lokhat, D. Rafatullah, M. Ganash, M. Kamal M. A. Ashraf, G. M. 2018. Essential oils: extraction techniques, pharmaceutical and therapeutic potential-a review. Curr. Drug Metab., 19(13): 1100-1110.

Bourgou, S. Rahali, F.Z. Ourghemmi, I. Saïdani Tounsi, M. 2012. Changes of Peel Essential Oil Composition of Four Tunisian Citrus during Fruit Maturation. Sci. World J., 1–10.

Cassel, E. Vargas, R. M. F. Martinez, N. Lorenzo, D. Dellacassa, E. 2009. Steam distillation modeling for essential oil extraction pro-cess. Industrial Crops and Products, 29(1), 171–176

Chanthaphon, S. Chanthachum, S. Hongpattarakere. T. 2008. J. Sci. Technol. 30 125–131

Chede, P.S. 2012. Phytochemical Analysis of Citrus sinensis Pulp. International Journal of Pharmacognosy and Phytochemical Research. 2012; 4: 221-223.

Chen, F. Du, X. Zu, Y. Yang, L. Wang, F. 2016. Microwave-assisted method for distillation and dual extraction in obtaining essential oil, proanthocyanidins and polysaccharides by one-pot process from Cinnamomi Cortex. *Separation and Purification Technology*, 164, 1–11. 10.1016/j.seppur.2016.03.018

Dao, T. P. Nguyen, D. C. Nguyen, D. T. Tran, T. H. Nguyen, P .T. N. Le, T. H .N. Nguyen, D. H. Nguyen, V. D. V. Bach, L. G. 2019. Extraction Process of Essential Oil From Pletranthus amboinicus Using Micro-wave-Assisted Hydrodistillation and Evaluation of It's Antibacterial Activity Asian J. Chem. 31 977–981

Dao, T.P. Quyen, N.T.C. Nhi, T.T.Y. Nguyen, C.C. Nguyen, T.T. Le, X.T. 2021. Response surface methodology for optimization studies of hydro-distillation of essential oil from pixie Mandarin (Blanco) peels. Pol. J. Chem. Technol. 23, 26–34.

Elzey, B. Norman, V. Stephenson, J. Pollard, D. Fakayode, S.O. 2016. Purity analysis of adulterated essential oils by FT-IR spectroscopy and partial-least-squares regression. Spectroscopy. 2016;31(8):26-37

Ferhat, M.A. Meklati, B.Y. Smadja, J. Chemat, F. 2006. An improved microwave Clevenger apparatus for distillation of essential oils from orange peel. J. Chromatogr. A, 1112(1–2), 121–126.

Golmakani, M. T. & Moayyedi, M. 2015. Comparison of heat and mass transfer of different microwave-assisted extraction methods of essential oil from Citrus limon (Lisbon variety) peel. *Food science & nutrition*, *3*(6), 506-518.

Golmakani, M.T. & Moayyedi, M. 2016. Comparison of microwave-assisted hydrodistillation and solvent-less microwave extraction of essential oil from dry and fresh *Citruslimon (Eureka variety*) peel. *J. Essent. Oil Res. 28*, 272–282.

Hojjati, M. Barzegar, H.2017. Chemical Composition and Biological Activities of Lemon (Citrus limon) Leaf Essential Oil. Nutrition and Food Sciences Research. 4: 15-24.

Hou, H.-S. Bonku, E.M. Zhai, R. Zeng, R. Hou, Y.-L. Yang, Z.-H. Quan, C. 2019. Extraction of Essential Oil from Citrus reticulate Blanco Peel and Its Antibacterial Activity against Cutibacterium acnes (Formerly Propionibacterium acnes). Heliyon 2019, 5, e02947. [CrossRef]

Jamil, N. Jabeen, R. Khan, M. Riaz, M. Naeem, T. 2015. Quantitative assessment of juice content, citric acid and sugar content in oranges, sweet lime, lemon and grapes available in fresh fruit market of quetta city. International Journal of Basic and Applied Sciences. 2015; 15: 21-24

Javed, S. Javaid, A. Nawaz, S. Saeed, M. K. Mahmood, Z. 2014. Phytochemistry, GC-MS analysis, antioxidant and antimicrobial potential of essential oil from five citrus species. Journal of Agricultural Science, 2014; 6: 201-208.

Jeong, D. Park, H. Jang, B.K. Ju, Y. Shin, M.H. Oh, E.J. Lee, E.J. Kim, S.R. 2021. Recent advances in the biological valorization of citrus peel waste into fuels and chemicals. Biores. Technol. 323, 124603

Knittel, J.J. & R.M. Zavod. 2008. Drug design and relationship of functional groups to pharmacologic activity. In T.L. Lemke and D. A. Williams (Eds.), Foye's principles of medicinal chemistry. New York: Lippincott Williams & Wilkins, 6th Ed., 26-53.

Kondo, M. Goto, M. Kodama, A. Hirose, T. 2000. Fractional extraction by supercritical carbon dioxide for the deterpenation of bergamot oil. *Industrial & engineering chemistry research*, *39*(12), 4745-4748.

Bach, L. G. Tran, T. V. Nguyen, T. D. Pham, T.V. Do. S.T. 2018. Enhanced adsorption of methylene blue onto graphene oxide-doped XFe2O4 (X = Co, Mn, Ni) nanocomposites: kinetic, isothermal, thermodynamic and recyclability studies, Research on Chemical Intermediates, vol. 44, no. 3, pp 1661–1687

Le, X. T. Ha, P. T. H. Phong, H. X. Hien, T. T. Ngan, T. T. K. 2020. Extraction of essential oils and volatile compounds of kaffir lime (Citrus hystrix DC) by hydrodistillation method. In *IOP Conference Series: Materials Science and Engineering* (Vol. 991, No. 1, p. 012024). IOP Publishing.

Liu, B. Fu, J. Zhu, Y. Chen, P. 2018. Optimization of microwave-assisted extraction of essential oil from lavender using response surface methodology. *Journal of Oleo Science*, 67, ess18019. 10.5650/jos.ess18019

Martínez-Abad, A. Ramos, M. Hamzaoui, M. Kohnen, S. Jiménez, A. Garrigós, M. C. 2020. Optimisation of sequential microwave-assisted extraction of essential oil and pigment from lemon peels waste. *Foods*, *9*(10), 1493.

Milojević, S. Stojanović, T. D. Palić, R. Lazić, M. L. Veljković, V. B. 2008. Kinetics of distillation of essential oil from comminuted ripe juniper (Juniperus communis L.) berries. Biochemical Engineering Journal, 39(3), 547–553

Mohanapriya, M. Ramaswamy, D.L. Rajendran, D.R. 2013. Health and medicinal properties of lemon (Citrus limonum). International Journal of Ayurvedic and herbal medicine. 3: 1095-1100.

Pathak, P.D. Mandavgane, S.A. Kulkarni, B.D. 2017. Fruit peel waste: characterization and its potential uses. Curr. Sci. 444–454

Pham, T.N. Phu, Nguyen, T.N. Duc, L.T. Nguyen, M.T. Toan, T.Q. Hong, Nhan, L.T. N-Vo, D.V. Vo, T.S. Bui, L.M. 2019. Response surface modeling and optimizing conditions for anthocyanins extraction from Hibiscussabdariffa L. (Roselle) grown in Lam Dong, Vietnam. IOP Conf. See. Mater. Sci. Eng. 544. DOI: 10.1088/1757-899X/544/1/012016

Romdhane, M. & Tizaoui, C. 2005. The kinetic modelling of a steam dis-tillation unit for the extraction of aniseed (Pimpinella anisum) essential oil. Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology, 80(7), 759–766

Satari, B. & Karimi, K. 2018. Citrus processing wastes: environmental impacts, recent advances, and future perspectives in total valorization. Resour. Conserv. Recycl. 129, 153–167.

Sir Elkhatim, K. A. Elagib, R. A. Hassan, A. B. 2018. Content of phenolic compounds and vitamin C and antioxidant activity in wasted parts of Sudanese citrus fruits. *Food science & nutrition*, *6*(5), 1214-1219.

Hien, T.T. Nhan, N.P.T. Nguyen, D.T. Ho, V.T.T. Bach, L.G. 2018. Optimizing the Pomelo Oils Extraction Process by Microwave-Assisted Hydro-Distillation Using Soft Computing Approaches, Solid State Phenomena, 2018, Vol. 279, pp. 217-221.

Tran, T.V. Bui, Q.T.P. Nguyen, T.D. Le, N.T.H. Bach, L.G. 2017. A comparative study on the removal efficiency of metal ions (Cu+2, Ni+2, and Pb2+) using sugarcane bagasse derived ZnCl2-activated carbon by the response surface methodology, Adsorption Science & Technology 2017, vol. 35(1–2), pp. 72–85

Tran, T.V. Bui, Q.T.P. Nguyen, T.D. Ho, V.T.T. Bach, L.G. 2017a. Application of response surface methodology to optimize the fabrication of ZnCl2- activated carbon from sugarcane bagasse for the removal of Cu2+, Water Science & Technology, vol. 75, no.9, 2017a, pp. 2047-2055

Toan, T. Q. Truc, T. T. Le, X. T. Quyen, N. T. C. Tran, T. H. 2020. Study on extraction process and analysis of components in essential oils of Vietnamese orange peel (Citrus sinensis) by microwave assisted hydrodistillation extraction. In *IOP Conference Series: Materials Science and Engineering* (Vol. 991, No. 1, p. 012125). IOP Publishing.

Tran, T. H. Dao, T. P. Lam, T. D. Toan, T. Q. Nguyen, T. D. Vo, D. V. N. Vy, T. A. 2019. New direction in research on extraction of Citrus aurantifolia (Lemon fruit) essential oil grown in Mekong Delta-Vietnam via microwave-assisted hydrodistillation. In *IOP Conference Series: Materials Science and Engineering* (Vol. 542, No. 1, p. 012038).

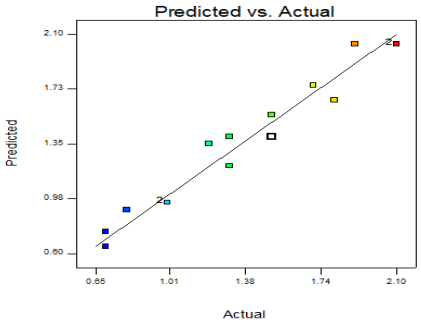
Tran, T. H. Nguyen, T. N. Q. Le, X. T. Phong, H. X. Long, T. B. 2021. Optimization of operating conditions of Lemon (Citrus aurantifolia) essential oil extraction by Hydro-distillation Process using Response Surface Methodology. In *IOP Conference Series: Materials Science and Engineering* (Vol. 1092, No. 1, p. 012094). IOP Publishing.

Tran, T.H. Quyen, N.T. Linh, H.T.K. Ngoc, T.T.L. Quan, P.M. Toan, T.Q. (2019a). Essential Oil from Vietnamese Mandarin (Citrus reticulata Blanco) Using Hydrodistillation Extraction Process and Identification of It's Components. Solid State Phenom. , 298, 100–105.

Yu, F. Wan, N. Zheng, Q. Li, Y. Yang, M. Wu, Z. 2021. Effects of ultrasound and microwave pretreatments on hydrodistillation extraction of essential oils from Kumquat peel. *Food Science & Nutrition*, *9*(5), 2372-2380.

Zaker, M.A. Sawate, A.R. Patil, B.M. Sadawarte, S.K.2016 Studies on Effect of Orange Peel Powder Incorporation on Physical, Nutritional and Sensorial Quality of Cookies. International Journal of Engineering Research and Technology. 5: 78-8

Zeleke, Z. 2022. Extraction of essential oil from lemon and orange peel by Clevenger apparatus: Comparative GC_MS analysis of chemical composition, from Debre Berehan Market town Amahara Region Ethiopia. *Ann. Biotechnol*, *5*, 1026.



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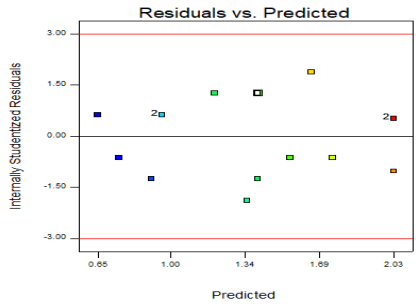

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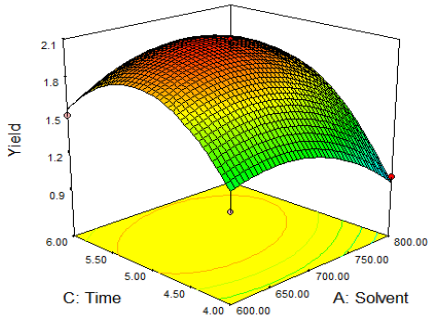

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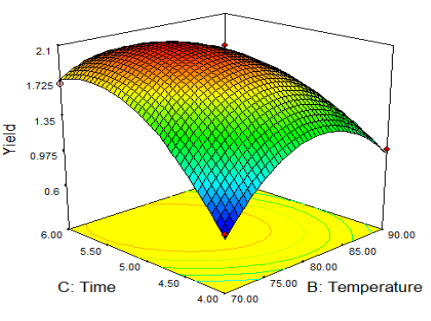

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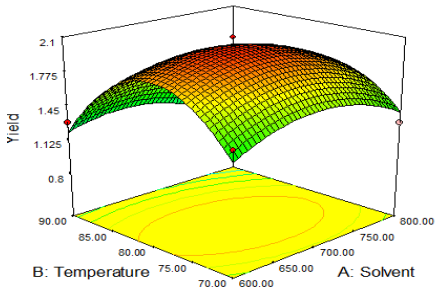

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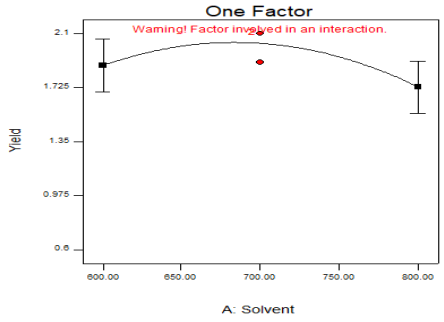

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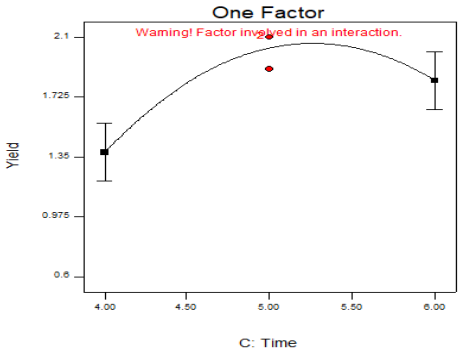

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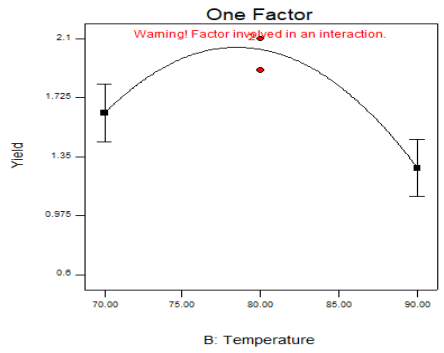
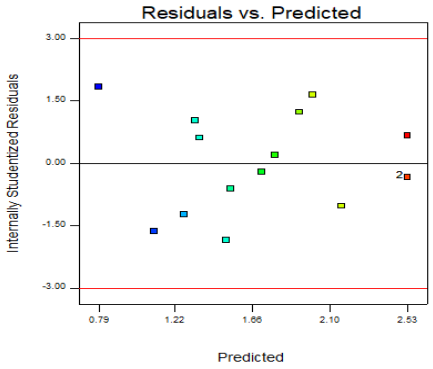


3(c)

Fig 1(a), 1(b) Normal plot of residual vs. predicated value of HD essential oil.

Fig 2(a), 2(b), 2(c) 3D response surface plot of interaction yield % of HD.

Fig 3(a), 3(b), 3(c) one factor analysis of HD extracted essential oil.



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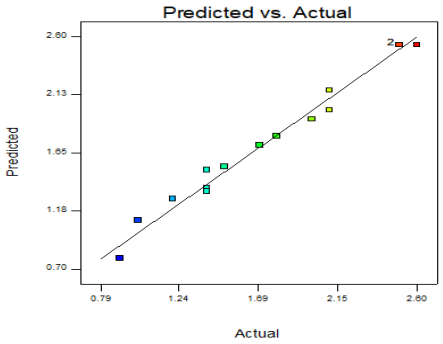

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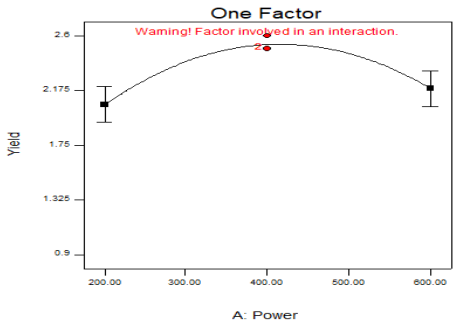

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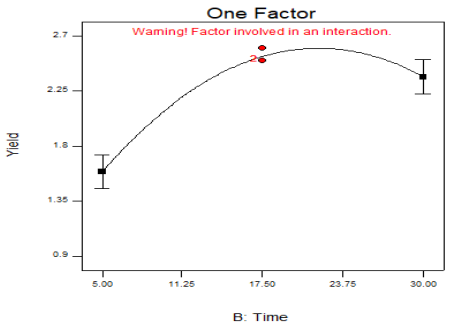

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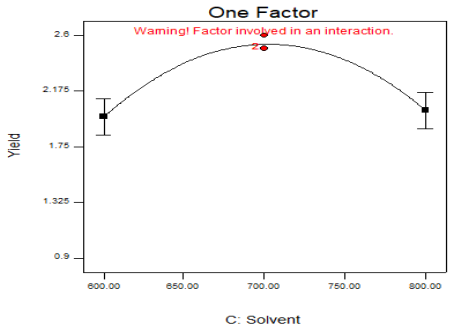

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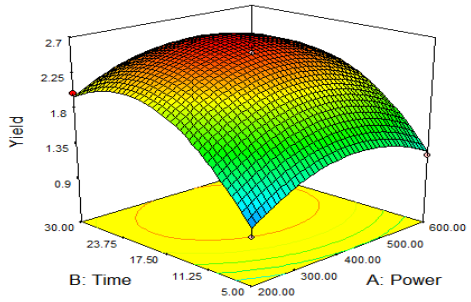

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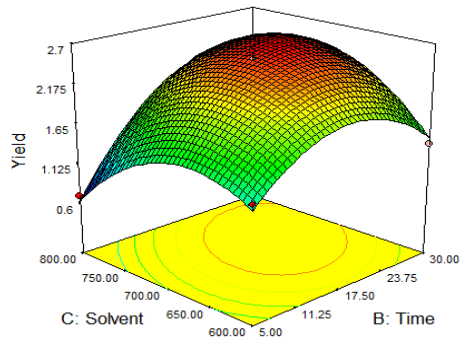

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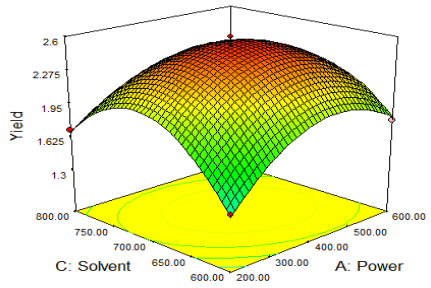

6(c)

Fig 4(a), 4(b) Normal plot of residual vs. predicated value of MAHD essential oil.

Fig 5(a), 5(b), 5(c) one factor analysis of MAHD extracted essential oil.

Fig 6 (a), 6(b), 6(c) 3D response surface plot of interaction yield % of MAHD.

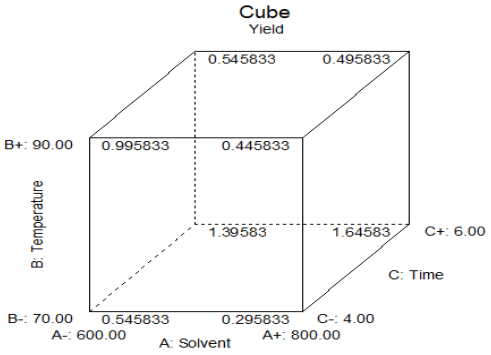

Fig 7 Graphical optimization of kinnow peel oil extraction yield (mL/100 g).

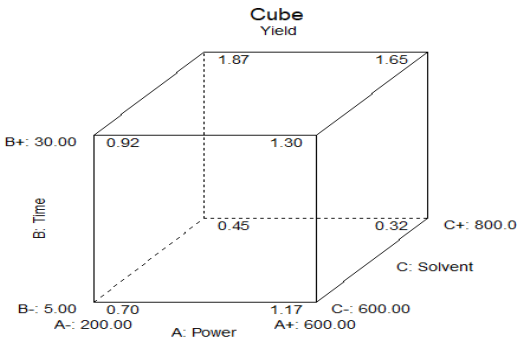

Fig 8 Graphical optimization of kinnow peel oil extraction yield (mL/100 g).

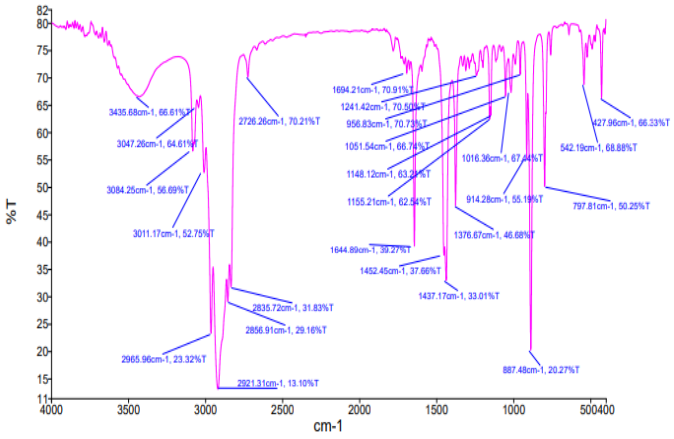

Fig 9 FT-IR spectrum of Kinnow peel oil extracted by HD.

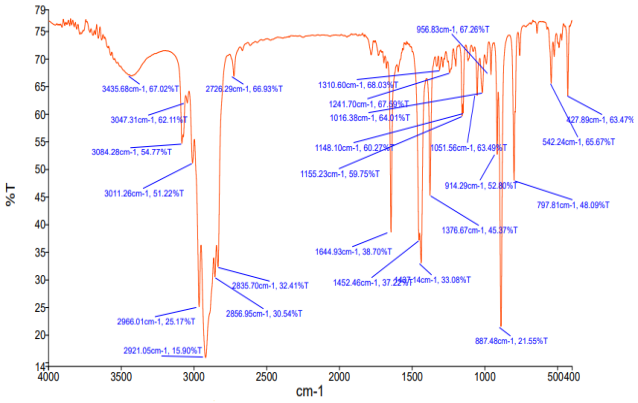

Fig 10 FT-IR spectrum of Kinnow peel oil extracted by MAHD.

Table 1 Experimental and predicated extraction efficiencies by hydrodistillation under different conditions for RSM model

Std	Run	Solvent (mL)	Temperature (°C)	Time (hr)	Actual Yield %	Predicated yield %
1	2	600	70	5	1.50	1.40
2	10	800	70	5	1.30	1.40
3	3	600	90	5	1.30	1.20
4	6	800	90	5	0.80	0.90
5	4	600	80	4	1.20	1.35
6	7	800	80	4	1.00	0.95
7	12	600	80	6	1.50	1.55
8	8	800	80	6	1.80	1.65
9	5	700	70	4	0.70	0.65
10	15	700	90	4	1.00	0.95
11	11	700	70	6	1.70	1.75
12	14	700	90	6	0.70	0.75
13	13	700	80	5	2.10	2.03
14	9	700	80	5	2.10	2.03
15	1	700	80	5	1.90	2.03

Table 2 Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of squares	dF	Mean Square	F-value	P-value	Comment
Model	3.08	9	0.34	13.52	0.0052	Significant
A-Solvent	0.045	1	0.045	1.78	0.2401	SD=0.16
B-Temperature	0.25	1	0.25	9.67	0.0266	Mean=1.37
C-Time	0.41	1	0.41	15.99	0.0103	CV(%)=11.59
AB	0.022	1	0.022	0.89	0.3892	R^2 =0.9605
AC	0.063	1	0.063	2.47	0.1771	AP-10.645
BC	0.42	1	0.42	16.68	0.0095	Pred R^2 =0.4828
A^2	0.19	1	0.19	7.65	0.0395	Adj R^2 =0.8895
B^2	1.24	1	1.24	48.89	0.0009	
C^2	0.68	1	0.68	26.84	0.0035	
Residual	0.13	5	0.025			
Lack of fit	0.10	3	0.033	2.50	0.2985	Not –significant
Pure error	0.027	2	0.013			

Cor total	3.21	14

Table 3 Experimental and predicated extraction efficiencies by microwave assisted hydro distillation under different conditions

Std	Run	Power (W)	Time (Min)	Solvent (mL)	Yield %	Predicated yield %
1	2	200	5.00	700	1.0	1.10
2	15	600	5.00	700	1.20	1.28
3	4	200	30.00	700	2.0	1.93
4	5	600	30.00	700	2.10	2.00
5	8	200	17.50	600	1.40	1.36
6	9	600	17.50	600	1.80	1.79
7	11	200	17.50	800	1.70	1.71
8	3	600	17.50	800	1.50	1.54
9	10	400	5.00	600	1.40	1.34
10	1	400	30.00	600	1.40	1.51
11	6	400	5.00	800	0.90	0.79
12	13	400	30.00	800	2.10	2.16
13	12	400	17.50	700	2.50	2.53
14	14	400	17.50	700	2.49	2.53
15	7	400	17.50	700	2.50	2.53

Table 4 Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of squares	dF	Mean Square	F-value	P-value	Comment
Model	4.10	9	0.46	30.76	0.0007	Significant
A-Power	0.031	1	0.031	2.11	0.2064	SD=0.12
B-Time	1.20	1	1.20	80.98	0.0003	Mean=1.74
C-Solvent	5.000E-003	1	5.000E-003	0.34	0.5867	CV(%)=7.00
AB	2.500E-003	1	2.500E-003	0.17	0.6989	R^2 =0.9822
AC	0.090	1	0.090	6.07	0.0570	AP-17.556
BC	0.36	1	0.36	24.27	0.0044	Pred R^2 =0.7383
A^2	0.60	1	0.60	40.66	0.0014	Adj R^2 =0.9503
B^2	1.13	1	1.13	76.44	0.0003	
C^2	1.03	1	1.03	69.70	0.0004	
Residual	0.074	5	0.015			
Lack of fit	0.067	3	0.022	6.75	0.1318	Not significant

Pure error	6.667E-003	2	3.333E-003
Cor total	4.18	14	

Table 5 - Infrared vibrations of HD, MAHD extracted essential oil

Link Present	X (cm^{-1})	T(%)in HD	T(%)in MAHD
N-H primary and secondary amines and amide stretch,	3435.68	66.61	67.02
N-H primary and secondary amines and amide stretch, Alkenes stretch	3084.25	56.69	54.77
N-H primary and secondary amines and amide stretch, C-H Alkenes stretch	3047.26	64.61	62.11
N-H primary and secondary amines and amide stretch	3011.17	52.75	51.22
C-H, C-H Alkanes stretch	2965.96	23.32	25.17
C-H Alkanes stretch	2921.31	13.10	15.90
C-H Alkanes stretch	2856.91	29.16	30.54
C-H Alkanes stretch	2835.72	31.83	32.41
C-H Aldehyde	2726.26	70.21	66.93
C=O Amide	1694.21	70.91	69.38
C=C Alkene	1644.89	39.27	38.70
$-CH_3$ bend	1452.45	37.66	37.22
$-CH_3$ bend	1437.17	33.01	33.08
$-CH_3$ bend	1376.67	46.68	45.37
C-O Alcohols, ether, ester , carboxylic acid, anhydrides	1241.42	70.50	67.59
C-O Alcohols, ether, ester , carboxylic acid, anhydrides	1155.21	62.54	59.75
C-O Alcohols, ether, ester , carboxylic acid, anhydrides	1148.12	63.21	60.27
C-O Alcohols, ether, ester , carboxylic acid, anhydrides	1051.54	66.74	63.49
C-O Alcohols, ether, ester , carboxylic acid, anhydrides	1016.36	67.44	64.01
Aromatic out-of-plane bend	956.83	70.73	67.28
Aromatic out-of-plane bend	914.28	55.19	52.80
Aromatic out-of-plane bend	887.48	20.27	21.55
Aromatic out-of-plane bend	797.81	50.25	48.09

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