# HEAT AND MASS TRANSFER ANALYSIS IN A SPOUTED BED DRYER COUPLED WITH A CYCLONE FOR PEPPER DRYING

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Degree of Doctor of Philosophy

Department of Chemical & Process Engineering

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Thesis submitted in partial fulfilment of the requirements for the degree Doctor of Philosophy in Chemical and Process Engineering

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## DECLARATION OF THE CANDIDATE AND SUPERVISOR

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Name of the supervisor: Prof(Mrs.) B.M.W.P.K Amarasinghe

## Abstract

This thesis outlines the analysis of heat and mass transfer process of drying of black pepper in a spouted bed coupled with a cyclone separator. Black pepper is a widely used spice and is well-known for its pungency and aroma. Experiments conducted with wetted black pepper reveals that conventional spouted bed has the higher drying rate, higher moisture diffusivity, lower drying time and lower activation energy compared to those of spouted beds equipped with porous draft tube and non-porous draft tube. Therefore, the conventional spouted bed was used to conduct the experiments to achieve the objectives of the study since it was identified as the optimum configuration of the spouted bed.

Spouting behaviour of raw black pepper was studied in the conventional spouted bed. The minimum spouting velocities of particular bed heights at ambient temperature were determined. Minimum spouting velocity of raw black pepper in the conventional spouted bed versus static bed height was correlated to a power form of function and the exponent of static bed height was 0.67. The effect of operational conditions; drying air temperature, air velocity and static bed height on drying kinetics of raw black pepper was analysed. The higher values of moisture removal rates were achieved when the dryer was operated with moderately high air temperatures, high air flow rates and shallow beds. Drying kinetic data of raw black pepper in the conventional spouted bed shows only falling rate periods. Effective moisture diffusivity values increased with increasing drying air temperature. The highest effective moisture diffusivity of $2.03\times10^{-10}$ $m^2/s$ was obtained at air temperature of 75 °C. Activation energy for drying of raw black pepper in conventional spouted bed was 38.59 kJ/kmol. Specific energy consumption was calculated and the specific energy consumption values increased with increasing air velocity and decreased gradually with increasing the static bed height.

Drying kinetic data obtained from experiments were fitted to five thin layer drying models. Results show that the Logarithmic model gives the best fit. In addition, four models were developed for black pepper drying in the conventional spouted bed by correlating drying constants and coefficients of Logarithmic model to stagnant bed height at specified temperatures; 45 °C, 55 °C, 65 °C, and 75 °C. Developed models can be used to estimate the drying time of black pepper in the conventional spouted bed dryer for given moisture reduction in the ranges of 0.14-0.22 m stagnant bed heights and in 2.37 m/s air velocity at specified temperatures.

Essential oil was extracted using hydro distillation from black pepper dried at five different drying conditions. The analysis of components by Gas Chromatography Mass Spectrometry technique shows that the black pepper essential oil comprised mainly monoterpenes and sesquiterpenes. Analysis of variance was conducted and the results show that variation of sesquiterpenes concentration in black pepper essential oil was significant while variations of monoterpenes, oxygenated terpenes and caryophyllene concentration were non-significant in black pepper essential oil with drying air temperature. In addition, the variation of essential oil yield is statistically significant with drying air temperatures. 65 °C drying air temperature provides consistent quality essential oil with high percentage of caryophyllene and higher oil yield.

Heat transfer coefficients for black pepper drying in the conventional spouted dryer were estimated for different drying conditions of unsteady state drying of black pepper dried from initial moisture content to final moisture content of 15% dry basis. Heat transfer coefficient varied from 35-68 $W/m^2K$ for the conditions under the investigation. Dimensional analysis was carried out and important dimensionless numbers were identified. A correlation was developed for heat transfer process as a function of dimensionless groups namely Reynolds number, Nusselt number, Gukhman number and static bed height to particle diameter with 0.791 of coefficient of determination. Heat transfer coefficients predicted from the developed correlation show a good agreement with the experimentally determined heat transfer coefficients.

Keywords: Black pepper, spouted bed, drying kinetics, heat and mass transfer, essential oil

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# TABLE OF CONTENT

## LIST OF FIGURES

# LIST OF TABLES

# LIST OF FIGURES IN APPENDICES

## LIST OF TABLES IN APPENDICES

# LIST OF ABBREVIATIONS

ANOVA - Analysis of Variance

ASTA - American spice trade association

CFD - computational fluid dynamics

CSA - Canadian spice association

CSB - conventional spouted bed

ESA - Europe spice association

GC-MS - Gas Chromatography Mass Spectrometry

MR – Moisture ratio

NCPHT & VA - National Committee on Post-Harvest Technology and Value Addition

$R^2$ - Coefficient of determination

RMSE - Root mean square error

SBNPDT - Spouted bed equipped with non-porous draft tube

SBPDT - Spouted bed equipped with porous draft tube

SEC - Specific energy consumption

SLCARP -"Sri Lanka Council for Agricultural Research Policy"

SSE - Sum of square error

VSD - variable speed drive

## Chapter 1

# 1. INTRODUCTION

### 1.1 Background to the research problem

Black pepper is the berries of a tropical vine botanically known as '*Piper nigrum L.*'. Dried black pepper is one of the largest commodity in the international spice trade. Global annual demand for black pepper is 250,000-300,000 MT in year 2017. Of the total world trade in spices, one third of total volume is black pepper. Brazil, India, Indonesia, Malaysia, Sri Lanka and Vietnam are the major pepper producing countries. In Sri Lanka during year 2006 to 2016, the average annual black pepper production is approximately 17,000 MT while average export is approximately 10,000 MT [1].

Black pepper is a widely used spice in food preparation all over the world. Moreover, black pepper is also used in pharmaceutical industry and cosmetic industry due to its aroma, pungency and other medicinal features such as antioxidant, anti-inflammatory, anti-bacterial and anti-asthmatic actions [2 , 3 , 4]. Black pepper is commonly available as dry seeds or in its powder form in the market.

The main pungent component in black pepper is piperine; $C_{17}H_{19}O_3N$ which is 2 trans, 4-trans piperidine amide of piperic acid. Piperine is non-volatile and can be isolated from solvent extraction (alcohol extraction) as oleoresins [5]. The essential oil of black pepper, which consists of volatile components obtained by the steam distillation or other methods, is a valuable additive in the food manufacturing industry such as sausages, canned meats, soups, beverages and liquors and also in perfumery and cosmetics industry. The quality of black pepper may be affected depending on factors such as maturity level, type of cultivars, season and post-harvest processing method [6].

Considering the post-harvest methods, drying is the most important unit operation as it affects the quality of the final product. After harvesting, pepper berries are removed from the spikes by either hand or using a mechanical thresher. These berries are then spread as a thin layer on mats and dried in the sun for five to six days depending upon the climate conditions. Delays in drying of black pepper after harvesting will cause growth of moulds on the berries and lowers the product quality. The best moisture content of black pepper to prevent the growth of moulds during storage is found to be 12-14% dry basis [7 , 8].

Sun drying is the commonly used method for drying of agricultural crops in tropical countries. However, the method has several limitations such as non-uniform sun light during the day and problems caused during the rainy seasons. Therefore, the use of alternative drying techniques becomes essential. Among the techniques used for drying of agricultural products, packed beds, fluidized beds, spouted beds and cross circulation drying using tray dryers are commonly used. Many researchers promote these drying methods due to their lower capital cost and maintenance cost, higher heat and mass transfer rates and their ability to produce quality product compared to high-end drying technologies such as freeze drying, drum drying and steam drying [9].

Spouted bed dryers are particularly suitable for heat sensitive materials such as agricultural products or polymeric granules. Regular circulation of particles in three hydrodynamic regions namely spout, fountain and annulus regions permit the use of higher temperature gas without the risk of thermal damage to the particles than those of the non-agitated driers. More information on spouted beds will be available in Chapter 2.

## 1.2 Research objectives

The overall objective of this research was to analyse the heat and mass transfer process of black pepper drying in the spouted bed dryer. Specific objectives are as follows:

1. Evaluation of the spouted bed dryer for black pepper drying process
   1.1. Study hydrodynamics of black pepper spouting.
   1.2. Analysing the effects of initial bed height, air temperature, air velocity and draft tube on drying.
   1.3. Examine optimum drying air temperature to achieve black pepper with maximum essential oil yield with consistent quality.
   1.4. Analyse the effect of drying air temperature on mass transfer characteristics namely effective moisture diffusivity.
2. Model heat transfer characteristics in the spouted bed dryer and validate the model using the experimental data
3. Develop suitable drying model to describe drying behaviour (drying kinetics).

## 1.3 Significant of the research

Black pepper has been identified as a high priority crop by National Committee on Post-Harvest Technology and Value Addition (NCPHT & VA) of Sri Lanka Council for Agricultural Research Policy (SLCARP). Furthermore, postharvest technologies for black pepper such as drying, processing, packaging and storage are also focused as research priority areas to be attended [10, 11].

Feasibility of using spouted bed dryer as a drying technique for black pepper drying is explored from this research. It is required to identify the optimum operational parameters such as air velocity, drying temperature and bed height to improve the performance of the drying process.

The drying kinetics data, heat and mass transfer characteristics identified for black pepper drying in the spouted bed, thin layer modelling and the non-dimensional model developed in this research can be utilized in agriculture industry or other researchers to optimize the drying operations in conjunctions with the various types of drying models such as computational fluid dynamics (CFD) models or other studies.

## 1.4 Structure of the dissertation

This thesis consists of nine chapters. Chapter 1 provides general overview of the study and the scope of the study. Chapter 2 provides the literature review of the study. Chapter 3 describes the methodology used to accomplish the objective of the study. The results and discussion of the study are discussed in Chapter 4 to 7. Chapter 4 provides the results of preliminary experiments conducted with wetted black pepper. Chapters 5 to 7 present the results and discussion of main experiments conducted with raw black pepper to accomplish the objectives. Chapter specific nomenclatures and abbreviations are given at the end of each chapter from Chapter 1 to 7. Chapter 8 presents the overall conclusion and the recommendations for future works. Finally, References and Appendices are presented.

### Abbreviations

NCPHT & VA - National Committee on Post-Harvest Technology and Value Addition

SLCARP - Sri Lanka Council for Agricultural Research Policy

CFD - computational fluid dynamics

**Chapter 2**

# 2. LITERATURE REVIEW

Many researchers have investigated on drying of agricultural crops. Various techniques have been experimented. Drying kinetics, heat and mass transfer have been studied extensively. This section covers a comprehensive review on drying theory, research conducted with spouted bed and drying models. In addition, conventional methods of black pepper drying, research conducted on black pepper essential oil and quality of black pepper are reviewed.

## 2.1 Principles & theory of drying

### 2.1.1 Moisture content

Moisture content of a material is described as either moisture content of dry basis (X) or moisture content of wet basis. They are expressed as shown in Equation 2.1 and 2.2.

$$\text{Moisture content (dry basis)} = \frac{\text{kg of moisture}}{\text{kg of dry solid}} \qquad (2.\ 1)$$

$$\text{Moisture content (wet basis)} = \frac{\text{kg of moisture}}{\text{kg of wet solid}} \qquad (2.\ 2)$$

### 2.1.2 Drying

Drying is the removal of moisture adhering to a material by vaporization. Moisture is located on the surface and in the interior of the material such as capillaries and interstices.

When a sample of wet material is dried in a stream of air from initial moisture content to equilibrium moisture content, typical variation of moisture content of the sample with time can be shown in Figure 2.1. Equilibrium moisture content ($X_e$) is the moisture content of the material in equilibrium with the air at given humidity and temperature. Measuring the slope of tangent drawn to the curve of Figure 2.1 or by determining rate of change moisture content (dX/dt), drying rate (N) can be determined.

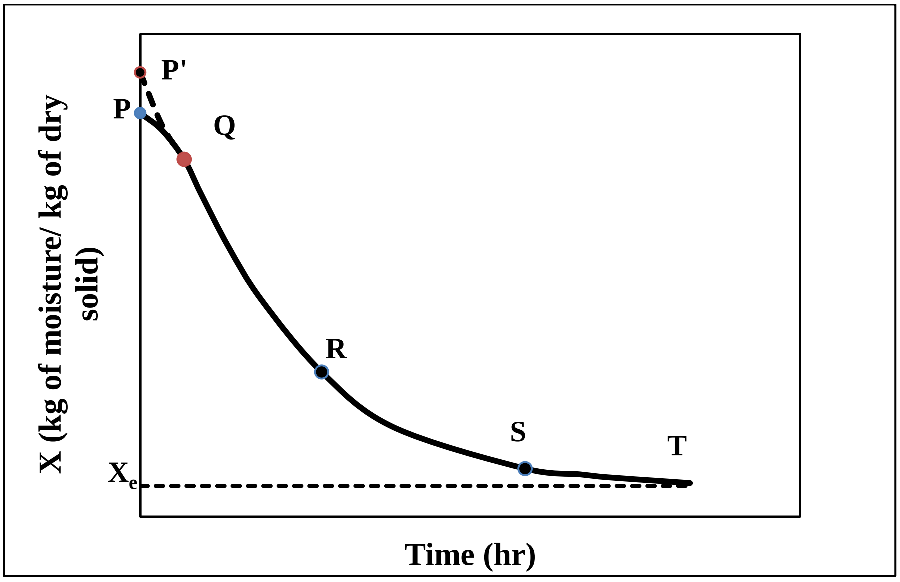



Figure 2.1: Moisture content vs. time of a material being dried in a dryer (Typical drying curve)

Drying rate, expressed in Equation (2.3) as mass of moisture evaporated per unit area per time depends on the way of moisture present in the material to be dried and the type of the material [12].

$$N = -\frac{W_d}{A}\frac{dX}{dt} \qquad (2.3)$$

Where

$W_d$ - mass of dried solid

A - cross section of the bed measured at right angles to the air flow

More information on drying can be obtained when the drying rate was plotted against moisture content of the material as in Figure 2.2. If the material is very wet, unbound moisture is available as a thin film of liquid on the surface of the solid. During the drying, the surface moisture is vaporized first. Even the moisture on surface is depleting, moisture concentration in depths is high. Due to high moisture diffusivity, liquid moisture in capillaries and interstices move to the surface rapidly where rate of drying remains constant at the value of $N_c$ as shown between points Q and R in Figure 2.2. Surface is saturated with moisture or thin layer of moisture remains on the surface of the material during the constant rate-drying period. Constant rate drying processes are called as externally controlled processes since externally controlled parameters govern the drying process [13]. Externally controlled parameters are operational conditions of drying process such as air temperature, air humidity, air velocity, etc.

The induction period or initial adjustment period shown in the period P′Q and PQ of Figure 2.1 and Figure 2.2 is usually ignored in many works due its rapidity. If the material to be dried is colder than the ultimate surface temperature, initial adjustment occurs by increasing drying rate as shown in curve PQ. If the material temperature is higher than the ultimate surface temperature, drying rate decreases as in curve P′Q.

When the moisture content reaches to the critical moisture content ($X_c$), material is unable to keep its thin layer of moisture on the surface and hot spots are appeared on the surface. This gives rise to the unsaturated surface drying, first part of the falling rate-drying period, between the points R and S. Eventually moisture available on surface is entirely evaporated at an average moisture content corresponding to point S.

On further drying, the moisture is expelled, because of concentration gradients exists between deeper part of the material and the surface. Rate of internal movement of moisture decreases as a result of reducing moisture concentration in the deeper parts of the material. In the later part of the falling rate drying period, from points S to T, rate of drying falls more rapidly than that of the first part of the falling rate-drying period. It shows that internal movement of moisture governs the drying rate in falling rate-drying period. Therefore drying processes having falling rate periods are called as internally controlled processes. Movement of moisture from depth to the surface is occurred due to many principles such as liquid diffusion, capillary movement, vapor diffusion, pressure, etc. [14].

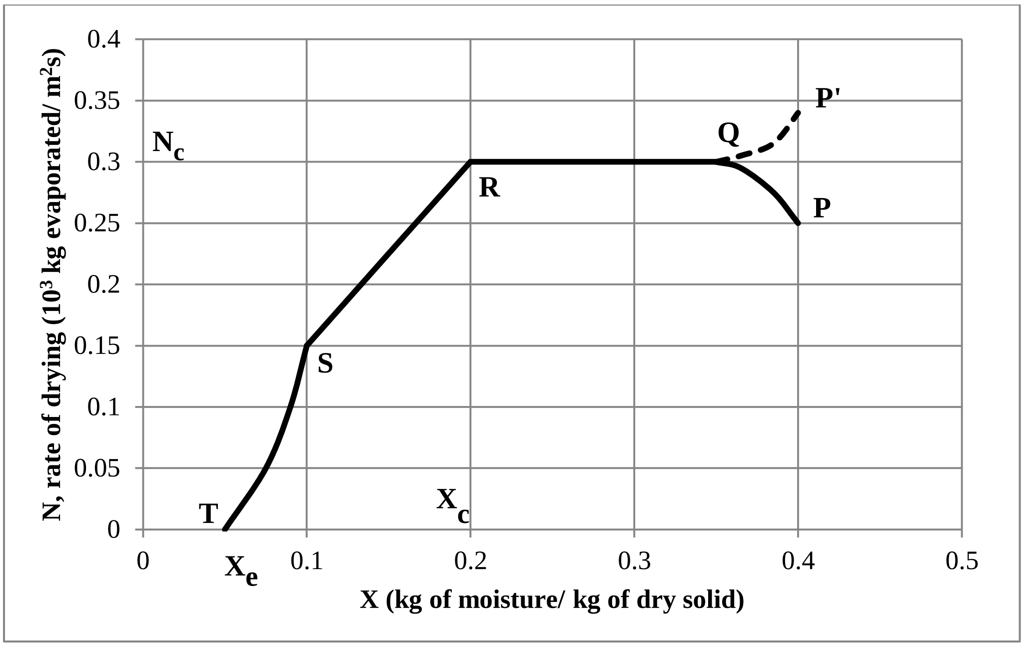



Figure 2.2: Typical drying rate curve including constant rate and falling rate drying conditions [14]

### 2.1.3 Moisture diffusivity

When a sample of wet material is dried, the drying rate can be constant or vary with time. In constant rate drying period, the surface of the solid is saturated with moisture and the rate of drying is controlled by the rate of water evaporation. In falling rate drying period, movement of moisture from interior to surface of the drying material is occurred mainly by diffusion and controls the rate of drying.

Effective diffusivity describes the potential of moisture diffusing from material inside to particle surface. Many researchers have estimated the effective moisture diffusivity ($D_{eff}$) of many materials for numerous type of material, dryer types and numerous operating conditions, but a few researchers have estimated the convective mass transfer coefficient of particle air interface. In most of the cases, moisture or mass transfer coefficient has been estimated for steady state or constant rate drying operations. To the best of the authors' knowledge, experimental techniques have not been used for estimating mass transfer coefficient of drying processes in unsteady state operations. If a reliable technology exists to measure the humidity of the particle air interface continuously with time, experimental mass transfer coefficients in unsteady state conditions can be easily determined.

Moisture diffusivity in a material depends on the type of material, porosity, shape, air temperature, initial moisture content, etc [15]. The general solution of Fick's equation can be derived for spherical particles as depicted in Equation 2.4 and it has been used by several researchers in order to obtain the effective moisture diffusivity of agricultural products [16, 17, 18].

$$MR = \frac{X_t - X_e}{X_0 - X_e} = \frac{6}{\pi^2} \sum_{i=1}^{n} \frac{1}{n^2} exp(-n^2 \pi^2 F_0) \quad (2.4)$$

Where

$F_0$ -Fourier number

MR -moisture ratio

t -time (s)

$X_e$ -equilibrium moisture content (kg of moisture /kg dry solids)

$X_o$ -initial moisture content (kg of moisture /kg dry solids)

$X_t$ –moisture content at time t (kg of moisture /kg dry solids)

Then Equation (2.4) is evaluated numerically for Fourier number $F_0$ as in Equation (2.5).

$$F_0 = \frac{D_{eff} t}{R_p^2} \quad (2.5)$$

Where

$D_{eff}$ -effective moisture diffusivity ($m^2/s$)

$R_p$- radius of the spherical particle (m)

The moisture ratio is simplified to $X_t/X_0$ neglecting $X_e$ term by some researchers, since $X_e$ term is relatively small compared to $X_t$ and $X_0$ and the continuous fluctuation of the relative humidity of drying air leading to change of equilibrium moisture content of the particle being dried [19]. By neglecting the terms beyond the first term of summations and replacing the Fourier number with proper variables, the Equation (2.6) can be obtained.

$$ln\ MR = ln\frac{X_t}{X_0} = ln\frac{6}{\pi^2} - \pi^2\frac{D_{eff}}{R_p^2}t \qquad (2.6)$$

Plotting $ln\frac{X_t}{X_0}$ vs time at a given air temperature will result in a straight line of slope $\pi^2\frac{D_{eff}}{R_p^2}$ which can be used to find the effective diffusivity. In literature, it is found that $D_{eff}$ has been expressed as a function of temperature in an Arrhenius type equation as given in Equation (2.7) [20, 17]:

$$D_{eff} = D_0 exp\left(-\frac{E_a}{RT}\right) \qquad (2.7)$$

Where

$D_0$ -pre exponential factor of Arrhenius equation

$E_a$ -activation energy (kJ/mol)

R -universal gas constant (kJ/mol K)

T -absolute drying air temperature (K)

The plot of $ln(D_{eff})$ versus $1/T$ is used to determine the $D_0$ and $E_a$.

### 2.1.4 Specific energy consumption

Specific energy consumption (SEC), the energy supplied to evaporate one kg of moisture is defined according to Equation (2.8) [21]

$$SEC = \left[\frac{Q(C_{pa}+C_{pv}Y_a)(T_d-T_{am})}{V_h}\right]\frac{t_{drying}}{m_v} \qquad (2.8)$$

Where

$C_{pa}$-specific heat capacity of air (J/kg°C)

$C_{pv}$-specific heat capacity of water vapour (J/kg°C)

$m_v$ - mass of water removal (kg)

Q - Air flow rate ($m^3$/s)

$T_{am}$ - ambient temperature (°C)

$T_d$ - drying air temperature at the inlet of the drying chamber ($^{o}C$)

$t_{drying}$ - Total drying time (s)

$V_h$ - humid volume or specific volume of air ($m^3$/kg of dry air)

$Y_a$ - humidity of air (kg of moisture/ kg of dry air)

### 2.1.5 Classification and selection of dryers

Dryers are normally categorized based on the method of heat transfer namely direct contact type and indirect contact type. Usually direct contact type dryers transfer heat by convection while indirect contact type transfers heat by conduction and radiation. In addition, dryers can be classified as either batch dryers or continuous dryers considering the method of operation. Furthermore, some researchers have classified either on the physical form of the feed or residence time of the product being dried in the dryer. Moreover, that some of the newer and novel dryers cannot be fit to the classification suggested in literature even they are not mentioned in most textbooks. About 50 types of dryers are widely used in practice to dry wide range of materials but more than 400 types of dryers have been cited in the literature [22]. Examples for some of the commonly used in the industry are rotary dryer, tray dryer, fluidized bed dryer, spray dryer, impingement dryer and flash dryer. Brief description of some of widely used dryers is provided in Table 1 of Appendix A**.**

There is no specified theory or principle for dryer selection. Many factors have to be considered to select a suitable dryer compromising among cost, efficiency, product quality and the clean environment. In addition, selection of suitable dryer for particular material is depending on the prior experience. Capital cost and operational cost, quality of the product, safety considerations, convenience of handling and installations have a direct impact on selecting a dryer for particular material. Quality of final product such as flavour retention of most farming crops depend on the method of drying and type of the operation such as batch or continuous mode.

Usually drying processes cause air pollution by emissions of dust, gases and water vapor. Therefore, dryers are coupled with dust collection equipment such as cyclone separators, bag filters, scrubbers and electrostatic precipitator. In addition, absorption, adsorption and incineration units can be used for treatment of noxious gaseous pollutants exhausting from dryers.

Despite of lack of data availability for design and applications of spouted bed, many researchers have investigated the use of spouted bed dryers for agricultural products. Spouted bed gives many advantages such as small space requirement and etc. Section 2.3 elaborates more information on spouted beds.

## 2.2 Drying of agricultural crops

Drying of agricultural crops, as a post-harvest method is a requisite for safe storage in order to prevent product contamination due to microbial attacks. Preservation of agricultural crops through drying, dates back centuries is based upon solar power. Wide varieties of crops such as grains, oil seeds, spices and some perishable crops such as fruits and vegetables are subjected to drying. Development of alternate drying technologies has begun due to limitation in sun drying in particular uncontrolled weather conditions and mass production.

Many investigations have been conducted on conventional drying methods as well as new drying techniques. Conventional drying methods such as packed bed, cabinet or tray drying, fluidized bed drying are convective air-drying techniques. Most of new drying methods consist of state of art equipments with high capital and operational cost namely freeze drying, vacuum, osmotic, microwave and combinations of some of the above.

However, drying contributes to the loss of aroma, flavour and nutritive quality of product and hence careful selection of the best-suited drying technique and condition for a given product is extremely important. Many researchers have compared the drying methods by analysing traditional quality parameters such as: colour, taste, bulk density and rehydration ratio of product while some researchers use standardization technique such as measuring levels of vitamins, bioactive material and minerals [23].

### 2.2.1 Black pepper drying

In case of black pepper drying, most widely used method of drying is solar drying. First pepper spikes are picked off from the fruiting branches of the vines at the correct stage and they are kept as such for a day for de-spiking. The most common pre-treatment for black pepper before drying is hot water blanching [24]. Blanching reduces the mold and other microbial contamination from the surface of the berries. In addition uniform glossy black color can be obtained to the product. After blanching, pepper is spread as a thin layer on mats or pavements for sun drying. Depending on the intensity of sun light, black pepper is dried in the sun for five to six days. Green color of the skin of the peppercorn is changed to black as a consequence of enzymatic reaction.

Solar dryers, cabinet dryers and flat-bed dryers are the commercially available artificial dyers in Sri Lanka. Renewable energy sources such as fuel wood, rice husk and saw dust as well as commercially available fossil fuels either kerosene or diesel is used as the fuel for hot air generation in the cabinet and flat-bed dryer [25]. Department of Export Agriculture of Sri Lanka recommends drying air temperature of black pepper in the artificial dryers should be in range of 55 $^{\circ}$C to 60 $^{\circ}$C. They emphasized that the drying air temperature should not exceed the 60 $^{\circ}$C since volatile compound in the black pepper can be evaporated with reducing the quality. In addition, they recommend not to conduct the drying operation continuously but intermittently [26].

Solar thermal energy is used as the heating medium in the solar dryers. Different sizes of solar dryers are available in the market ranging from 10 to 60 kg of raw black pepper capacity. Chambers with green houses also used to dry large quantities of black pepper. Black pepper can be dried using solar dryers at low cost or no cost [26].

The cabinet dryer consists of two main components namely the tray drying chamber and the hot air generating unit. Hot air is entered into the drying cabinet supplied by an air blower. Maximum capacity of the cabinet dryer with bio mass driven air heater is approximately 300 kg of raw black pepper while total drying time would be round 18 to 20 hours. The cabinet dryer with kerosene driven air heater has maximum capacity of 450 kg of raw black pepper with around 12 hours of drying time. Positions of the trays during the drying operation have to be changed periodically to overcome the non-uniform drying [26].

The flat bed dryer also consists of two main components namely hot air generating unit and the drying chamber with a base of perforated metal plate. The raw black pepper is packed in the drying chamber and hot air passes through the perforated plate at the base by means of an air blower. Particles are mixed periodically to achieve uniform drying. Flat bed dryer with bio mass driven air heater has capacity of 1000 kg to 1500 kg while drying time would be 18 hrs to 20 hrs. Usually flat bed dryers are widely used since they have higher capacity and availability in market at low cost. Also the flat dryer is popular due to ease of operation in loading, unloading and mixing compared to the cabinet dryer [26].

## 2.3 Spouted beds

### 2.3.1 Introduction to spouted beds

Spouted beds are gas-particle contactors which has been applied not only for drying of granular materials, paste with inert particles, solutions and suspensions but also in a wide range of operations and chemical processes, such as blending of solids, coating, granulation, cooling, combustion and pyrolysis, [27, 28]. Numerous experimental and theoretical investigations on spouted beds during the past five decades have been carried out with various types of particles such as bio mass particles namely barley, millet [29],carrot cubes [30], paddy [31], soy bean [32] corn [33], saw dust, etc. [34] and non-bio mass particles such as glass beads [35], sand [36].

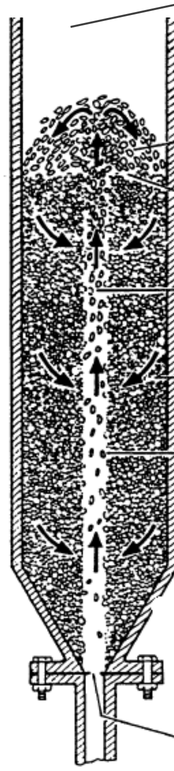



Figure 2.3 : Schematic diagram of a conventional spouted bed [37]

A typical conventional spouted bed dryer is illustrated in Figure 2.3. This representation shows the fluid inlet, the upward movement of solids in the spout region and subsequent descending in the annulus region and the fountain region. The particles can be loaded either batch wise or continuous mode.

Heat carrying gas is introduced vertically upward in to the bed through the centrally located opening at the bottom of the vessel. Hot air jet causes a stream of particle to rise rapidly through the hollowed central core or spout within the bed of solid. Particles after rising to a height above the surface of the surrounding packed bed or annulus, rain back as a fountain on to the annulus [37].

Particles in the annulus region slowly move downwards and fluid from the spout leaks into the annulus and percolates through the moving packed bed and, to some extent inward as a loosely packed bed. The gaseous streams flowing away through annulus and spout region enter the fountain region, and both streams are mixed with each other and flow away the dryer through the fluid outlet of the dryer [36].

Pneumatic transport in the spout-region and the moving bed in the downcomer are the two distinct hydrodynamic regions depicted in a spouted bed. Below mentioned two hydrodynamic conditions have to be fulfilled to achieve a stable spouting regime in a spouted bed.

i. The bed depth must be lower than the maximum spoutable bed depth
ii. The gas flow rate has to be exceeding the minimum spouting velocity

Spouted bed dryer is suitable to handle coarse particles such as Group -D particles in the Geldart classification of particles [38]. Figure 1 and Table 2 of Appendix A gives more information on Geldart classification. Major difference between the spouted bed dryer and the fluidized bed dryer is the particle flow pattern. In a spouted bed the fluid is moving through the spout region using a nozzle rather than a perforated distributor as in a fluidized bed [39].

Ordinary fluidized bed experiences an oscillatory and more random particle flow pattern while particles in the spouted bed move upwards through the spout and come down through the annulus. Some of the key characteristics of gas spouted and gas fluidized beds dryers are compared in Table 3 in Appendix A.

The conventional spouted bed dryer is characterized by a cylindrical vessel with a conical base. It has undergone various modifications to improve its performance [27] such as spouted beds of different geometries [40], spout- fluid beds [41], insertion of either draft tubes [42] or draft plates [33], multiple spouts, etc. [43]. Spouted bed vessels may have several geometries such as cylindrical, conical-cylindrical, two dimensional (slot rectangular), triangular, paraboloid based and etc. Figure 2.4 shows different geometric configurations of spouted beds including conical- cylindrical, conical, two dimensional and triangular spouted bed.

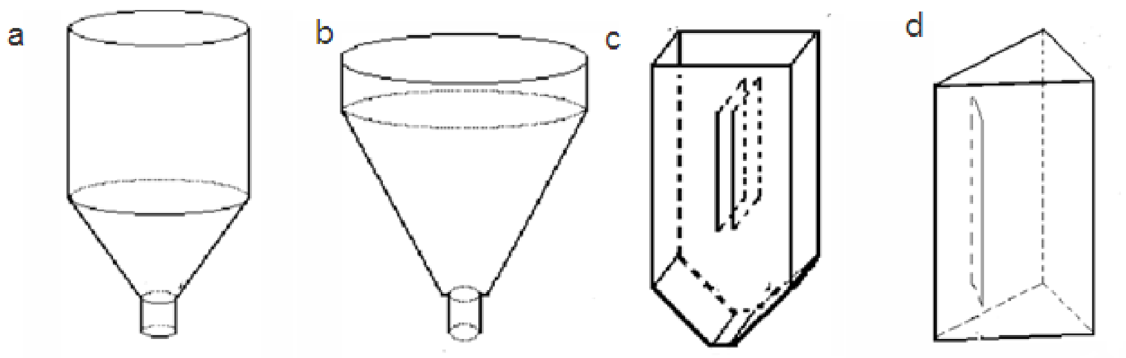
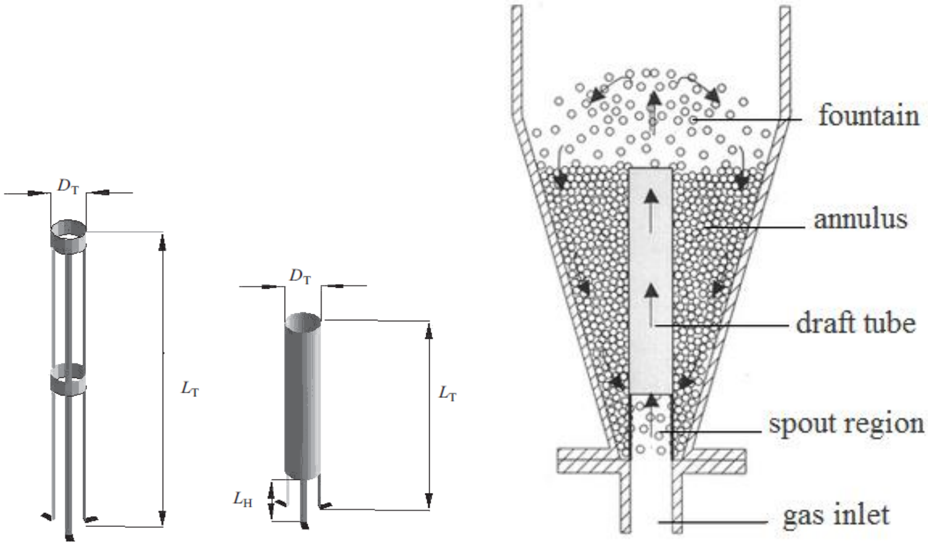



Figure 2.4-: Spouted bed Configurations: (a) conventional, (b) conical (c) two dimensional with draft plate and (d) triangular spouted bed [27]

While particles moving down through the annulus region, they can enter into the spout region resulting a random behaviour of particles. Insertion of an axially positioned tube can reduce the random behaviour of the particles and improves the solid circulation and stability of spouting [45]. Different types of tubes namely non porous draft tubes, porous draft tubes and open sided draft tubes have been used for different processes. Diameter of the draft tube ($D_T$), entrainment height ($L_H$), length of the draft tube ($L_T$) and opening ratio of porous draft tube are key design parameters for draft tube. Solid circulation, particle cycle time, gas distribution are governed by entrainment height. In addition, the hydrodynamic parameters such as minimum spouting velocity and operational pressure drop are also functions of the type of draft-tube used [46]. Usually draft tube diameter is selected as similar to the diameter of the spout without a draft tube or diameter is equal to or larger than the that of the inlet gas nozzle [37]. Figure 2.5 (a) and (b) show non porous draft tube and open sided draft tubes used by Altzibar et al. Figure 2.5 (c) shows a non porous draft tube fitted conical spouted bed also. [46].




(a) (b) (c)

Figure 2.5: (a) open sided draft tube (b) non porous draft-tube (c) draft tube fitted conical spouted bed [46]

The characteristics of the conventional spouted bed versus spouted bed with non-porous draft tube and spouted bed with porous draft tube are listed in Table 4 of Appendix A for more information.

Spouted bed has good solid mixing and relatively large air velocity helps to maintain the constant product temperature. As a consequence of it spouted beds can eliminate the possibility of overheating when the moisture content of material is low at the end of drying period [47].

### 2.3.2. Minimum spouting velocity

Knowledge of minimum spouting velocity of a specific type of material is mandatory to design and scale up of a spouted bed. In conventional spouted beds, minimum spouting velocity can be determined by using the plot of pressure drop versus superficial gas velocity with increasing and decreasing the superficial gas velocities. In contrast to the conventional spouted beds, the hydrodynamics of the conical spouted beds are quite different. Minimum spouting velocity of conical bed is the gas velocity at the onset of internal spouting, which corresponds to the pressure peak point on the curve of the pressure drop versus superficial gas velocity obtained by increasing and decreasing the superficial gas velocity as shown in Figure 2.7.

Numerous correlations are available for determination of minimum spouting velocity of spouted bed systems as shown in Equation 2.9 to Equation 2.14 of Table 2.1. Among them, Equation 2.9; Mathur- Gishler correlation is the simplest predictor of the minimum spouting velocity for wide variety of solid materials, bed dimensions and nozzle diameters [37]. Moreover, Table 5 of Appendix A shows more details about existing correlations.

Further majority of spouted bed studies are also limited to experimental columns of diameter having 300 mm or less and studies on column of 1 m or larger in diameter are rare [48]. Consequently, Lim and Grace (1987) studied the hydrodynamics of a spouted bed column of diameter 0.91 m and found that the minimum spouting velocity is not well predicted by the correlations developed for smaller vessels.

The minimum spouting velocity of a spouted bed without draft tube is higher than that of a system with a draft tube. A spouted bed with open sided draft tube requires much higher values of minimum spouting velocity comparing to a spouted bed with non-porous daft tube [46, 45, 49].

Table 2.1:Correlations for minimum spouting velocity

| **Author** | **correlation** | **Equation no** |
|---|---|---|
| Mathur and Gishler 1955 [50] | $U_{ms} = \left(\frac{d}{D}\right)\left(\frac{D_i}{D}\right)^{1/3}\sqrt{\frac{2gH(\rho_p-\rho)}{\rho}}$ | 2. 9 |
| Fane and Mitchell (1984) [48] | $U_{ms} = 2.0\ D^n\left(\frac{d_p}{D}\right)\left(\frac{D_i}{D}\right)^{1/3}\sqrt{\frac{2gH(\rho_p-\rho)}{\rho}}$ | 2. 10 |
| Wu et al. (1987) [51] | $\frac{U_{ms}}{\sqrt{2gH_o}} = 10.6\left[\frac{d_p}{D_c}\right]^{1.05}\left[\frac{D_o}{D_c}\right]^{0.266}\left[\frac{H_o}{D_c}\right]^{-0.095}\left[\frac{\rho_s-\rho}{\rho}\right]^{0.256}$ | 2. 11 |
| Olazar et al. (1992) [52] | $(Re_o)_{ms} = 0.126Ar^{0.5}\left(\frac{D_b}{D_o}\right)^{1.68}\left(\tan\frac{\gamma}{2}\right)^{-0.57}$ | 2. 12 |
| San José et al., (2007) [53] | $(Re_o)_{ms} = 0.126Ar^{0.5}\left(\frac{D_b}{D_o}\right)^{1.68}\left[\tan\frac{\gamma}{2}\right]^{-0.57}\left(\frac{H_o-l_d}{H_o}\right)^{0.45}\left(\frac{D_i}{D_i-d_d}\right)^{0.17}$ | 2. 13 |
| Altzibar et al. (2009) [54] | $(Re_o)_{ms} = 0.204Ar^{0.475}\left(\frac{H_o}{D_o}\right)^{1.240}\left(\frac{L_H}{D_T}\right)^{0.168}\left(\tan\frac{\gamma}{2}\right)^{-0.135}$ | 2. 14 |

### 2.3.3. Maximum spoutable bed height

There are three mechanisms, which causes spouting to become unstable for a given limit of height. They are fluidization of solids in the upper surface of the annular zone, choking of spout and propagation of surface instability created at the base of the bed [55]. Therefore, maximum spoutable bed height is an important parameter when improving the volumetric processing capacity and as well as the scale up operation. Several researchers have studied maximum spoutable height in spouted beds and various correlations were developed for the prediction as shown in Table 6 in Appendix A [37, 56].

### 2.3.4. Pressure drop

Numerous researches have been carried out to investigate the pressure drop in spouted beds of different geometries with different types of particles and fluids. Various correlations are available in the literature for determination of maximum pressure drop of spouted bed operation as shown in Table 7 in Appendix A.

When the gas flow rate is increased, certain pressure drop is built up through the bed of particles. The change in pressure drop with increasing and decreasing flow is caused by the different packing conditions of the bed particles. Figure 2.6 shows the photographic sequence of an evolution of spouting process of polyethylene terephthalate (PET) chips performed in a squared-based half sectional 0.2 m side unit by group of researchers [56]. Figure 2.7 describes the consequent hydrodynamic evolution of spouting process, which express the pressure drop versus flow rate hysteresis between an increasing and the decreasing flow of spouted bed.

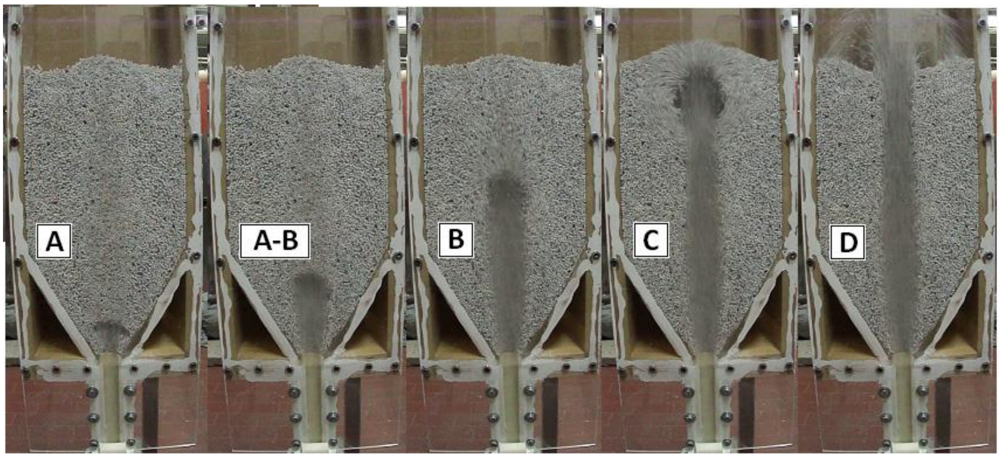



Figure 2.6: Photographic sequence of the evolution of a spouting process of PET chips performed in a squared-based half sectional 0.2 m side unit [56]

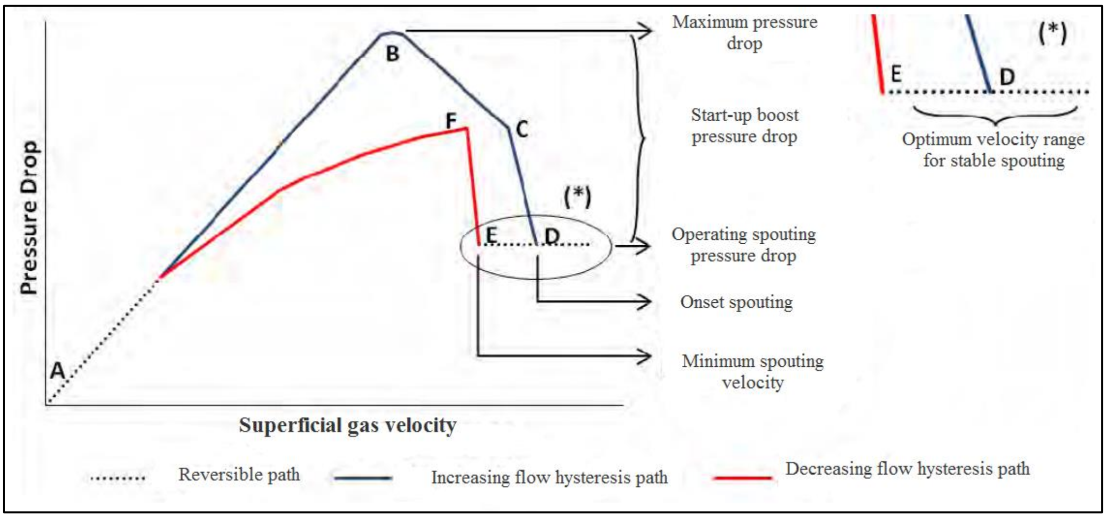



Figure 2.7: Pressure drop versus. flow rate hysteresis between an increasing and the decreasing flow in a spouted bed of PET chips [56]

## 2.4 Dimensionless models for analysis of heat transfer in spouted bed dryers

Designing of a dryer and evaluation of drying time and drying rate require the knowledge of heat and mass transfer. Mathematical models which used to simulate the temperature and moisture content of the material and the drying gas during a drying process requires the input of heat and mass transfer coefficients.

Many studies have been carried out on analysis of heat and mass transfer in spouted bed dryers. However, the consistency of the heat transfer coefficients estimated from the existing correlations is very poor. Some shortcomings are appeared on them such as assuming the whole drying period is a constant rate drying period. When heat transfer coefficients are estimated from existing correlations, difference of one or more orders of magnitude occurs for same value of input parameters. Many existing correlations are not concerned about the flow pattern of the gas and particles and the quality of spouting [57].

Generally, Nusselt number (Nu) is used to express the heat and mass transfer coefficient as a function of one or more dimensionless groups such as Reynolds number (Re), Prandlt number (Pr), the ratio of dryer vessel diameter to particle diameter, the ratio of vessel diameter to static bed height, etc. The knowledge of interfacial surface area, heat flow and the driving force; temperature difference is required to calculate the heat transfer coefficients between the particle and fluid stream [57].

Many authors have interpreted their drying processes have only constant rate drying period without analysing the surface behaviour of the material being dried. Very limited literature is available to determine the drying process is in whether constant rate or falling rate drying period by direct measurement of surface behaviour. However many investigations have been conducted by analysing surface temperature and drying kinetics [58].

In many recent research works of computational fluid dynamics (CFD) modelling of spouted bed drying, existing correlations have been used to evaluate the heat transfer coefficient [59]. However, most of the existing correlations were developed based on either the external control conditions or in the steady state conditions. Therefore, it is questionable to achieve good agreement with experimental value and the simulated value because some drying processes have falling rate drying periods as well.

A number of investigations on heat transfer between particle and fluid in spouted bed dryers are those of among the works of Prachayawarakorn et al. [39], Kmiec [60], Kudra et al. [61], El-nass et al. [62], Rocha et al. [63], etc. In case of spouted beds which supplies additional heat or remove heat out of the bed, wall to bed heat transfer coefficient were evaluated by some workers [64 , 65].

Fluid to particle heat transfer coefficient was evaluated and several correlations were developed by many researchers either applying dimensional analysis or empirically. Equation 2.15 to Equation 2.21 in Table 2.2 show the correlations associated with heat transfer of spouted beds [60 , 63].

Equation 2.15 was developed after analysis of simultaneous heat and mass transfer during batch drying of silica gel and activated carbon in spouted bed by Kmiec assuming the overall process had the constant rate dying period [60]. Prachayawarakorn et al. developed two correlations; Equation 2.16 and Equation 2.17 for heat transfer coefficient for downcomer (annulus) and spout regions separately for continuous drying of agricultural materials in spouted bed with draft plates [39]. Oliveira and Feire studied continuous drying of liquid materials in conical spouted bed [66]. One of the hypotheses used by them was that drying took place at the external control condition that is called as constant drying rate period. Owing to great deviation of experimentally obtained heat transfer coefficient with values obtained from existing correlations, they developed a correlations using non-linear regression as shown in Equation 2.19. Dimensionless equation for heat transfer coefficient shown in Equation 2.20 in Table 2.2 was developed by Kudra et al., for particulate drying in two dimensional spouted bed in the region of constant rate drying period [61].

Table 2.2 : Correlation associated with heat transfer in spouted beds

| **Author** | **Correlation** | **Equation no** |
|---|---|---|
| Kmiec (1975) [60] | $Nu = 0.897Re^{0.464}Pr^{0.333}Ar^{0.116}\left(\tan\frac{\theta}{2}\right)^{-0.813}\left(\frac{H_0}{d_p}\right)^{-1.19}\emptyset^{2.261}$ | 2. 15 |
| Prachayawarakorn et al. (2006) [39] | $Nu = 42.07Re_{p,d}^{0.454}\left(\frac{H_d}{d_p}\right)^{-1.006}$ | 2. 16 |
| Prachayawarakorn et al. (2006) [39] | $Nu = 0.4Re_{p,s}^{0.779}\left(\frac{H_s}{d_p}\right)^{-0.81}$ | 2. 17 |
| Englart et al (2009) [67] | $Nu = 0.0030Re^{0.836}Pr^{0.333}Ar^{0.236}\left(\frac{D_0}{d_p}\right)^{3.35}\left(\frac{D_b}{d_p}\right)^{-4.121}\left(\frac{\dot{m}_w}{\dot{m}_g}\right)^{0.600}\emptyset^{-0.918}$ | 2. 18 |
| Oliveira & Feire (1996) [66] | $Nu = 0.000625\left(\frac{W_l}{W_g}\right)^{1.189}Re_i^{0.991}Gu^{-1.855}Cl^{0.264}Ar^{-0.004}Pr^{0.333}/A$ | 2. 19 |
| Kudra et al. (1989) [61] | $Nu = 1.975Re^{0.64}\left(\frac{H}{d_p}\right)^{-1.20}\left(\frac{H}{w}\right)^{0.45}\left(\frac{s}{d_p}\right)^{0.26}$ | 2. 20 |
| Reger et al (2011) [27] | $Nu = 0.0597Re^{2}Ar^{-0.438}Gu^{0.61}\left(\frac{H}{d_p}\right)^{-1}$ | 2. 21 |

## 2.5 Drying models

Mathematical modelling of drying processes describes the behaviour of drying. They are used to estimate the drying time and temperature profile of the material being dried and the drying gas for selected moisture reduction without operating a real dryer [68]. Furthermore, mathematical modelling generates data to scale up, design and control of existing dryers to identify optimum dimensions of the dryer and operational parameters [69].

Early studies on spouted bed was focused on analysis of effect of operating conditions (drying temperature, bed height and particle diameter) and contactor geometry (air inlet diameter and cone angle) on drying behaviour and hydrodynamic behaviour of gas and particulates. However many number of recent studies on spouted bed drying have mainly focused on numerical simulation of drying behaviour using modelling [27].

According to the Passos et al., published models for drying of solids in a spouted bed dryer can be categorized into three levels namely zero level, one level and two level modelling [27]. Zero level models, which consist of simple algebraic equations, are based on the application of simple mass and energy balances for both gas and solid phases at the inlet and outlet of the dryer. In zero level models, once both inlet gas phase and solid phase conditions and outlet solid phase conditions are known, outlet air conditions can be determined.

One level models are composed of overall mass and energy balance for the both gas and solid phases at the inlet and outlet of the dryer and the sorption curve of solids [36].

Two level models include the conservation of mass and momentum equation and additional closure laws to describe the solid stress, interfacial forces and turbulence of two phases. Particle -particle and particle-fluid interactions are considered using these additional closure laws. Two level models are categorized into 2 types; A and B. In 2A models, gas and water vapour mixture assumed to be behaved as a continuous mixture while particulate solids are to be considered as a discrete phase. 2B models are complex and they consider the gas and solid particulate flow in three directions while only statistically mean particle path and main gas flow direction are considered for 2 A model. Computational fluid dynamics (CFD) packages are being used for solving of 2B model equations as they are more complex.

Application of Computational fluid dynamics (CFD) improves the understanding of hydrodynamic behaviour of spouted beds. CFD has been applied to conventional, conical ,two dimensional spouted beds [70], spouted fluid beds [30] and spouted bed with either draft tubes or plates [71] to get an accurate prediction of drying behaviour. Computer packages 'Fluent', 'Comsol Multi Physics', etc have been used to facilitate the model [30, 72, 73].

So far, there have been many numbers of mathematical models in literature to describe the drying behaviour of many agricultural products. However another concise analysis of drying model by Jittanit et al. showed that models can be categorized as empirical models ,semi empirical models and models based on heat and mass balances, etc. [69]. Among them, thin layer drying models which frequently having a semi empirical relationship are popular within many researchers. Although thin layer drying models are popular, many of them are limited to specific equipment, dryer configuration and specific material and operational conditions. Thin layer drying modes are widely applied by many researchers due to its simplicity and lack of required data [74].

Thin layer drying models are useful in designing new drying equipments, improving existing drying processes and for prediction of drying time accurately [75]. Furthermore, they contribute to get an understanding about the heat and mass transfer of the drying systems [15].

Thin layer drying models are categorized as theoretical, semi theoretical and empirical models [74]. They describe the variation of moisture ratio (MR) of the material with the time during the drying process. Ficks' second law of diffusion is the most widely applied theoretical model for drying and it considers the internal resistance to transfer moisture between the drying material and the air. Semi theoretical and empirical models consider the external resistance to moisture transfer between material and the air. However, they can be applied within a range of operational parameters such as drying temperature, air flow rate, initial moisture content, and for a particular drying material that they developed. Numerous semi theoretical and empirical models are available in literature to fit the data of drying kinetics of many agricultural products. Some of them are listed as shown in Equation 2.22 to Equation 2.33 in Table 2.3. The Newton model, Page model, Henderson and Pabis model, Two component model and Logarithmic model are some of semi theoretical models while Wang and Sing model and Thompson model are empirical models available in literature. Coefficients of some thin layer models have been correlated to operational parameters of the process such as drying temperature, air velocity, etc. [76, 77, 78, 79].

Table 2.3:Thin layer drying models

| **Model name** | **Model** | **Equation no** | **Reference** |
|---|---|---|---|
| Newton | $MR = \frac{X_t - X_e}{X_0 - X_e} = e^{-kt}$ | 2. 22 | [80] |
| Page | $MR = \frac{X_t - X_e}{X_0 - X_e} = e^{-kt^n}$ | 2. 23 | [81] |
| Modified Page | $MR = \frac{X_t - X_e}{X_0 - X_e} = e^{(-kt)^n}$ | 2. 24 | [81] |
| Henderson and Pabis | $MR = \frac{X_t - X_e}{X_0 - X_e} = ae^{-kt}$ | 2. 25 | [82] |
| Logarthmic | $MR = \frac{X_t - X_e}{X_0 - X_e} = ae^{-kt} + b$ | 2. 26 | [76] |
| Two compartment | $MR = \frac{X_t - X_e}{X_0 - X_e} = ae^{-k_1 t} + be^{-k_2 t}$ | 2. 27 | [80] |
| Abbasi et al. ( Modified Middilli-Kucuk) | $MR = \frac{X_t - X_e}{X_0 - X_e} = ae^{-kt^n} + b$ | 2. 28 | [81, 75] |
| Midillli - Kucuk | $MR = \frac{X_t - X_e}{X_0 - X_e} = ae^{-kt^n} + bt$ | 2. 29 | [75] |
| Hii et al. | $MR = \frac{X_t - X_e}{X_0 - X_e} = ae^{-k_1 t^n} + be^{-k_2 t^n}$ | 2. 30 | [83] |
| Wang and Sing model | $MR = \frac{X_t - X_e}{X_0 - X_e} = 1 + at + bt^2$ | 2. 31 | [84] |
| Verma et al. (modified two term exponential) Model | $MR = \frac{X_t - X_e}{X_0 - X_e} = aexp(-k_1 t) + (1 - a)exp(-k_2 t)$ | 2. 32 | [75 ,81] |
| Thompson model | $MR = \frac{X_t - X_e}{X_0 - X_e} = alnMR + b(lnMR)^2$ | 2. 33 | [75] |

a, b, k, $k_1$, $k_2$ and n are drying coefficients and constants

Thin layer drying models are applied when either thin layer of material is maintained or the air velocity is high enough to cause good solid mixing to have uniform drying. Moreover, the operating conditions of the drying process such as air temperature and humidity are kept constant throughout the process [85].

According to Kuck et al., 67 potential thin layer drying models are available in the literature from 2003 to 2013 [75]. Goodness of fit was evaluated under 28 performance assessment criteria. Coefficient of determination($R^2$), root mean square error (RMSE), reduced chi square ($\chi^2$), mean relative percentage error, standard error of estimate are among the most used benchmarks. In order to evaluate the goodness of fit, many researchers used highest values of either coefficient of determination or modelling efficiency, and lowest values of one of these parameters such that reduced chi-square, the root mean square error and the mean relative percentage error [75].

Mathematical modelling on thin layer drying processes has been conducted on many agricultural products such as cocoa [83], mint, parsley [86], apple [87], green pepper [19], banana [88], eggplant [89], leek slices [90], jackfruit [91], etc. Most of the drying processes were conducted using an air ventilated oven [83], open sun drying [86], packed bed and fluidized bed dryers [92, 93].

According to Jittanit et al., thin layer drying models are applied to spouted bed drying process since regular circulation of particles in the spouted bed achieves uniform moisture content and uniform temperature of samples [80]

A limited published literature is available for analysis of thin layer models in spouted bed drying process [79, 77, 33, 32].The thin layer drying models are evaluated for spouted bed dryers considering the product type, drying parameters such as temperature [80], air velocity, bed depth [79], etc. It was hardly found for considering the configuration of the draft tubes. Although many researches have been carried out on mathematical modelling of drying of agricultural crops, published data available on black pepper drying in spouted beds is very limited.

## 2.6 Scale up

Scaling up of a spouted bed can be approached in two ways either changing the geometry of the conventional spouted bed or modifying the spouting operation [94]. The first approach implies increasing the size of a single unit or changing geometry of conventional spouted bed in to two dimensional spouted bed or conical spouted bed. Later is concerned to insertion of auxiliary device such as draft tube, draft plate, mechanical devices or introduce additional fluid in the annular region. Design and constructions of both options have to be conducted carefully to minimize heat loss, investment and operating cost since they have some advantages and drawbacks. Table 8 of Appendix A shows more information on scale up of spouted beds.

## 2.7 Research on black pepper essential oil

Essential oil of black pepper contains the volatile organic compounds. They which imparts the flavor and perfumery to the black pepper have been studied by various researchers [95, 96]. The volatile oil component of black pepper contains terpene hydrocarbons and oxygenated terpenes. 90% of terpene hydrocarbon consists of monoterpene and sesquiterpenes. The chemical formula of monoterpene and sesquiterpene are $C_{10}H_{16}$ and $C_{15}H_{24}$ respectively. Terpene hydrocarbons possess main desirable attributes of black pepper flavor. Oxygenated compounds which present less than 4%, imparts the characteristic musty, moldy odor and off flavor of black pepper [96].

A research conducted by Mccarron *et. al.* found that β -Pinene and Carryophellene (β caryophyllene) and Sabinene were commonly available compounds in Sri Lankan and Indian black pepper derived essential oil [6]. Another study reported by Menon et. al. added three more compounds to the main components of Indian black pepper oil namely delta-3 Carene, Limonene and α-Pinene. They analyzed four selected cultivars of black pepper and identified 55 components of volatile organic compounds [95]. Buckle et al. have recommended the local Sri Lankan cultivars for perfumery industry than Indian and Sarawak cultivars since Sri Lankan cultivars were rich in β caryophyllene which is the abundant component of sesquiterpene hydrocarbons [97]. According to Mccarron et al. and Buckle et al., the composition of black pepper oil depends on the geographical conditions and varietal variations and post-harvest methods. In fact recent studies carried out with comprehensive gas chromatography–mass spectrometry (GC-MS) has identified more than 300 compounds in essential oil derived from black pepper [98]. In a recent research of Jelen and Gracka, 273 components have been identified [96].

## 2.8 Quality of black pepper

Depending on the country, specification for quality requirement of black pepper is varied. ASTA (American spice trade association), ESA (Europe spice association, CSA (Canadian spice association) are some of authorized associations pertaining to assure quality of spices and herbs in the global market. Table 9 of Appendix A consists of some specifications required for black pepper defined by several institutes related to spice and herb.

According to the European spice association (ESA) specifications of quality minima for black pepper should have 12% w/w of moisture content and minimum 2% v/w of volatile oil content for trading within the Europe [99]. Table 10 of Appendix A consists of the quality standards approved by the Sri Lanka Standard Institute.

## Chapter specific nomenclature

a, b, k, $k_1$, $k_2$ & n - drying coefficients and constants

A -cross section of the bed measured at right angles to the air flow

Ar - Archimedes number

Cl - liquid concentration in the material (kg/kg)

$C_{pa}$ and $C_{pv}$ - specific heat capacity of air and vapour respectively (J/kg$^{\circ}$C)

D, $D_c$ - diameter of the column (m)

$d$, $d_p$ - particle diameter , horizontally projected diameter

$D_0$ -pre exponential factor of Arrhenius equation

$D_b$ - upper diameter of the stagnant bed in conical spouted bed

$D_{eff}$ -effective moisture diffusivity ($m^2/s$)

$D_i$- gas inlet diameter (m)

$D_T$ , $d_d$ -diameter of draft tube (m)

$E_a$ -activation energy (kJ/mol)

$F_0$ -Fourier number

Gu- Guckhman number

$H$, $H_o$ -static bed depth (m)

$H_d$ static bed height in downcomer region (m)

$H_s$ static bed height in spout region (m)

$H_T$- tube height (m)

$L_H$ -entrainment height (m)

$L_T$ , $l_d$ - total height of the draft tube

$m_v$- mass of water removal (kg)

$\dot{m}_g$- mass flow rate of the gas (kg/s)

$\dot{m}_w$- mass flow rate of the liquid (kg/s)

N - drying rate or (mass moisture evaporated/(area)(time) ($kg/m^2s$)

Nu- Nusselt number

Pr- Prandlt number

Q- air flow rate ($m^3/s$)

R -universal gas constant (kJ/mol K)

Re - Reynolds number

$(Re_o)_{ms}$ - Reynolds number of minimum spouting, referred to gas inlet

$R_p$ -radius of the spherical particle (m)

s - slot width in two dimensional draft tubes (m)

T -absolute temperature (K)

t -time (s)

$T_{am}$ - ambient temperature ($^{o}$C)

$T_d$- inlet air temperature to the drying chamber or drying temperature ($^{o}$C)

$t_{drying}$ - Total drying time (s)

$U_{ms}$ - minimum spouting velocity (m/s)

$V_h$ - humid volume or specific volume of air ($m^3$/kg of dry air)

W - bed width (m)

$W_d$ - mass of dried solid

$W_g$ - gas mass velocity (m/s)

$W_l$ -liquid mass velocity (m/s)

X - moisture content dry basis

$X_0$ - initial moisture content (kg/kg dry basis)

$X_c$ - critical moisture content

$X_e$ -equilibrium moisture content (kg/kg dry basis)

$X_t$ -moisture content at time t (kg/kg dry basis)

$Y_a$ - humidity of air (kg of moisture/ kg of dry air)

Φ - particle shape factor, Φ>1

$\gamma, \theta$ - angle of the conical base of the contactor, degrees

$\rho$ - density of air or fluid

$\rho_p, \rho_s$- density of particle, $kg/m^3$

**Abbreviations**

SEC - specific energy consumption

ASTA - American spice trade association

ESA - Europe spice association

CSA - Canadian spice association

MR - moisture ratio

**Chapter 3**

# 3. METHODOLOGY

This chapter describes the material preparation for spouted bed experiments, experiments for determination of spouting behavior of black pepper, black pepper drying experiments, determination of heat transfer coefficient, methodology of dimensional analysis of heat transfer process and mathematical model development of spouted bed drying process.

## 3.1 Experimental methods

In this section, experiments conducted to accomplish the objectives of this study are described, including the materials, equipment, instruments and operational parameters used.

A number of experiments were carried out to study the spouting behavior and drying of black pepper to accomplish the objectives stated in Chapter 1. The experiments are categorized in to two sections as preliminary experiments and major experiments. Preliminary experiments were conducted to identify the best configuration of spouted bed among two types of draft tube fitted spouted beds and the conventional spouted bed. Major experiments were conducted to examine optimum spouted bed parameters to achieve black pepper with maximum essential oil yield, to model heat transfer characteristics and to develop mathematical model to describe drying behavior.

Preliminary experiments were conducted using wetted black pepper and section 3.1.2 describes the preparation of wetted black pepper. Preliminary experiments are categorized as:

- Finding minimum spouting velocity
    - In conventional spouted bed
    - In spouted bed with internal devices
        - Non-porous draft tube fitted spouted bed
        - Porous draft tube fitted spouted bed

- Drying experiments
    - In conventional spouted bed
    - In spouted bed with internal devices
        - Non-porous draft tube fitted spouted bed
        - Porous draft tube fitted spouted bed

Major experiments were conducted in the conventional spouted bed using raw black pepper and section 3.1.1 describes the methods used to handle raw black pepper prior to experiments. Major experiments are categorized as:

- Finding minimum spouting velocity
- Drying experiments
- Extraction of essential oil

**3.1.1 Handling of raw black pepper for experiments**

Raw black pepper (matured, unripe green colour) with their spikes collected from a farm located in Gampaha District of Sri Lanka was used for conducting major experiments. The initial moisture content of raw black pepper seeds ($X_0$) was 3.50 kg moisture/kg of dry solids (350%). The raw black pepper were stored in a refrigerator at 2-5 °C to avoid spoilage. Required amount of raw black pepper was taken out of the refrigerator around one hour before the experiment. Then seeds were removed from their spikes manually and allowed to reach the room temperature.

The Precision balance; VWR ECN 611-2300 with reading accuracy of 0.01g was used to measure the required amount of seeds. Figure 3.1 shows a tray of raw black pepper with their spikes and prepared black pepper seeds for experiments.

Figure 3.1: Raw black pepper preparation for experiments (a) black pepper spikes (b) raw black pepper seeds

### 3.1.2 Preparation of wetted black pepper

Since black pepper is a seasonal crop and it is not available throughout the year, wetted black pepper was used to conduct the preliminary experiments. Preliminary experiments were conducted to determine the best configuration of the spouted bed among the draft tubes fitted spouted bed and the conventional spouted bed. Effect of configuration of draft tubes such as draft tube diameter ($D_T$), entrainment height ($L_H$) and draft tube height ($H_T$) on drying kinetics were analysed by conducting drying experiments with the wetted black pepper.

Dried black pepper was purchased from Jayantha Agrochemicals of Galle, Sri Lanka. Dried black pepper usually has moisture content 8-15% dry basis. They were rewetted to moisture content around 80% dry basis, as described in next paragraph.

Dried black pepper seeds were wetted by adding distilled water. Dried black pepper was put in to a polypropylene container and predetermined amount of distilled water was added and mixed to wet the surface of the particles and absorb more water. Then they were kept in a refrigerator at 3-5 $^{\circ}$C temperature for 5-6 days in the tightly closed container, until black pepper particles reached to the stable conditions. Samples of black pepper were taken out and moisture content was measured daily using the direct and indirect measuring methods.

### 3.1.3 Determination of moisture content of black pepper particles

Moisture content of the solid is the key parameter for investigations in drying processes. Moisture content is determined by direct methods or indirect methods [100].

The direct method consists of drying known sample of solid material in a drying oven at 102 °C -105 °C until the weight of the samples becomes constant and measurement of sample weight before and after the drying process. Then the moisture content, X (% dry basis) is given by Equation (3.1).

$$X(\%drybasis) = \frac{W_w - W_d}{W_d} \times 100 \qquad (3.1)$$

Where

$W_w$- initial weight of the sample (kg)

$W_d$-weight of sample after drying in the oven (kg)

For the direct measurement of moisture content, a drying oven; A lab Tech LDO-060E with reading accuracy of 0.5 °C was used to dry black pepper samples. Weight of black pepper samples were measured by a portable digital balance; KERN PCB 350-3 in the range of 0-300g and accuracy of ± 0.001g.

Digital Moisture Analyzer (Citizen, MB 200X), with reading accuracy of ±0.01 kg/kg was used for the indirect measurement of moisture of the black pepper seeds.

### 3.1.4 Experiment set up and equipment

A laboratory scale spouted bed dryer was designed and got fabricated by Mega Heaters (Pvt) ltd, Kottawa, Sri Lanka. The dryer consists of an air blower with variable speed drive (VSD) to control the airflow, air heater with control unit, spouted bed contactor, temperature measurement sensors, a U tube manometer and a cyclone separator as shown in Figure 3.2 and Figure 3.3.

The cyclone separator is reverse flow and used to capture entrained fine particles. The spouted bed contactor is a cylindrical vessel with conical bottom. The dimensions of the spouted bed column are: the diameter of the cylindrical column

($D_c$) or diameter of the upper section of the conical base, 0.15 m; angle of conical section, 60° and the height of the conical section 0.069 m. The gas inlet diameter ($D_i$) can be set for any of three values; 0.029 m, 0.035 m and 0.05 m. The total height of the vessel (conical bottom plus cylindrical column) is approximately 1.07 m. A perforated plate is fixed at the bottom of the spouted bed column which prevents black pepper seeds entering the gas inlet tubes. The dryer could be adjusted to any preferred drying air temperature between room temperature to 120 °C. The particles to be dried are packed in the spouted bed column. The desired drying air temperature is attained by electric heater and the temperature control unit.

The entire dryer is made of stainless steel. The bottom of the cone section of the spouted bed dryer is connected to the heater and blower while the reverse flow cyclone separator is channelled to top of spouted bed contactor to capture entrained fine particles. Tables 3.1 summarizes the geometric factors of spouted bed set up.

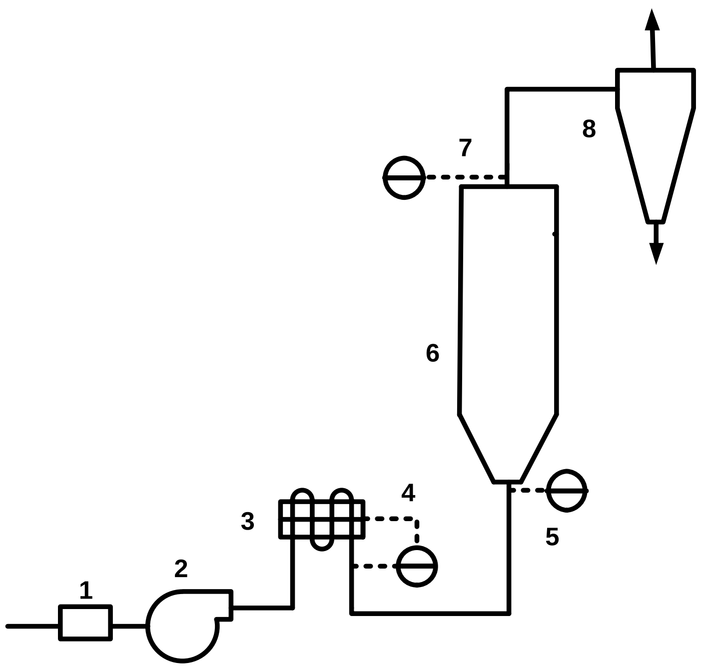



Figure 3.2: Schematic diagram of the spouted bed drying experiment Set up;
1-VSD, 2-Blower, 3,4-Air heater with temperature control system, 5,7- Temperature indicators, 6- Spouted bed column, 8- Cyclone separator

The blower is operated by a 2.2 kW motor and the air heater has a capacity of 12 kW. Pressure measurements were carried out by means of a U tube water manometer. Two Pt100 thermometers are located at the spouted bed inlet and outlet to measure the temperatures of the inlet and exit air. In all experiments, the fluctuations of temperature were within ±1$^{\circ}$C.

Five temperature sensors; DS18B20-PAR with ± 0.5 $^{\circ}$C accuracy were placed inside the spouted bed. Temperature sensors are compatible with Arduino development boards and coding was done to communicate with sensors. Arrangement of temperature sensors are shown in Figure 3.4. Schematic diagram of arrangement of temperature sensors in spouted bed column is shown in Figure 4 in Appendix C. Measurements of temperature inside the spouted bed were used for the modelling of heat transfer to determine the heat transfer coefficients.

Figure 3.3: Image of spouted bed drying experiment set up

Figure 3.4: Arrangement of temperature sensors inside the spouted bed contactor

Table 3.1: Geometric factors of the spouted bed

| spouted bed -Stainless steel | | | | |
|---|---|---|---|---|
| Column diameter | $D_C$ (m) | 0.15 | | |
| Cone angle | Γ (deg) | 60 | | |
| Height of the cylindrical sections | $H_L$ (m) | 1 | | |
| Height of the cone sections | $H_c$ (m) | 0.07 | | |
| Gas Inlet diameters | $D_i$ (m) | 0.049 | 0.035 | 0.024 |
| Cone base diameter | $D_o$ (m) | 0.05 | | |

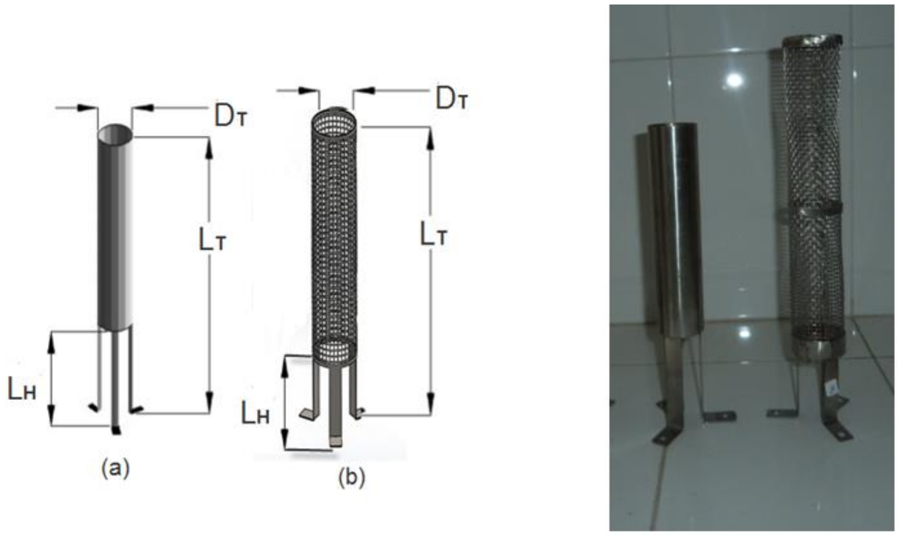
Air velocity at the inlet was measured by means of EXTECH CFM Thermo anemometer model 407113 with an accuracy of ±2 %. Relative humidity of air at outlet of the dryer and the ambient air were measured by Thermo-Hygrometer Model GMK-920HT with an accuracy of ± 2%.

The draft tubes are cylindrical tubes with three arms made of stainless steel and placed collinear with the axis of cylinder. Two types of draft tubes were used separately. They are namely porous draft tube and nonporous draft tubes having similar configuration except to the perforations as explained in section 2.3. Figure 3.5 (a) and (b) illustrates non-porous and a porous draft tubes respectively.

The draft tube was fixed using its three arms at the bottom of the vessel collinear with the axis of spouted bed column. The conical base of the dryer allows fitting a draft tube at the inlet of conical section as shown in Figure 3.6. Distance between the base of the arm and the base of the tube is called as the entrainment height. As per the literature, dimensional parameters of a draft tube is categorized as diameter of draft tube ($D_T$), entrainment height ($L_H$), tube height ($H_T$=$L_T$-$L_H$), width of the arm where $L_T$- total height of the draft tube [46].

Width of arm was kept constant during this study while changing the other parameters. Sixteen draft tubes with different configuration have been used. Seven of them were non-porous and other nine were porous. Table 3.2 & 3.3 show the dimensions of both types of draft tubes used.

Figures of all the equipment and instruments used for experiments are listed in Appendix B. More information on spouted bed contactor, draft tube and the reverse flow cyclone separator are also available in Appendix C.




(a) (b) (c)

Figure 3. 5: a) non porous draft tube (b) porous draft tube [101] and (c) Image of both type od draft tubes

Figure 3. 6: A porous draft tube is ready to fit into the spouted bed contactor

Table 3.2: Dimensions of non-porous draft tubes

| Draft tube no | Draft-tube diameter ($D_T$) (m) | Drat-tube entrainment height ($L_H$ ) (m) | Draft-tube height ($H_T$) (m) |
|---|---|---|---|
| 1 | 0.035 | 0.060 | 0.016 |
| 2 | 0.035 | 0.080 | 0.016 |
| 3 | 0.035 | 0.060 | 0.020 |
| 4 | 0.035 | 0.060 | 0.024 |
| 5 | 0.035 | 0.030 | 0.016 |
| 6 | 0.029 | 0.030 | 0.016 |
| 7 | 0.050 | 0.030 | 0.016 |

Table 3.3: Dimensions of porous daft tubes

| Draft tube no | Draft-tube diameter ($D_T$) (m) | Drat-tube entrainment height ($L_H$ ) (m) | Draft-tube height ($H_T$) (m) |
|---|---|---|---|
| 1 | 0.050 | 0.030 | 0.016 |
| 2 | 0.060 | 0.030 | 0.016 |
| 3 | 0.070 | 0.030 | 0.016 |
| 4 | 0.035 | 0.040 | 0.016 |
| 5 | 0.035 | 0.060 | 0.016 |
| 6 | 0.035 | 0.080 | 0.016 |
| 7 | 0.035 | 0.060 | 0.020 |
| 8 | 0.035 | 0.060 | 0.024 |
| 9 | 0.035 | 0.060 | 0.080 |

### 3.1.5 Preliminary experiments

Spouting behavior of wetted black pepper was studied to determine the minimum spouting velocity of the spouted bed of three different configurations namely conventional spouted bed , spouted bed with porous drat tube and spouted bed with non-porous draft tube fitted systems. Experiments were conducted for a selected bed height; 16 cm of wetted black pepper. Way of determining minimum spouting velocity is similar to those of the experiments conducted with raw black pepper in conventional spouted bed. More details are elaborated in section 3.1.6.1.

Effects of geometric factors such as height, diameter and height of entrainment zone of draft tubes on drying were determined. Samples of wetted black pepper with initial stagnant bed height of 16 cm were dried in spouted bed fitted with different draft tubes at their minimum spouting velocity at 75 °C drying temperature. Seven non-porous draft tubes with different dimensions and nine porous draft tubes with different dimensions were used.

Drying experiments with wetted black pepper were conducted using three configurations of spouted bed. A number of experiments were conducted in a limited range of drying conditions to identify the best configuration. Experimental conditions are summarized in Table 3.4 to Table 3.6. When analysing the effect of spouted bed configurations, two superficial air velocities were used. Air velocity was set at their minimum spouting velocities and in a higher velocity; 0.89 m/s to ensure the stable spouting operation with all possible bed heights without pneumatic transport of particles out to the cyclone separator.

Table 3.4: Operating conditions of preliminary experiments conducted to analyze the effect of spouted bed configuration at minimum spouting air velocity

| **Configuration** | **Air velocity (m/s)** | **Stagnant bed height (cm)** | **Temperature (°C)** |
|---|---|---|---|
| Conventional spouted bed | 0.74 | 16 | 55, 65, 75 |
| *Non porous draft tube fitted spouted bed | 0.51 | 16 | 55, 65, 75 |
| *Porous draft tube fitted spouted bed | 0.58 | 16 | 55, 65, 75 |
| * $D_T$= 0.035m, $L_H$ = 0.06 m, $L_T$= 0.26 m | | | |

Table 3.5: Operating conditions of preliminary experiments conducted to analyze the effect of spouted bed configuration at superficial velocity of 0.89 m/s

| **Configuration** | **Air velocity (m/s)** | **Stagnant bed height (cm)** | **Temperatur e (°C)** |
|---|---|---|---|
| Conventional spouted bed | 0.89 | 16 | 75 |
| *Non porous draft tube fitted spouted bed | 0.89 | 16 | 75 |
| *Porous draft tube fitted spouted bed | 0.89 | 16 | 75 |
| * $D_T$= 0.035m, $L_H$ = 0.06 m, $L_T$= 0.26 m | | | |

Table 3.6: Operating conditions of preliminary experiments conducted to analyze the effective moisture diffusivity of black pepper in three spouted bed configuration

| **Configuration** | **Air velocity (m/s)** | **Stagnant bed height (cm)** | **Temperature (°C)** |
|---|---|---|---|
| Conventional spouted bed | 0.74 | 16 | 45, 55, 65, 75 |
| *Non porous draft tube fitted spouted bed | 0.51 | 16 | 45, 55, 65, 75 |
| *Porous draft tube fitted spouted bed | 0.58 | 16 | 45, 55, 65, 75 |
| * $D_T$= 0.035m, $L_H$ = 0.06 m, $L_T$= 0.26 m | | | |

### 3.1.6 Major experiments with raw black pepper

According to the results of preliminary experiments with different spouted bed configurations, best configuration was selected as the conventional spouted bed. Therefore major experiments were conducted with raw black pepper in conventional spouted bed to achieve following goals of the study.

- Determination of minimum spouting velocity
- Effect of operational parameters on drying kinetics
- Examine optimum drying air temperature to achieve black pepper with maximum essential oil yield with consistent quality.
- Analyse the effect of drying air temperature on mass transfer characteristics namely effective moisture diffusivity.
- Model the heat transfer in the spouted bed dryer and validate the model using the experimental data
- Develop suitable drying model to describe the drying behaviour

### 3.1.6.1 Determination of spouting behavior of raw black pepper

Spouting behavior of raw black pepper was studied to determine the minimum spouting velocity and maximum pressure drop of the spouted bed of selected bed heights; 7 cm, 14 cm, 18 cm and 22 cm. All the experiments were conducted using ambient air.

Spouted bed contactor was filled with raw black pepper particles up to the required static bed height. Air flow rate was increased in small increments by adjusting the variable frequency drive connected to the blower. Airflow velocity and total pressure drop across the spouted bed contactor were recorded simultaneously. Air flow rate was increased gradually and air velocity and pressure drop measurements were recorded. Once the bed is in fully spouted bed condition, the airflow rate was reduced gradually and the total pressure drop was recorded. Total pressure drop is the pressure drop caused mainly due to the black pepper bed and the perforated plate fixed at the bottom of the spouted bed contactor.

Pressure drop across the perforated plate fixed at the bottom of the spouted bed contactor was measured in the absence of solid particles over a same range of air velocities. The true pressure drop across the bed of particles was determined by subtracting the measured empty bed pressure drop from total pressure drop value [13].

Then the minimum spouting velocity at the selected bed heights of raw black pepper was determined using the plots of pressure drop versus air velocity at ambient temperature.

### 3.1.6.2 Effect of operational parameters on drying kinetics

The dryer was operated at hot air temperatures between 45 $^{\circ}$C to 75 $^{\circ}$C and stagnant bed heights of 7-20 cm of raw black pepper. Air velocity was maintained at 1.60 m/s, 1.97 m/s and 2.37 m/s. During drying process, samples were collected in selected time intervals and moisture content was measured using the direct method as described in section 3.1.3. The drying experiments were conducted until the moisture of the black pepper reached to less than 15%.

Experiments were conducted as described below to determine the effect of drying temperature on drying kinetics. Raw black pepper samples were dried in a spouted bed dryer at 4 different temperatures; 45 $^{\circ}$C, 55 $^{\circ}$C, 65 $^{\circ}$C and 75 $^{\circ}$C keeping other parameters constant. The initial stagnant bed height was 14 cm and the airflow rate was maintained at 2.37 m/s.

Effect of air velocity on drying kinetics was determined by drying 14 cm initial stagnant bed height of raw black pepper samples in the spouted bed dryer at three different air velocities; 1.60 m/s, 1.97 m/s and 2.37 m/s keeping drying temperature at 65 $^{\circ}$C.

Initial static bed height was varied as 7 cm, 14 cm and 20 cm keeping drying temperature at 65$^{\circ}$C and air velocity at 2.37 m/s to determine the effect of initial stagnant bed height on drying.

Airflow with superficial velocity of 2.37 m/s was used for the experiments conducted to analyze the effect of drying temperature and bed height. Air velocity of 2.37 m/s was selected to have stable spouting operation with all possible bed heights. Since 2.37 m/s was below the terminal velocity of dried black pepper particle and it was also above the minimum spouting velocity of maximum spoutable bed height (25 cm) of the spouted bed column used for the current investigation. All the experiments were duplicated. Terminal velocity of black pepper is 9.1 m/s and it was calculated from the equation available in Appendix H.

### 3.1.6.3 Drying experiments for modeling of heat transfer

The dryer was operated at hot air temperatures between 45 $^{\circ}$C to 75 $^{\circ}$C and stagnant bed heights of 7-24 cm of raw black pepper. Air velocity was maintained from 1.59 m/s to 2.60 m/s where all the experiments were conducted beyond the minimum spouting condition and also below the entrainment velocity of black pepper particles respective to their stagnant bed height. Superficial air velocity and inlet gas temperature were kept constant during the drying operation.

Drying experiments were conducted until the moisture of the black pepper reached to less than 15%. 48 experiments were conducted and data was gathered for estimation of heat and mass transfer coefficients.

During drying process, samples were collected in selected time intervals and moisture content was measured using the direct method [100]. Temperature and relative humidity of exhaust air of the dryer and temperature of the bed were measured to estimate the heat transfer coefficient. Due to excellent mixing and heat transfer occur in the spouted bed, gas and particle temperature profile in the spout and annulus regions are almost identical and equal to the bed average temperature [102]. Therefore, temperature of the bed was determined from the average of the temperature measurements of five sensors located inside the bed.

Gas flow rate and inlet gas temperature is kept constant throughout the experiment. Therefore, humidity of inlet gas is also constant assuming that there is no fluctuation of humidity and temperature of the ambient air.

#### 3.1.6.4 Drying experiments for development of model to describe drying behavior

The dryer was operated at hot air temperatures between 45 °C to 75 °C and stagnant bed heights of 14 - 22 cm of raw black pepper. The air velocity was maintained at 2.37 m/s since it was above the minimum spouting velocity of 22 cm stagnant bed height of raw black pepper. The selected velocity was well below the terminal velocity of black pepper. During the drying process, samples were collected in selected time intervals and moisture content was measured using the direct method. The drying experiments were conducted until the moisture of the black pepper reached 15 % dry basis.

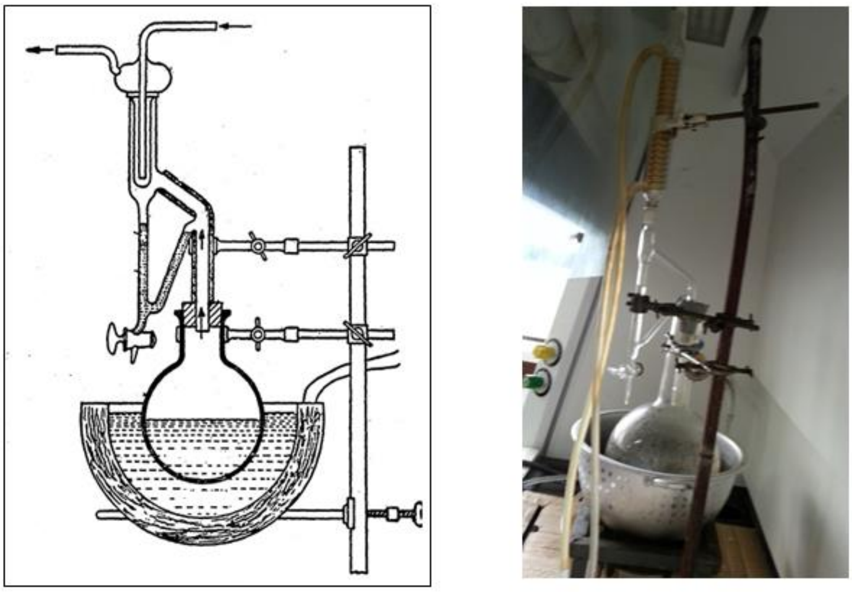
All the experiments described in section 3.1.6.1 to 3.1.6.4 were duplicated and average of results are presented and described in Chapter 5.

### 3.1.6.5 Experiments for determination of optimum drying air Temperature

Experiments were conducted as described below to determine the effect of drying temperature in the spouted bed on quality of black pepper and to compare sun drying with the spouted bed drying.

A fresh sample of raw black pepper was dried in sun for several days to reduce the moisture content up to 15%. 14 cm stagnant bed height of raw black pepper was dried in conventional spouted bed just above the minimum spouting velocity of 1.43 m/s at different hot air temperatures; 45 $^{\circ}$C, 55 $^{\circ}$C, 65 $^{\circ}$C and 75 $^{\circ}$C. Solar dried black pepper and samples of black pepper dried in the spouted bed were used to extract essential oil.

After drying, all the black pepper samples were packed in air proof dark polythene bags to avoid the contact of oxidative agents with dried seeds and stored in a refrigerator at 3-5 $^{\circ}$C until they were used for oil extraction. Extraction apparatus consists of a heating mantle, oil bath and 5 L round bottom flask with Clevenger type volatile oil trap and a condenser as shown in Figure 3.7 (a) and (b).



(a) (b)

Figure 3.7: (a) Schematic diagram of extraction apparatus (b) Photograph of extraction apparatus

Dried black pepper was chopped and placed in round bottom flask of extraction apparatus with 2 L of distilled water and boiled for 3 - 4 hr. Essential oil was collected in the graduated Clevenger type volatile oil trap. Collected oil was allowed to cool and the volume of the essential oil was measured using graduated scale on the oil trap as shown in Figure 3.8 and 3.9. Oil extraction experiments were conducted for sundried and spouted bed dried black pepper. All the experiments were replicated four times.

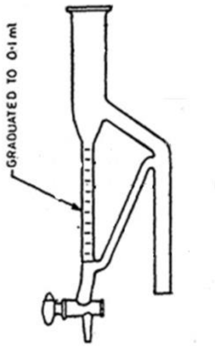
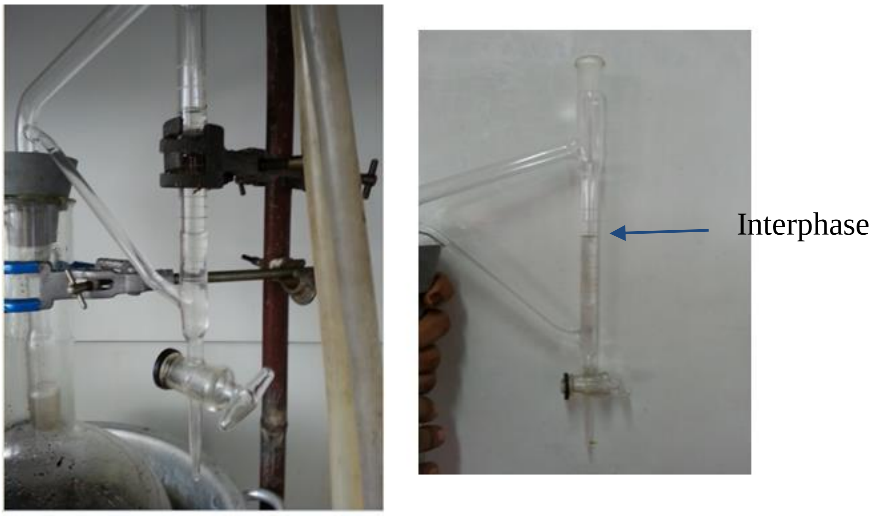



Figure 3.8: Clevenger type oil trap




(a) (b)

Figure 3.9: (a) Clevenger type oil trap in experiment set up (b) interphase of oil and water in oil trap

The oil samples were subsequently analysed using Gas Chromatography Mass spectrometry(Agilent, American 7890A/5975C GC-MS system) equipped with a fused silica capillary Agilent Technology 5% phenyl dimethyl siloxane column. The injector temperature was 25 $^{\circ}$C, and the oscillatory temperature was 100 $^{0}$C. A volume of 2μl of oil was injected in split mode (split ratio of 1:100). The initial temperature was kept at 70 $^{\circ}$C for 2 min, and the temperature was gradually increased to 270 $^{\circ}$C at a heating rate of 5 $^{\circ}$C/min. Figure 8 in Appendix III shows an image of Agilent, American 7890A/5975C GC-MS system.

Components in essential oil were identified according to the NIST (National Institute of Standards and Technology). Microsoft Excel 2010 and IBM SPSS Statistics 20 (IBM, Armonk, US) were used for the analysis of volatile oil components of essential oil derived from black pepper. In order to investigate the significance of the drying temperature on quality and oil yield of black pepper, analysis of variance (ANOVA) was conducted at 95% confidence level.

### 3.1.7 Summary of experimental conditions

Drying conditions used in major experiments were summarized in Table 3.5.

Table 3.7 : The conditions used in drying experiments with conventional spouted bed

| **Objective of Experiments*** | **Air velocity (m/s)** | **Stagnant bed height (cm)** | **Temperature ($^{\circ}$C)** |
|---|---|---|---|
| Determination of minimum spouting velocity | | 7, 14, 18, 22 | ambient temperature |
| Effect of drying temperature- extraction of essential oil | 2.37 | 14 | 45, 55, 65, 75, sun drying |
| analyzing diffusivity | 2.37 | 14 | 45, 55, 65, 75 |
| Effect of bed height | 2.37 | 7, 14, 20 | 65 |
| Effect of air velocity | 1.60, 1.97, 2.37 | 14 | 65 |
| Drying kinetics | 1.60, 1.97, 2.37 | 7, 14, 18, 20 | 45, 55, 65, 75 |
| Thin layer modeling | 2.37 | 14, 18, 20, 22 | 45, 55, 65, 75 |
| Heat and mass transfer analysis | 1.6-2.37 | 7-22 | 35-75 |

*Material: Raw black pepper ; Configuration: conventional spouted bed; Initial moisture content: 350 d.b%

## 3.2 Model for heat transfer

### 3.2.1 Determination of heat transfer coefficient

The model used to define heat transfer coefficient is derived by applying energy balance to the spouted bed dryer. The main assumptions adopted in the model are as followings.

- Black pepper particles are assumed to be spherical, isotropic (uniformity in all orientations) and identical.
- Physical properties of the dry matter remain constant with time.
- Particles are well mixed in the spouted bed and each particle remove same amount of moisture with time and receive same heat flux from hot gas with time.
- Dryer is well insulated.
- Heat is flown from hot gas to particles only. Conduction of heat and moisture from particle to particle is negligible.
- Air that leaves the dryer is not in thermal equilibrium with the solid particles.
- Particle shrinkage is negligible.
- There is no accumulation of air inside the bed.
- Latent heat of moisture is assumed as constant throughout the process.

Drying rate at time t, N(t) of spouted bed dryer is expressed as kg of moisture evaporated per unit area of bed cross section per unit time.

$$N(t) = \frac{W_b\left(-\frac{dX}{dt}\right)}{S_B} \qquad (3.1)$$

where

$N(t)$ - Drying rate at time t (kg of moisture evaporated /$m^2$s)

$W_b$ - mass of dry solid (kg)

$S_B$ - cross section of the bed measured at right angles to the direction of air flow ($m^2$)

The general energy balance can be written as Equation 3.2 for either closed or open system between two instant of time since energy cannot be destroyed or generated [103].

*Energy accumulation =energy input streams - energy output streams* (3.2)

*Energy accumulation = final energy of system- initial energy of system* (3.3)

Spouted bed drying process described in this work is a semi batch process where drying material does not cross the boundary but hot gas stream enters into the dryer and exits continuously. Figure 3.10 shows typical schematic diagram for unsteady state spouted bed drying process.

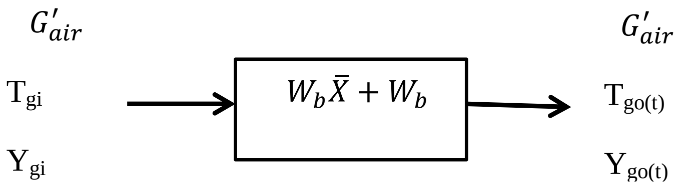



Figure 3. 10: Schematic diagram for unsteady state spouted bed drying process

Where

$G'_{air}$- dry air flow rate (kg of dry air/s)

$T_{gi}$- inlet gas temperature (°C)

$T_{go}(t)$ – outlet gas temperature at time t (°C)

$W_b$- mass of dry solid (kg)

$\bar{X}$- mean moisture content of the solid over the drying period (kg moisture/ kg dry solid)

$Y_{gi}$ -humidity of air at the inlet of dryer (kg of moisture/ kg of dry air)

$Y_{go(t)}$ -humidity of air at the outlet of the dryer at time t (kg of moisture/ kg dry air)

When considering right hand side of the Equation 3.2 for unsteady state spouted bed dryer, only the hot gas stream crosses the boundaries. Therefore right hand side (RHS) may be written using the net energy given by hot air and the energy transferred out by the system during moisture evaporation.

Energy balance was applied as follows to obtain an expression for heat transfer coefficients with combination of Equation 3.2 and Equation 3.3.

$$\left(W_b C_{ps} + W_b \bar{X} C_{pw}\right)\frac{dT_{b(t)}}{dt} = \eta G'_{air} c_{pav}\left(T_{gi} - T_{go(t)}\right) - W_b \lambda \left(-\frac{dX(t)}{dt}\right) \quad (3.4)$$

$\left(W_b C_{ps} + W_b \bar{X} C_{pw}\right)\frac{dT_{b(t)}}{dt}$ expresses the thermal energy required to raise the temperature of bed. $W_b \lambda \left(-\frac{dX(t)}{dt}\right)$ expresses the thermal energy required to vaporise the moisture from bed of particle. $\eta G'_{air} c_{pav}\left(T_{gi} - T_{go(t)}\right)$ expresses the thermal energy given for the drying process by hot air stream.

$$\left(W_b C_{psw}\right)\frac{dT_{b(t)}}{dt} + W_b \lambda \left(-\frac{dX(t)}{dt}\right) = \eta G'_{air} c_{pav}\left(T_{gi} - T_{go(t)}\right) \quad (3.5)$$

$$C_{pav} = C_{pa} + \bar{Y} C_{pv} \quad (3.6)$$

$$C_{psw} = C_{ps} + \bar{X} C_{pw} \quad (3.7)$$

Where

$C_{pa}$- specific heat of dry air (J/kg°C)

$C_{pav}$- heat capacity of 1kg of dry air and associated water vapour (J/kg°C)

$C_{ps}$ - Specific heat of dry solid, (J/kg°C)

$C_{psw}$- Specific heat of wet solid, (J/kg of dry solid °C)

$C_{pv}$ -specific heat of vapour, (J/kg °C)

$C_{pw}$ -specific heat of water in solid, (J/kg °C)

$\bar{Y}$- mean air humidity, (kg moisture/ kg dry air)

H - Particle to air heat transfer efficiency

$T_{b(t)}$ - mean temperature of the bed (°C)

X - moisture content of solid( dry basis) (kg of moisture/ kg of dry solid)

λ- Latent heat of water (J/kg )

If the thermal equilibrium between exit gas and bed solid is not achieved, it is convenient to use a gas to particle heat transfer coefficient [13]. Then heat transferred by hot gas is shown in Equation 3.8.
η =1; since no heat losses

$$G'_{air} c_{pav} \left(T_{gi} - T_{go(t)}\right) = h_p S_p \Delta T_{Lm} \qquad (3.8)$$

Heat transfer area $S_p$ is the surface area of the particles and $\Delta T_{Lm}$ is the logarithmic mean temperature difference defined in Eq. (3.9).

$$\Delta T_{Lm} = \frac{\left(T_{gi} - T_{b(t)}\right) - \left(T_{go(t)} - T_{b(t)}\right)}{\ln \frac{\left(T_{gi} - T_{b(t)}\right)}{\left(T_{go(t)} - T_{b(t)}\right)}} \qquad (3.9)$$

$$\left(W_b C_{psw}\right) \frac{dT_{b(t)}}{dt} + W_b \lambda \left(-\frac{dX(t)}{dt}\right) = h_p S_p \Delta T_{Lm} \qquad (3.10)$$

Where

$h_p$ - overall heat transfer coefficient ($W/m^2K$)

$S_p$ - interfacial surface area of particles where heat transfer ($m^2$)

Sensible heat gain is neglected as $\left(W_b C_{psw}\right) \frac{dT_{b(t)}}{dt} \ll W_b \lambda \left(-\frac{dX(t)}{dt}\right)$ (3.11)

$$W_b \lambda \left(-\frac{dX(t)}{dt}\right) = h_p S_p \Delta T_{Lm} \qquad (3.12)$$

$$h_p = \frac{-W_b \lambda \int_{X_1}^{X_2} dX}{S_p \int_{t=0}^{t=t} \Delta T_{Lm} \, dt} \qquad (3.13)$$

Heat transfer coefficient ($h_p$) were obtained by solving Equation 3.13 using graphical method for particular time period. Observed data of logarithmic mean temperature difference of the bed ($\Delta T_{Lm}$) vs time should be plotted and the area under the curve gave the value of the integral in the denominator of Equation 3.13. Nevertheless area under the curve of logarithmic mean temperature difference ($\Delta T_{Lm}$) vs time evaluated directly using the MATLAB codes.

### 3.2.2 Dimensional analysis of heat transfer process

Prior to dimensional analysis of the heat transfer process, fundamental dimensions should be identified. Fundamental dimensions which is used to express momentum transfer are length, time and mass. They are symbolized as L, t and M respectively. Dimensional analysis of energy problems requires two more fundamental dimensions, namely heat and temperature and symbolized as Q and T [104].

Considering the heat transfer process in drying of black pepper in spouted bed dryer, the important variables, their symbols and dimensions are listed in Table 3.6

Table 3.8: Important variables for heat transfer of black pepper in the spouted bed dryer

| | **Variable** | **Symbol** | **Dimensions** |
|---|---|---|---|
| 1 | Air velocity | U | $Lt^{-1}$ |
| 2 | Static bed height | H | L |
| 3 | Particle diameter | $d_p$ | L |
| 4 | Gas viscosity | $\mu_g$ | $ML^{-1}t^{-1}$ |
| 5 | Air thermal conductivity | $k_g$ | $QL^{-1}t^{-1}T^{-1}$ |
| 6 | Air inlet temperature | $T_{gi}$ | T |
| 7 | Temperature difference of gas inlet and gas inlet wet bulb temperature | $T_{gi}$-$T_{gi,w}$ | T |
| 8 | air density | ρ | $ML^{-3}$ |
| 9 | Heat transfer coefficient-fluid to particle | $h_p$ | $QL^{-2}t^{-1}T^{-1}$ |

Where

L, M, Q, T, t - Dimensions of length, mass, heat, temperature and time respectively

Then dimensional matrix for heat transfer processes is formed by tabulating exponents of the fundamental dimensions. Dimensional analysis was carried out according to Buckingham pi theorem and important dimensionless numbers were identified [104]. A Possible correlation was developed using IBM SPSS Statistics 20 by non-linear multiple regression. Results are presented and described in Chapter 7**.**

## 3.3 Drying model development

Experiments related to accomplish the objective of developing a suitable model to describe drying behaviour is described in section 3.1.6.4. Gathered data of moisture content vs time of the black pepper during the drying process were used to model the drying behavior of wetted and raw black pepper.

### 3.3.1 Mathematical modeling

Moisture content was normalized to dimensionless parameter; moisture ratio (MR).

Moisture ratio is calculated as follows:

$$MR = (X_i - X_e)/(X_o - X_e) \qquad (3.14)$$

$X_e$, $X_i$ and $X_o$ are equilibrium moisture content, i$^{th}$ experimental moisture content and initial moisture content respectively.

Moisture ratio vs time were used for model development. They were fitted to five thin layer drying models namely Newton model, Page model, Henderson and Pabis model, Two compartment model and Logarithmic model which were recalled in Table 3.7. These models are the basic models among large number of thin layer models and they are widely used by many researchers.

Table 3.9: Selected thin layer drying models used for analysis

| **Model name** | **Model** | **Equation no** |
|---|---|---|
| Newton | $MR = \frac{X_t - X_e}{X_0 - X_e} = e^{-kt}$ | 2. 34 |
| Page | $MR = \frac{X_t - X_e}{X_0 - X_e} = e^{-kt^n}$ | 2. 35 |
| Henderson and Pabis | $MR = \frac{X_t - X_e}{X_0 - X_e} = ae^{-kt}$ | 2. 36 |
| Logarithmic | $MR = \frac{X_t - X_e}{X_0 - X_e} = ae^{-kt} + b$ | 2. 37 |
| Two compartment | $MR = \frac{X_t - X_e}{X_0 - X_e} = ae^{-k_1 t} + be^{-k_2 t}$ | 2. 38 |

a, b, k, $k_1$, $k_2$ and n are drying coefficients and constants

The moisture ratio is simplified to $X_t/X_0$ neglecting $X_e$ term since $X_e$ term, is relatively small compared to $X_t$ and $X_0$ and the continuous fluctuation of the relative humidity of drying air leading to change of equilibrium moisture content of the particle being dried [19, 76]. The software Matlab 2011 was used to facilitate the model fitting.

The performance of these models were compared using three statistical parameters coefficient of determination ($R^2$), Root mean square error (RMSE) and sum of square error (SSE). The statistical values were evaluated using Equation 3.20 to Equation 3.22 [75].

$$\mathrm{SSE} = \sum_{i=1}^{n} \left(\mathrm{MR}_{pre,i} - \mathrm{MR}_{exp,i}\right)^2 \qquad (3.15)$$

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} \left(\mathrm{MR}_{pre,i} - \mathrm{MR}_{exp,i}\right)^2}{N}} \qquad (3.16)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n} \left(MR_{pre,i} - MR_{exp,i}\right)^2}{\sum_{i=1}^{n} (\mathrm{MR}_{exp,i} - \mathrm{MR}_{exp_{mean}})^2} \qquad (3.17)$$

Where

$MR_{exp,I}$ - $i^{th}$ experimental moisture ratio

$MR_{exp,mean}$ - mean of experimental moisture ratios

$MR_{pre,I}$ - $i^{th}$ predicted moisture ratio

N - Number of observation

According to the statistical analysis, best thin layer model which can describe the drying behaviour of black pepper in spouted bed dryer was selected. Since developed models can be used only for specified drying conditions, four models were developed to describe the drying behaviour of raw black pepper in conventional spouted bed. Drying constants and coefficients of best selected model were correlated to bed height at specified drying temperatures using the regression analysis.

**Chapter specific nomenclature**

a, b, k, $k_1$, $k_2$, n - drying coefficients and constants

$C_{pa}$ - specific heat of dry air (J/kg°C)

$C_{pav}$- heat capacity of 1kg of dry air and associated water vapour (J/kg°C)

$C_{ps}$ - specific heat of dry solid, (J/kg°C)

$C_{psw}$ - Specific heat of wet solid, (J/kg of dry solid °C)

$C_{pv}$ - specific heat of vapour, (J/kg °C)

$C_{pw}$ - specific heat of water in solid, (J/kg °C)

$D_c$ - diameter of the column (m)

$D_i$- gas inlet diameter (m)

$D_o$ - cone base diameter (m)

$d_p$ - particle diameter (m)

$D_T$ -diameter of draft tube (m)

$G'_{air}$- dry air flow rate (kg of dry air/s)

H, $H_o$- static bed height (m)

$H_l$ - height of cylindrical column (m)

$h_p$ - overall heat transfer coefficient fluid to particle (W/$m^2$K)

$H_T$ - tube height (m)

$k_g$ -Air thermal conductivity (J/msK)

L, M, Q, T, t - Dimensions of length, mass, heat, temperature and time respectively

$L_H$ -entrainment height (m)

$L_T$ - total height of the draft tube

$MR_{exp,i}$- i[th] experimental moisture ratio
$MR_{exp,mean}$ - mean of experimental moisture ratios
$MR_{pre,I}$ - i[th] predicted moisture ratio
N- number of observation

N(t)-Drying rate at time t (kg of moisture evaporated /$m^2$s)

$S_B$ - cross section of the bed measured at right angles to the direction of air flow ($m^2$)

$S_p$ - interfacial surface area of particles where heat transfer ($m^2$)

$T_{b(t)}$ - mean temperature of the bed (°C)

$T_{gi}$, $T_d$- drying air temperature or inlet gas temperature (°C)

$T_{gi,w}$- gas inlet wet bulb temperature (°C)

$T_{go}$(t) - outlet gas temperature at time t (°C)

U - Superficial air velocity (m/s)

$W_b$ - mass of dry solid (kg)

$W_d$ -weight of sample after drying in the oven (kg)

$W_w$ - initial weight of the sample (kg)

X- moisture content of solid( dry basis) (kg of moisture/ kg of dry solid)

$X_{e,}$ -equilibrium moisture content

X -moisture content dry basis (%)

$X_o$ -initial moisture content

$X_t$ -moisture content at time t

$\bar{X}$ - mean moisture content of the solid over the drying period (kg moisture/ kg dry solid)

$Y_{gi}$ - humidity of air at the inlet of dryer (kg of moisture/ kg of dry air)

$Y_{go(t)}$ - humidity of air at the outlet of the dryer at time t (kg of moisture/ kg dry air)

$\bar{Y}$ - Mean air humidity, (kg moisture/ kg dry air)

$\mu_g$ - Viscosity of air (kg/ms)

$\Delta T_{Lm}$ - Logarithmic mean temperature difference

$\eta$ - Particle to air heat transfer efficiency

$\lambda$ - Latent heat of water (J/kg )

$\rho$ - density of fluid/air ($kg/m^3$)

**Abbreviations**

ANOVA - Analysis of variance

$R^2$ - Coefficient of determination

RMSE - Root mean square error

SSE - Sum of square error

VSD - variable speed drive

**Chapter 4**

# 4. RESULTS AND DISCUSSION ON PRELIMINARY EXPERIMENTS

This chapter describes the outcome of preliminary experiments conducted with wetted black pepper. Preliminary experiments were conducted using three configurations of spouted bed dryer namely, conventional spouted bed (CSB), and spouted bed equipped with non-porous draft tube (SBNPDT) and spouted bed equipped with porous draft tube (SBPDT). Minimum spouting velocity, drying kinetics and diffusivity of wetted black pepper drying in three configurations are analysed and presented. Furthermore, results of mathematical modelling of wetted black pepper drying in above-mentioned three configurations are presented and discussed.

## 4.1 Minimum spouting velocity

Prior to conducting the drying experiments, minimum spouting velocities of wetted black pepper for two bed loadings in three configurations of spouted bed were determined. Plots of pressure drop versus air velocity were used to determine minimum spouting velocity. As indicated in Table 4.1, spouted bed equipped with non-porous draft tube (SBNPDT) has the lowest minimum spouting velocity followed by the spouted bed equipped with porous draft tube (SBPDT) for a particular bed height.

In the spouted bed equipped with non-porous draft tube, air stream is not percolated in to the annulus region from the spout region as in other two configurations. Therefore, energy required to disrupt the packing is achieved by low airflow rate compare to other two configurations. Conventional spouted bed has the highest minimum spouting velocity. In all cases, minimum spouting velocity increases with increasing stagnant bed heights due to increase of energy required to disrupt the packing. Altzibar et al. also stated that the conical spouted bed equipped with non-porous draft tube had low minimum spouting air velocity compared to the conical spouted bed without draft tube. In addition, minimum spouting velocity was approximately proportional to the stagnant bed of cylindrical spouted beds [46]. More information on determination of minimum spouting velocity from plot of pressure drop versus air velocity is given in section 5.1 for experiments conducted with raw black pepper.

Table 4.1: Minimum spouting velocity

| **Configuration** | **Stagnant bed height; H (m)** | **Minimum spouting velocity; $U_{ms}$ (m/s)** |
|---|---|---|
| CSB | 0.16 | 0.74 |
| | 0.10 | 0.50 |
| SBPDT[b] | 0.16 | 0.58 |
| | 0.10 | 0.44 |
| SBNPDT[b] | 0.16 | 0.51 |
| | 0.10 | 0.43 |
| [b] $D_T$= 0.035m, $L_H$ = 0.06 m, $L_T$= 0.26 m | | |

## 4.2 Effect of draft tube configurations on drying

Drying experiments were conducted to identify the effect of draft tube configuration on drying. Spouted bed equipped with different dimensions of non-porous and porous draft tubes were used. Geometrical parameters of draft tubes such as diameter ($D_T$), entrainment height ($L_H$) and tube height ($H_T$) were changed. Drying experiments were conducted until black pepper attained 15% dry basis moisture content from their initial moisture content of 70-80 %. Drying time is defined as the time taken to dry black pepper from initial moisture content to 15 % moisture content.

Use of higher air flow rate is unproductive for spouted bed setting and considering the cost and energy involved, many researches have been conducted at minimum spouting conditions to ensure the regular movement of particles in the three hydrodynamic regions of the bed; spout, annulus and fountain [31]. Therefore, all the drying experiments were conducted using airflow rates just above the minimum spouting conditions. Results of experiments conducted to analyze the effect air velocity on drying kinetics will be presented on section 4.3.

### 4.2.1 Effect of diameter of draft tube

Seven non-porous draft tubes and nine porous draft tubes with different dimensions were used for the analysis. Dimensions of those draft tubes are presented in Table 3.2 and Table 3.3 in Chapter 3.

Three porous draft tubes with diameter of 0.05 m, 0.06 m and 0.07 m and non-porous draft tubes of diameter 0.029 m, 0.035 m and 0.048 m were used. The draft tube diameter is usually chosen to be similar or larger than the diameter of gas inlet nozzle to achieve stable spouting [37]. Therefore gas inlet diameter of spouted bed equipped with non-porous draft tube was set as 0.029 m and a porous draft tube was set as 0.05 m for this study.

Effect of diameter of draft tube on drying kinetics of black pepper was analysed and drying kinetics data are shown in Figure 4.1 to Figure 4.4. When draft tube diameter is increased keeping other parameters (entrainment height and tube height) constant, drying time was decreased and rate of moisture removal was increased. The amount of pepper particles that can enter into the spout region is higher in larger diameter draft tubes than those of smaller diameter draft tubes, and hence intensive heating takes place inside the spout. Therefore drying time decreases.

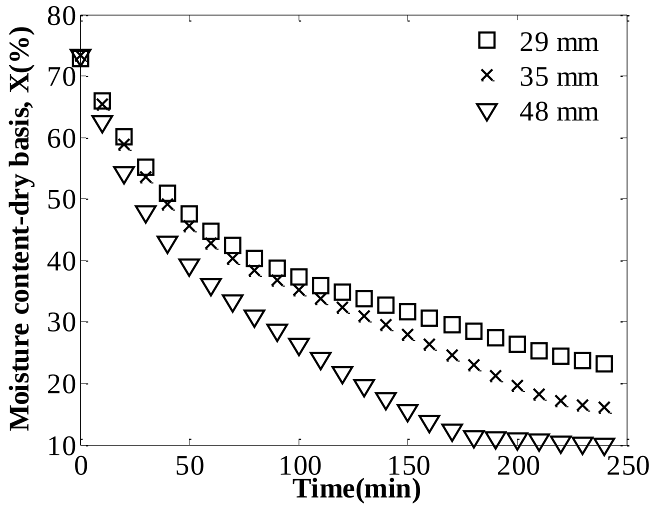



Figure 4.1: Effect of diameter of non-porous draft tube on drying of wetted black pepper under minimum spouting conditions in SBNPDT;
$T_d$ = 55 °C, $H_o$=0.16 m, Di = 0.029 m, $L_H$ = 0.03 m, $H_T$= 0.16 m

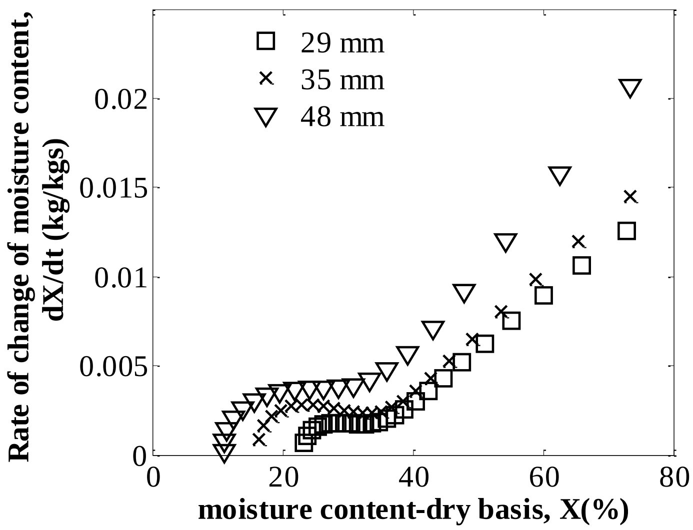



Figure 4.2: Rate of change of moisture content vs. moisture content;
of diameter of non- porous draft tube on drying of wetted black pepper under minimum spouting conditions in SBNPDT. $T_d$ = 55 °C, H =0.16 m, $D_i$=0.029 m, $L_H$ = 0.03 m, $H_T$= 0.16 m

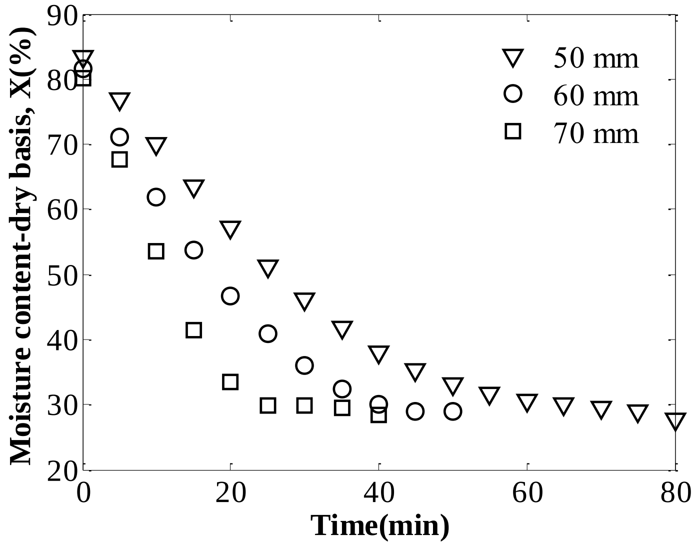



Figure 4.3: Effect of diameter of porous draft tube on drying of wetted black pepper under minimum spouting conditions in SBPDT; $T_d$ = 55 °C, H =0.16 m, $D_i$ =0.05 m, , $L_H$ = 0.03 m, $H_T$= 0.16 m

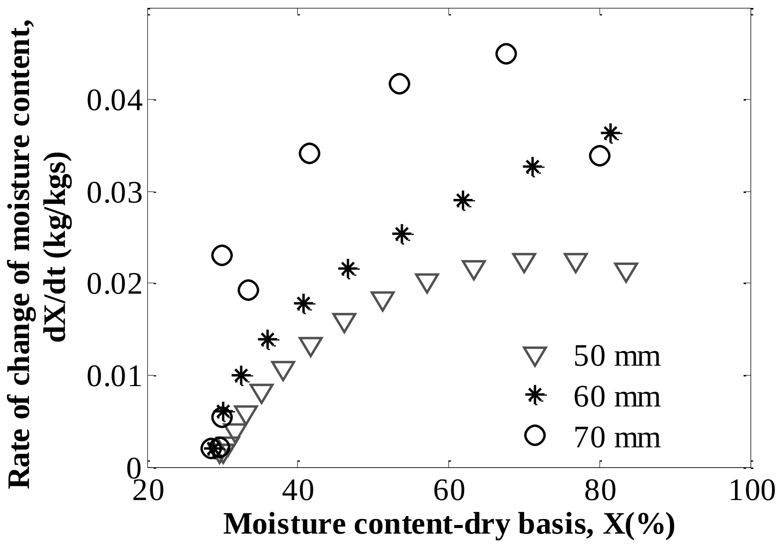



Figure 4.4: Rate of change of moisture content vs. moisture content;
Effect of diameter of porous draft tube on drying of wetted black pepper under minimum spouting conditions in SBPDT; $T_d$ = 55 °C, H =0.16 m, $D_i$ =0.05 m, $L_H$=0.03 m, $H_T$= 0.16 m

### 4.2.2 Effect of entrainment height of draft tube

Three non-porous draft tubes and three porous draft tubes of same diameter and tube height having different values entrainment heights were used to analyse the effect of entrainment height on drying kinetics of black pepper. Figure 4.5 to Figure 4.8 illustrate the drying curves for different entrainment heights of both draft tubes. Increase in entrainment height significantly affected in the moisture removal rate in both systems. For spouted bed equipped with non-porous draft tube, lowest drying time of 110 min was recorded for the black pepper dried at 0.08 m entrainment height at the combination of 75 °C drying air temperature and 0.16 m of non-porous draft tube height. However, for the same geometric configurations when the entrainment height was 0.06 m and 0.03m drying time were greater than 150 min.

The reason for the highest drying rate in the case of 0.08 m entrainment height is due to the fact that when the entrainment height is larger, more number of particles can enter through the draft tube to spout region and hence the spout region in which most of the heat and mass (moisture) transfer occurs [105].

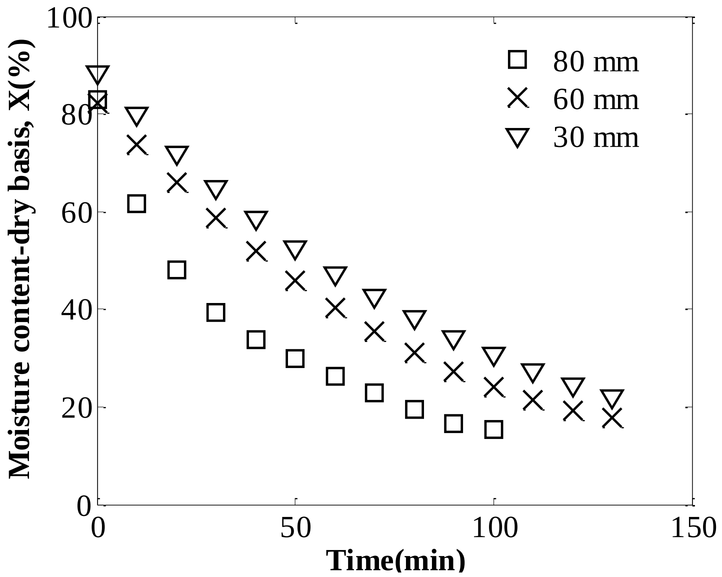



Figure 4.5: Effect of entrainment height of non- porous draft tube on drying of wetted black pepper under minimum spouting conditions in SBNPDT; $T_d$ = 75 °C, H =0.16 m, $D_i$ =0.035 m, $H_T$= 0.16 m, $D_T$= 0.035 m

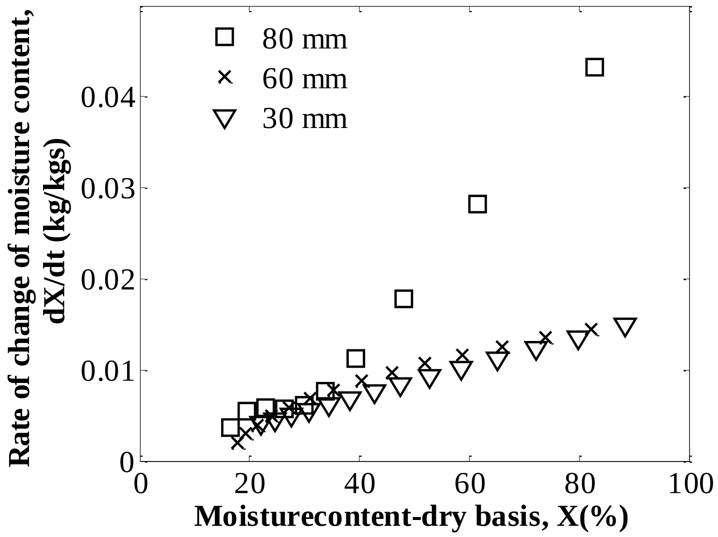



Figure 4.6: Rate of change of moisture content vs. moisture content.
Effect of entrainment height of non- porous draft tube on drying of wetted black pepper under minimum spouting conditions in SBNPDT; $T_d$ = 75°C, H =0.16 m, $D_i$ =0.035 m, $H_T$= 0.16 m, $D_T$= 0.035 m

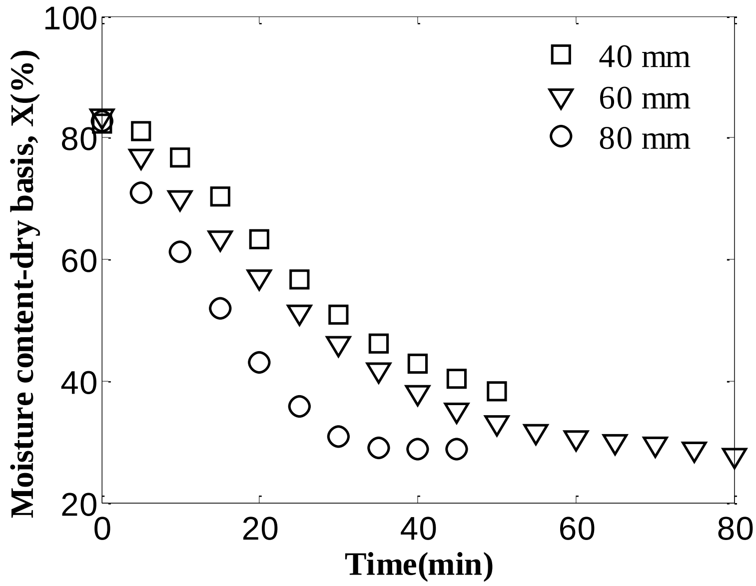



Figure 4.7: Effect of entrainment height of porous draft tube on drying of black pepper under minimum spouting conditions in SBPDT; $T_d$ = 75 °C, H =0.16 m, $D_i$ =0.05m, $H_T$= 0.16 m, $D_T$= 0.035m

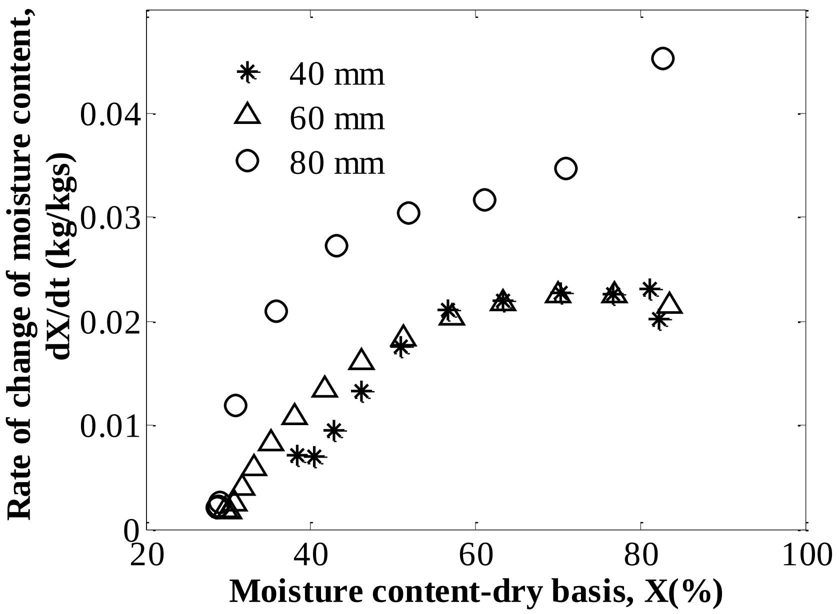



Figure 4.8: Rate of change of moisture content vs. moisture content.
Effect of entrainment height of porous draft tube on drying of wetted black pepper under minimum spouting conditions in SBPDT;
$T_d$=75 °C, H=0.16 m, $D_i$ =0.05 m, $H_T$= 0.16 m, $D_T$= 0.035 m

### 4.2.3 Effect of height of draft tube

Effect of height of draft tubes on drying kinetics is shown in Figure 4.9 to Figure 4.12. A drying time of 150 min was noticed when the draft tube height was kept 0.16 m, and whereas it was 100 min at a draft tube height of 0.24 m at 75 °C air temperature and entrainment height of 0.06 m at the minimum spouting conditions for non- porous draft tube fitted spouted bed. The drying rate was also increased with increasing draft tube height under investigation. In case of 0.24 m height draft tube, the rate of moisture removal was faster than those of other two due to longer exposure of particles to the heated air in the spout region [106]. Similar effect is also shown for porous draft tube fitted spouted bed. The drying rate was also increased with increasing porous draft tube height.

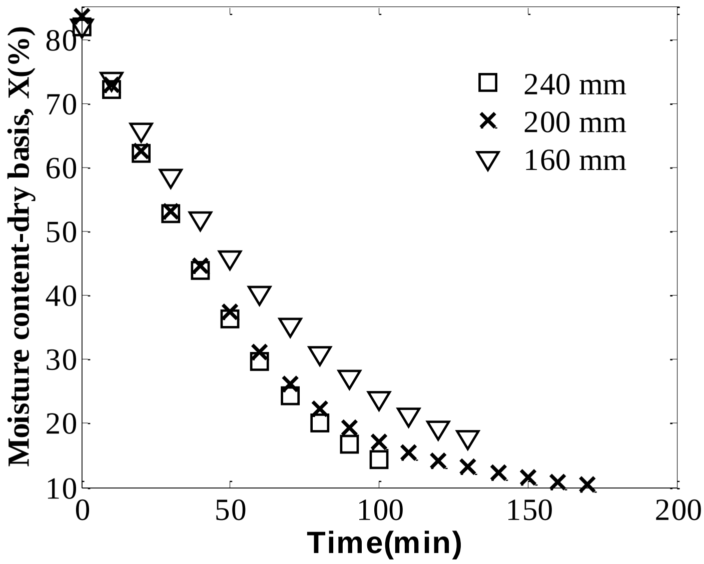



Figure 4.9: Effect of tube height of non- porous draft tube o drying of wetted black pepper under minimum spouting conditions in SBNPDT;
$T_d$ = 75 ˚C, H =0.16 m, $D_i$ =0.035 m, $L_H$= 0.06 m, $D_T$= 0.035 m

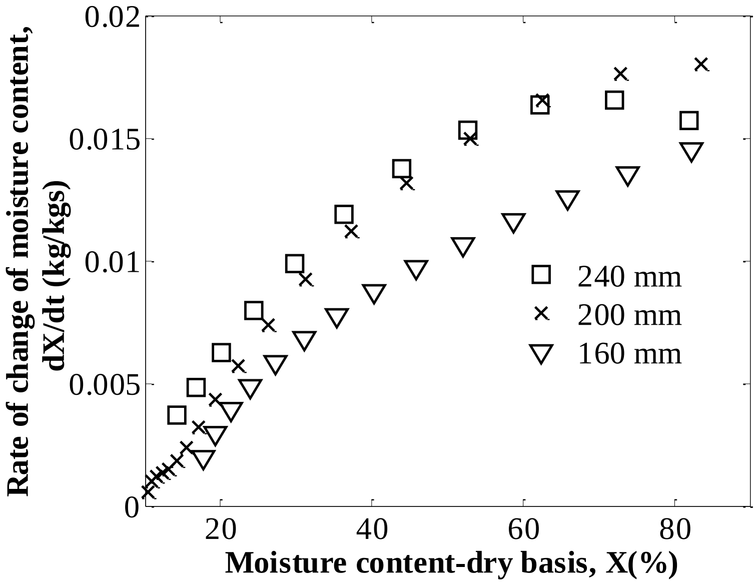



Figure 4.10: Rate of change of moisture content vs. moisture content
Effect of tube height of non- porous draft tube on drying of wetted black pepper under minimum spouting conditions in SBNPDT; $T_d$ = 75 ˚C, H =0.16 m, $D_i$ =0.035 m, $L_H$= 0.06 m, $D_T$= 0.035 m

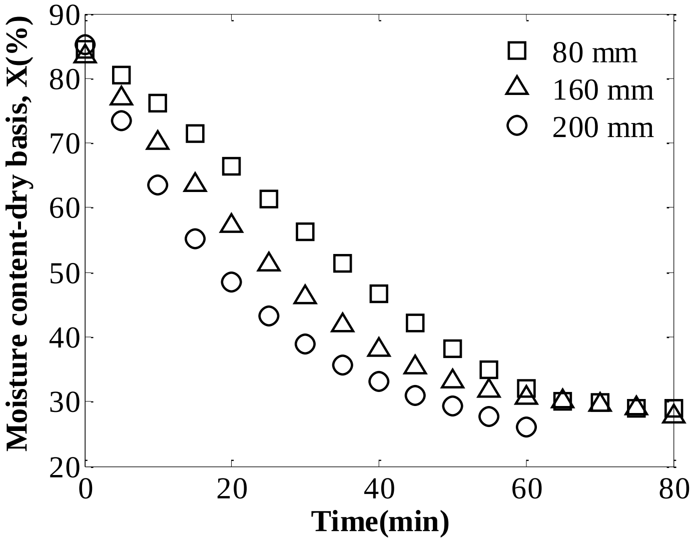



Figure 4.11: Effect of tube height of porous draft tube on drying of black pepper under minimum spouting conditions in; $T_d$= 75 ˚C, H =0.16 m, $D_i$ =0.05 m, $L_H$= 0.06 m, $D_T$= 0.035 m

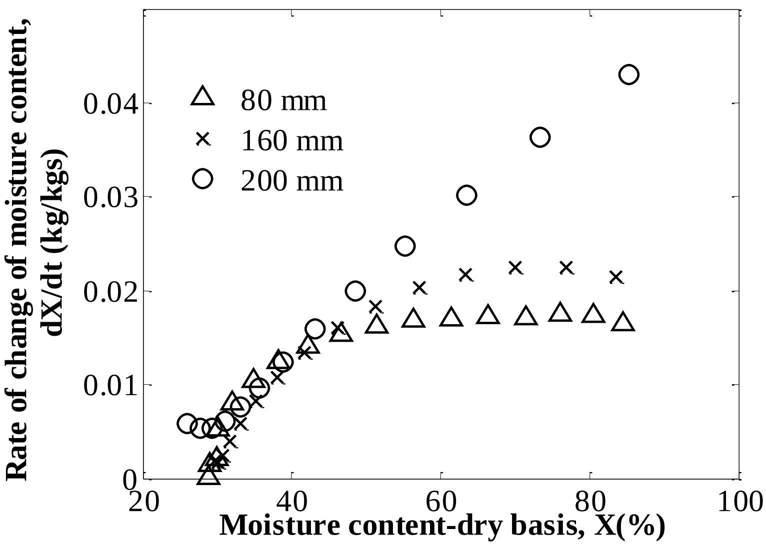



Figure 4.12: Rate of change of moisture content vs moisture content
Effect of tube height of non- porous draft tube on drying of wetted black pepper under minimum spouting conditions in SBPDT; $T_d$ = 75 ˚C, H =0.16 m, $D_i$ =0.05 m, $L_H$= 0.06 m, $D_T$= 0.035 m

As a summary, analysis of Figure 4.1 to Figure 4.12 shows that the drying rate of black pepper is influenced by the geometric factors of both type of draft tubes such as diameter, entrainment height and height of the draft tube.

## 4.3 Effect of air velocity on drying kinetics for spouted bed configurations

Effect of air velocity on drying kinetics of wetted black pepper in three spouted bed configurations was analysed. Experiments were conducted at two velocities namely, minimum spouting velocity ($U_{ms}$) of each configuration and 0.89 m/s ($v_1$) at 75 °C drying air temperature for 16 cm of static bed height. Latter is quite higher velocity where particles will not transport pneumatically away from the drying chamber. Drying time of respective experiments, percentage of increase in air velocity and percentage of time reduction due to use of higher air flow rate are shown in Table 4.2. Percentage of time reduction and percentage of increase in air velocity were calculated using Equation 4.1 and 4.2.

$$\% \text{ of time reduction} = \frac{t_{U_{ms}} - t_{v_1}}{t_{U_{ms}}} \times 100 \qquad (4.1)$$

$$\% \text{ of increase in air velcity} = \frac{v_1 - U_{ms}}{U_{ms}} \times 100 \qquad (4.2)$$

Where

$t_{U_{ms}}$- drying time when air velocity is set to minimum spouting velocity

$t_{v_1}$- drying time when air velocity is set to $v_1$

Table 4.2: Drying time of black pepper at different spouted bed configurations at different air velocities

| Air velocity / Dryer Configuration | Drying time (minutes) | | % of increase in air velocity | % of time reduction |
|---|---|---|---|---|
| | $U_{ms}$ | $v_1$ | | |
| Conventional bed | 54 | 49 | 20.27 | 9.26 |
| Spouted bed with porous draft tube | 100 | 92 | 53.45 | 8.00 |
| Spouted bed with non-porous draft tube | 105 | 100 | 74.51 | 4.76 |

High air velocity decreases the drying time of black pepper as shown in Table 4.2, Figure 4.13 and Figure 4.14 with increasing drying rate. This is due to the fact that at high air velocity or air flow rate, solid circulation rate is high. Therefore particles get more exposure to hot air in spout region than that of particles in spouted bed of low velocity. Circulation rate of particle is the number of cycles where a particle moves through spout, fountain and annulus region per unit time. However, percentage of time reduction is below 10 % for the three configurations. Therefore using high velocity air flow is not a good solution considering the energy and cost involved. Figure 4.13 and Figure 4.14 show the change of moisture ratio and moisture content of black pepper with time respectively while experiments were going on.

### 4.4 Effect of spouted bed configurations on drying kinetics

Effect of configuration of spouted bed on drying kinetics of wetted black pepper were analysed at minimum spouting condition for three different drying temperatures and results are shown in Figure 4.15 and Figure 4. 16. Installation of both types of draft tubes in the spouted bed dryer reduces the minimum spouting velocity of black pepper compared to that of conventional spouted bed dryer as shown in Table 4.1. However, considering the drying process, non-porous draft tube fitted system requires longer drying time and shows low drying rate due to gas by passing through the spout without percolating into the annulus region. All the drying rate curves are characterized by falling rate periods. According to Figure 4. 16, conventional spouted bed experiences the highest drying rate followed by porous drat tube fitted system while non-porous draft tube fitted spouted bed has the lowest drying rate. Solid particles are less exposed to the hot air in the annular region of the spouted bed equipped with draft tubes and hence show lower drying rates compared to the conventional spouted bed dryers [107].

Table 4.3: Drying time of spouted bed configurations at different drying temperatures

| Drying air temperature / Dryer configuration | Drying time (minutes) | | |
|---|---|---|---|
| | 55°C | 65°C | 75°C |
| Conventional bed | 100 | 75 | 54 |
| Spouted bed with porous draft tube | 230 | 160 | 100 |
| Spouted bed with non- porous draft tube | 310 | 170 | 105 |

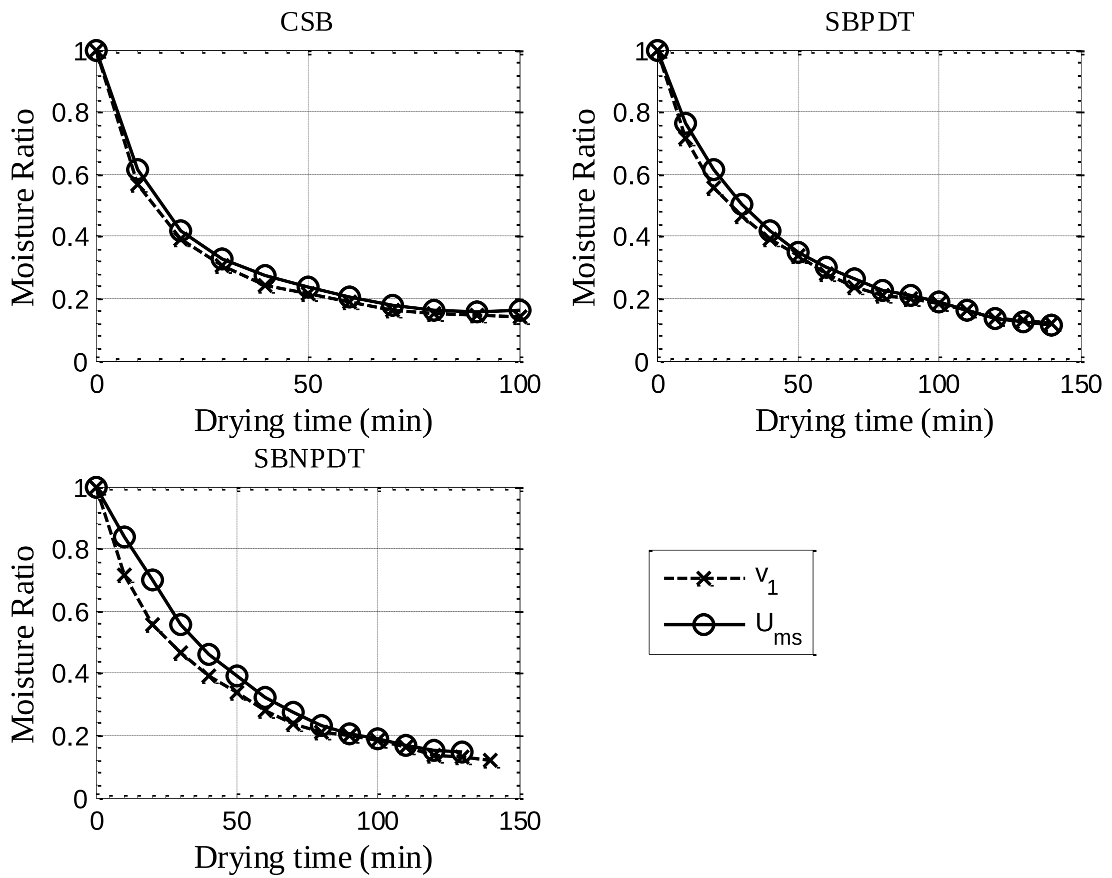



Figure 4.13: Effect of air velocity on drying kinetics of black pepper when dried in CSB, SBPDT and SBNPDT. Experiment conditions: $T_d$ = 75 ˚C, $D_o$ =0.035 m, H = 0.16 m, $D_T$= 0.035 m, $L_H$ = 0.06 m, $L_T$= 0.26 m

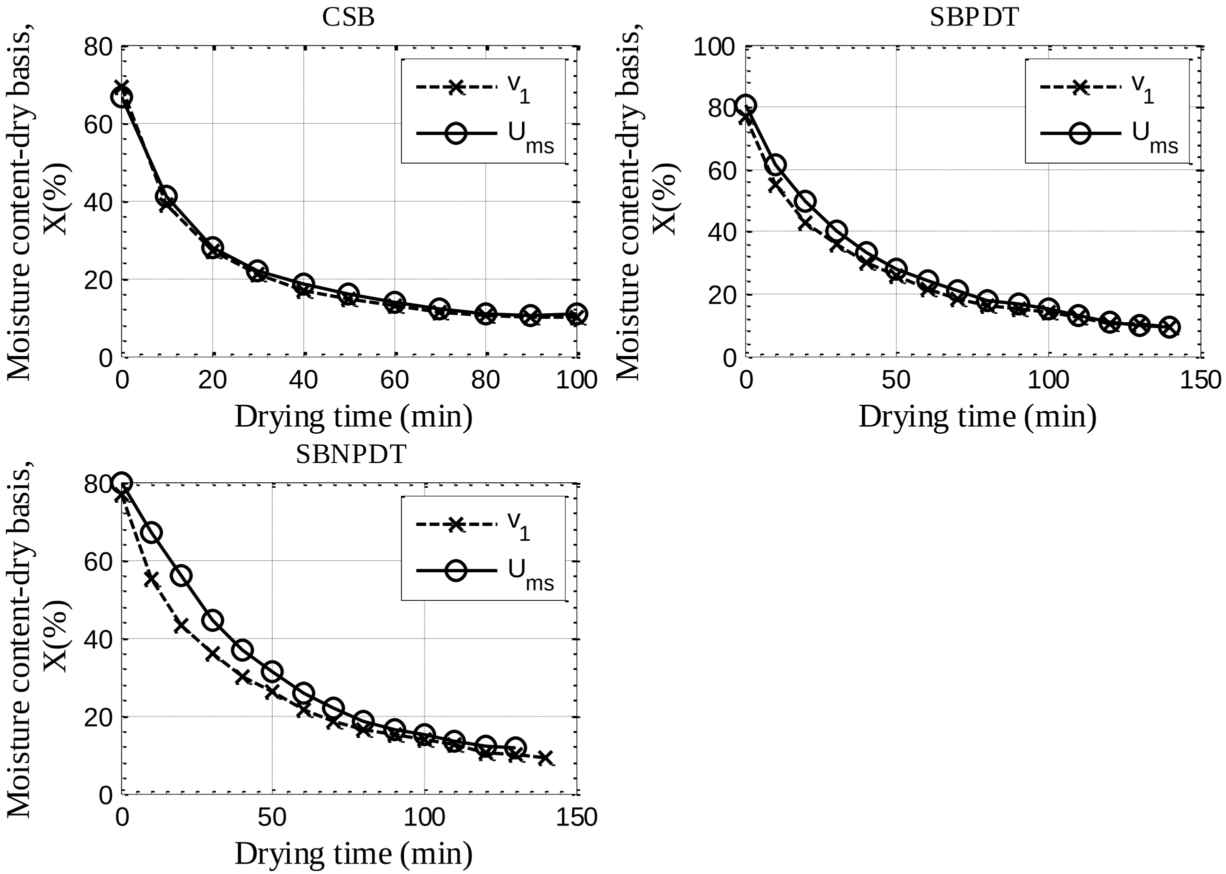



Figure 4.14: Effect of air velocity on drying kinetics of black pepper when dried in CSB, SBPDT and SBNPDT. Experiment conditions: $T_d$ = 75 ˚C, $D_o$ =0.035 m, H = 0.16 m, $D_T$= 0.035 m, $L_H$ = 0.06 m, $L_T$= 0.26 m

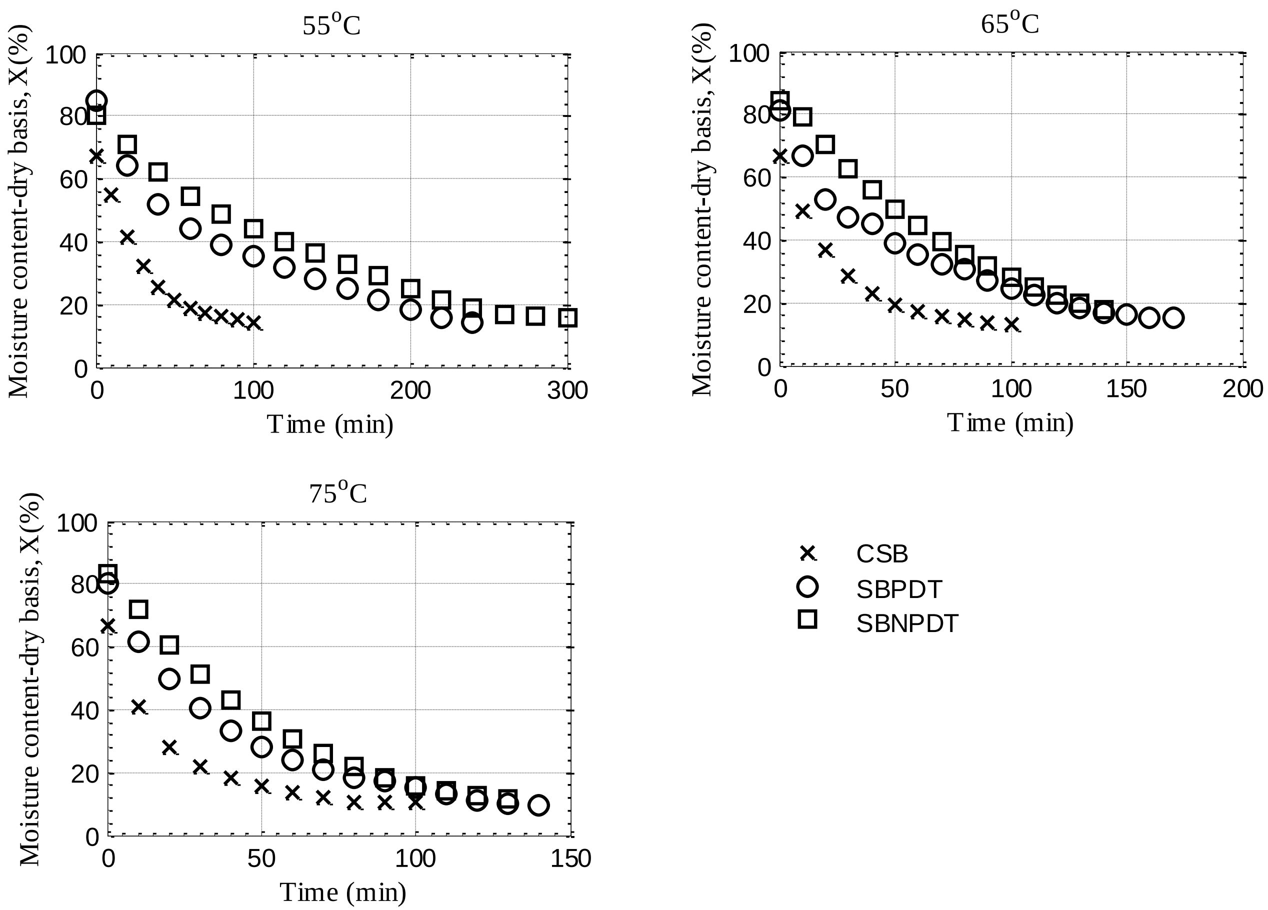



Figure 4.15: Effect of spouted bed configuration on drying kinetics of black pepper when dried in CSB, SBPDT and SBNPDT at minimum spouting conditions. Experiment conditions: $D_o$ =0.035 m, H = 0.16 m, $D_T$= 0.035 m, $L_H$ = 0.06 m, $L_T$= 0.26 m

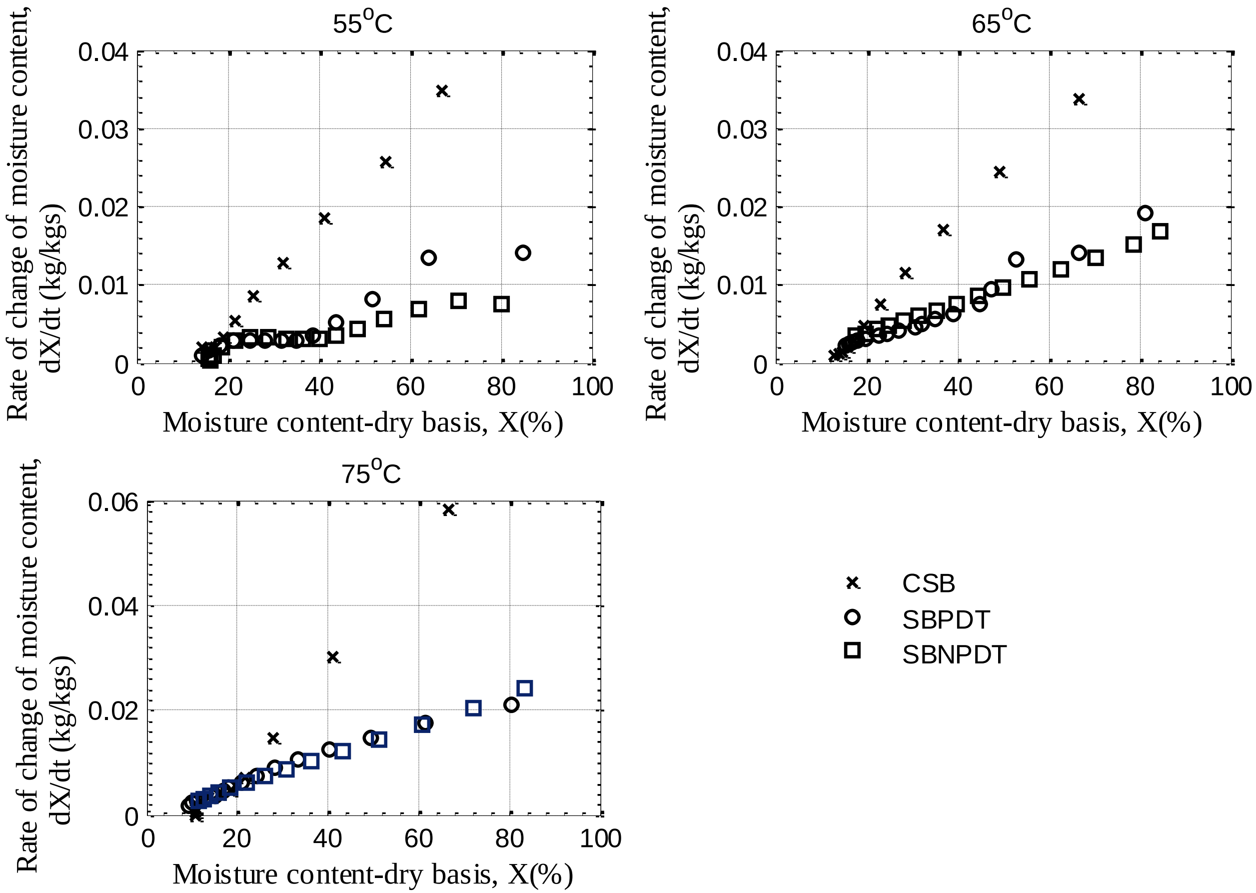



Figure 4. 16: Rate change of moisture content vs. moisture; Effect of spouted bed configuration on drying kinetics of black pepper when dried in CSB,SBPDT and SBNPDT at minimum spouting conditions; Experiment conditions: $D_o$ =0.035 m, H = 0.16 m, $D_T$= 0.035 m, $L_H$ = 0.06 m, $L_T$= 0.26 m

### 4.5 Diffusivity of wetted black pepper for three spouted bed configurations

Initial static bed height of 16 cm wetted black pepper were dried under minimum spouting conditions in three spouted bed configurations as mentioned in Chapter 3. Experiments were conducted at 4 different drying air temperatures: 45 °C, 55 °C, 65 °C, and 75 °C. During experiments, black pepper samples were collected in selected time intervals for determination of moisture content. Natural logarithm of moisture ratio (Ln (MR)) was plotted against time (t) for each drying temperatures as shown in Figure 4.17 to Figure 4.19.

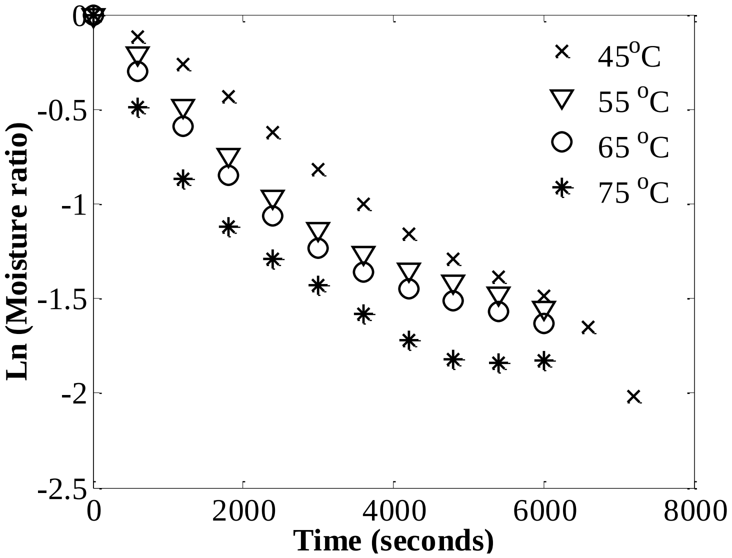



Figure 4.17: Ln (Moisture ratio) vs. drying time of wetted pepper dried in conventional spouted bed dryer Experiment conditions: H =0.16m, $D_i$ =0.035 m

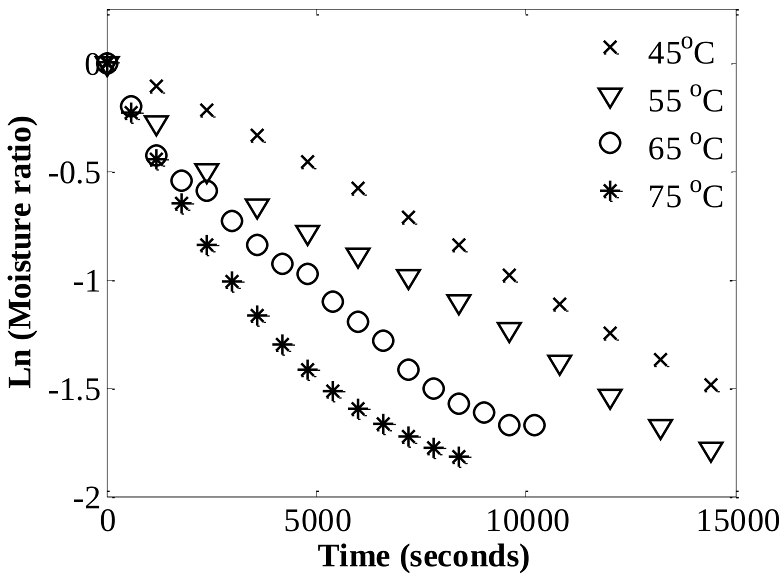



Figure 4.18: Ln (Moisture ratio) vs. drying time of raw pepper dried in porous draft tube fitted spouted bed dryer; Experiment conditions: H =0.16 m, $D_i$ =0.035 m, $L_H$= 0.06 m, $D_T$= 0.035m, $H_T$= 0.02 m

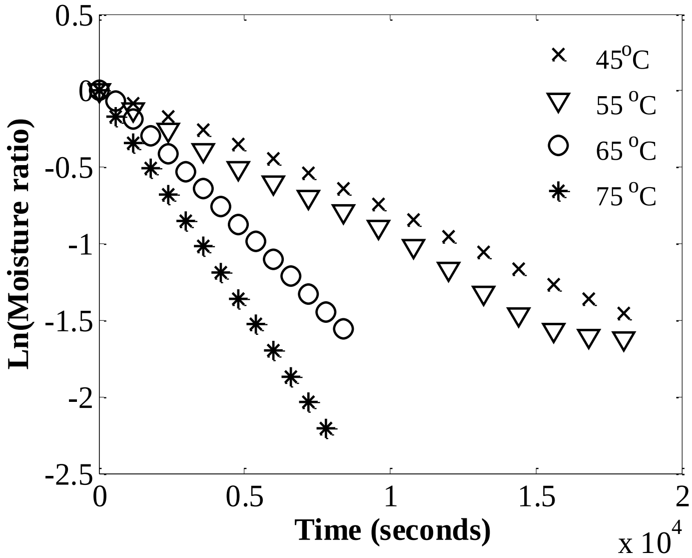



Figure 4.19: Ln (Moisture ratio) vs. drying time of wetted pepper dried in non-porous draft tube fitted spouted bed dryer; Experiment condition: H =0.16 m, $D_i$ =0.035 m, $L_H$= 0.06 m, $D_T$= 0.035 m, $H_T$= 0.02 m

Effective diffusivity ($D_{eff}$) of black pepper at different drying temperatures was calculated using the plot of Ln (MR) vs. time using Equation 2.5 as mentioned in section 2.13. As per Table 4.4 to Table 4. 6, effective diffusivity of black pepper was increased with increasing drying air temperatures. As stated in Chapter 5, drying rate or moisture removal rate is increased with increasing drying air temperatures. This is due to the fact that at high drying temperature, drying air provides high external heat fluxes leading to higher moisture diffusivities and hence higher drying rate [108]. Effective diffusivity values were ranged from $5.64\times 10^{-11}$ to $2.05\times 10^{-10}$ for above-mentioned drying air temperatures in three spouted bed configurations.

Table 4.4: Effective moisture diffusivity of wetted black pepper dried in conventional spouted bed at different temperatures

| **Drying air temperature $T_d$ (°C)** | **Effective diffusivity $D_{eff}$ ($m^2/s$)** |
|---|---|
| 45 | $9.59 \times 10^{-11}$ |
| 55 | $1.30 \times 10^{-10}$ |
| 65 | $1.57 \times 10^{-10}$ |
| 75 | $2.26 \times 10^{-10}$ |

Table 4.5: Effective moisture diffusivity of wetted black pepper dried in porous draft tube fitted spouted bed at different temperatures

| **Drying air temperature $T_d$ (°C)** | **Effective diffusivity $D_{eff}$ ($m^2/s$)** |
|---|---|
| 45 | $6.85 \times 10^{-11}$ |
| 55 | $9.59 \times 10^{-11}$ |
| 65 | $1.37 \times 10^{-10}$ |
| 75 | $1.71 \times 10^{-10}$ |

Table 4. 6: Effective moisture diffusivity of wetted black pepper dried in non-porous draft tube fitted spouted bed at different temperatures

| **Drying air temperature $T_d$ ($^{\circ}C$)** | **Effective diffusivity $D_{eff}$ ($m^2/s$)** |
|---|---|
| 45 | $4.11 \times 10^{-11}$ |
| 55 | $6.30 \times 10^{-11}$ |
| 65 | $8.90 \times 10^{-11}$ |
| 75 | $1.37 \times 10^{-11}$ |

Ln ($D_{eff}$) vs. reciprocal of absolute drying air temperature ($1/T_d$) given in Kelvin were plotted in Figure 4.20 to obtain the pre-exponential factor ($D_0$) and activation energy ($E_a$) as mentioned in Equation 2.6 using the Arrhenius type relationship. Table 4.7 listed the pre exponential factor and activation energy of wetted black pepper drying process in three spouted bed configurations.

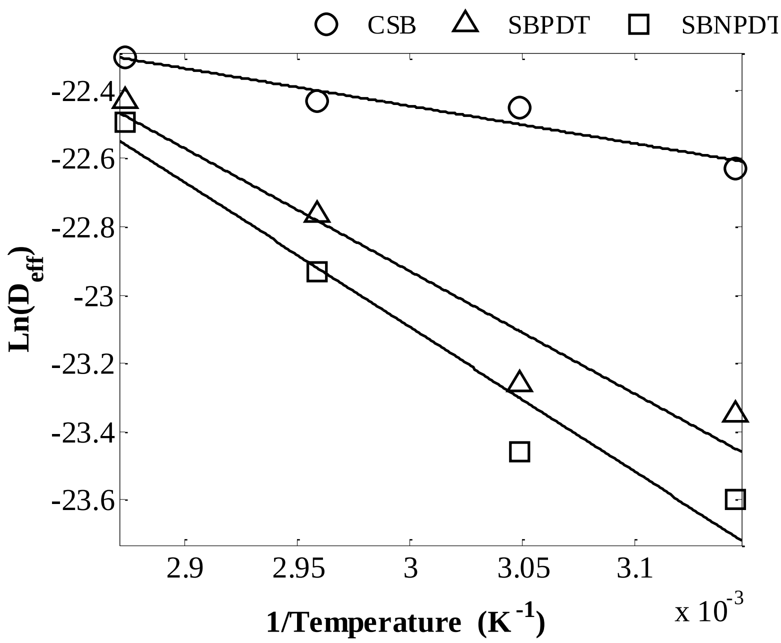



Figure 4.20: Ln ($D_{eff}$) vs. $1/T_d$ of wetted pepper dried in three spouted bed configurations; Experiment conditions: H =0.16 m, $D_i$ =0.035 m, $L_H$= 0.06 m, $D_T$= 0.035 m, $H_T$= 0.02 m

According Table 4.7, pre-exponential factor of black pepper dried in conventional spouted bed is the lowest followed by porous draft tube fitted bed while black pepper dried in non-porous draft tube fitted experienced the highest value. Activation energy refers to the minimum energy requirement to overcome the barrier for the moisture diffusion [109] . Activation energy for black pepper drying in conventional spouted bed is 9.13 kJ/mol which is the lowest of three configurations analysed followed by spouted bed with porous draft tube while non-porous draft tube fitted spouted bed has the highest activation energy of 35.21 kJ/mol.

Markowski et al. also used tempered barley for drying experiments in a spouted bed dryer at 30 °C -45 °C drying temperatures and found that the time of barley drying depend on the drying air temperature. The effective diffusivities of barley in their study were in the range of 2.20 - 4.52 × $10^{-11}$ $m^2/s$ [110]. Furthermore, Chapter 5 will present the information on effective diffusivity, pre-exponential factor and activation energy of raw black pepper and other agricultural products.

Table 4.7: Pre -exponential factor and activation energy of wetted black pepper dried in different spouted bed configurations

| **spouted bed configurations** | **Pre -exponential factor Do ($m^2/s$)** | **Activation energy $E_a$ (KJ/mol)** |
|---|---|---|
| conventional bed | 1.41× $10^{-6}$ | 25.37 |
| SBPDT | 3.56× $10^{-6}$ | 28.61 |
| SBNPDT | 4.00× $10^{-5}$ | 36.39 |

Equation 2.7 in chapter 2 stated the magnitude of effective diffusivity as a function of exponent ($E_a/RT$). When recalling the meaning of RT, it indicates the average kinetic energy of molecules. Therefore the exponent indicates the ratio of activation energy to kinetic energy of molecules participated in the drying process. When the ratio is too large, effective diffusivity value becomes smaller due to the negative

sign. Also high temperature and low activation energy favor large effective diffusivity thus speed up the drying process [111]. Moreover these $E_a$ and RT terms occur in an exponent; their effects on effective diffusivity are quite significant.

According to the results, effective diffusivity of black pepper not only depends on drying air temperature but also on the configuration of the spouted bed dryer.

## 4.6 Decision on selecting the optimum configuration for experiment with raw black pepper

Although minimum spouting velocity is low, spouted bed equipped with draft tubes experiences longer drying time than that of the conventional spouted bed. Hence, it can cause degradation of volatile compounds in the black pepper during long drying periods. Furthermore, either tube plugging or agglomeration of the drying material or any other foreign substance can disrupt the operation.

Conventional spouted bed experiences higher drying rates and higher effective diffusivity values compared to both draft tube fitted configurations. Therefore, conventional spouted bed dryer was selected as the best configuration of spouted bed among draft tube fitted system to continue drying experiments with raw black pepper.

## 4.7 Mathematical modeling of drying kinetics of wetted black pepper in three spouted bed configurations

3 kg of wetted black pepper were dried in the spouted dryer with 3 different configurations; namely conventional dryer (without draft tube), non-porous daft tube fitted dryer and porous draft tube fitted dryer. The dimensions of draft tubes used were: diameter of draft tube ($D_T$), 0.035m, entrainment height ($L_H$), 0.06 m and height of the draft tube,($L_T$) 0.26 m.

Drying kinetic data were fitted to selected five thin layer drying models using curve fitting tool of Matlab 2011. The results of fitting experimental data to thin layer models and the summary of the statistical analyses are presented in Table 4.8 to Table 4.10. The higher value of $R^2$ and lowest value of SSE and RMSE, the better the goodness of fit [92].

It was observed that the Logarithmic model presented the highest $R^2$ values with lower RMSE and SSE values for spouted bed dryer provided with non- porous draft tube at 55 °C, 65 °C and 75 °C drying air temperature.

Page model, Logarithmic model and Two compartment model possessed $R^2$ values greater than 0.99 with small values of RMSE and SSE values for conventional spouted bed dryer and the spouted bed equipped with porous draft tube at 75 °C.

Two compartment model was the best fitted model with 0.9975 of highest $R^2$ and 0.0156 of lowest RMSE value for conventional bed at 55 °C drying temperature. Logarithmic model found best with highest $R^2$ and lowest RMSE values for spouted bed equipped with non-porous draft tube bed at 55 °C drying temperatures while well-known Page model showed the best results with 0.9972 of $R^2$ and 0.0134 of RMSE for spouted bed equipped with porous draft tube at 55 °C drying air temperature.

Drying constants of thin layer drying models are presented in Table 4.9. For many cases drying constants of selected thin layer drying models for spouted bed drying process are in same order of magnitude with values available in literature [86,80].

Table 4.8: Results of statistical analysis for three spouted bed configurations at 55 ˚C drying air temperature

| **Conventional bed** | | | | |
|---|---|---|---|---|
| **Model** | **Equation** | $\mathbf{R^2}$ | **RMSE** | **SSE** |
| Newton | $MR = \exp(-0.0206t)$ | 0.9629 | 0.0508 | 0.0258 |
| Page | $MR = \exp(-0.0463\, t^{0.7923})$ | 0.9832 | 0.0360 | 0.0117 |
| Henderson & Pabis | $MR = 0.9604\exp(-0.0196t)$ | 0.9665 | 0.0509 | 0.0233 |
| Two compartment | $MR = 0.0526\exp(0.0114t) + 0.9623\exp(0.0281t)$ | 0.9975 | 0.0156 | 0.0171 |
| Logarithmic | $MR = 0.8408\exp(-0.0336t) + 0.1792$ | 0.9966 | 0.0173 | 0.0024 |
| **Spouted bed with porous draft tube** | | | | |
| **Model** | **Equation** | $\mathbf{R^2}$ | **RMSE** | **SSE** |
| Newton | $MR = \exp(-0.0086t)$ | 0.9516 | 0.0535 | 0.0344 |
| Page | $MR = \exp(-0.0336t^{0.7158})$ | 0.9972 | 0.0134 | 0.0020 |
| Henderson & Pabis | $MR = 0.9116\exp(-0.0077t)$ | 0.9719 | 0.0426 | 0.0200 |
| Two compartment | $MR = 0.4282\exp(-0.0077t) + 0.4834\exp(-0.0077t)$ | 0.9719 | 0.0471 | 0.0200 |
| Logarithmic | $MR = 0.8054\exp(-0.0123t) + 0.1562$ | 0.9871 | 0.0303 | 0.0092 |
| **Spouted bed with non- porous draft tube** | | | | |
| **Model** | **Equation** | $\mathbf{R^2}$ | **RMSE** | **SSE** |
| Newton | $MR = \exp(-0.0060\, t)$ | 0.9937 | 0.0197 | 0.0058 |
| Page | $MR = \exp(-0.0093\, t^{0.9138})$ | 0.9970 | 0.0141 | 0.0028 |
| Henderson & Pabis | $MR = 0.9633\exp(-0.0196t)$ | 0.9971 | 0.0138 | 0.0027 |
| Two compartment | $MR = 0.5077\exp(-0.0046t) + 0.4555\exp(-0.073t)$ | 0.9971 | 0.0149 | 0.0027 |
| Logarithmic | $MR = 0.9396\exp(-0.0061t) + 0.0294$ | 0.9973 | 0.0137 | 0.0024 |

Table 4.9: Results of statistical analysis for three spouted bed configurations at 65 ˚C drying air temperature

| **Conventional bed** | | | | |
|---|---|---|---|---|
| **Model** | **Equation** | **$R^2$** | **RMSE** | **SSE** |
| Newton | $MR = \exp(-0.0233t)$ | 0.9426 | 0.0622 | 0.0386 |
| Page | $MR = \exp(-0.0730t^{0.7018})$ | 0.9883 | 0.0295 | 0.0078 |
| Henderson & Pabis | $MR = 0.9291\exp(-0.0213t)$ | 0.9538 | 0.0588 | 0.0311 |
| Two compartment | $MR = 0.1563\exp(0.0157t) + 0.8464\exp(-0.03843$ | 0.9998 | 0.0043 | 0.0002 |
| Logarithmic | $MR = 0.8206\exp(-0.0399t) + 0.1831$ | 0.9998 | 0.0043 | 0.0002 |
| **Spouted bed with porous draft tube** | | | | |
| **Model** | **Equation** | **$R^2$** | **RMSE** | **SSE** |
| Newton | $MR = \exp(-0.0130t)$ | 0.9466 | 0.0532 | 0.0425 |
| Page | $MR = \exp(-0.0444t^{0.717})$ | 0.9961 | 0.0148 | 0.0031 |
| Henderson & Pabis | $MR = 0.906\exp(-0.0115t)$ | 0.9713 | 0.0404 | 0.0229 |
| Two compartment | $MR = 0.253\exp(-0.0082t) + 0.7512\exp(-0.0091t)$ | 0.9974 | 0.0131 | 0.0021 |
| Logarithmic | $MR = 0.7889\exp(-0.0190t) + 0.1712$ | 0.9879 | 0.0273 | 0.0097 |
| **Spouted bed with non- porous draft tube** | | | | |
| **Model** | **Equation** | **$R^2$** | **RMSE** | **SSE** |
| Newton | $MR = \exp(-0.0109t)$ | 0.9906 | 0.0247 | 0.0085 |
| Page | $MR = \exp(-0.0098t^{1.025})$ | 0.9908 | 0.0253 | 0.0083 |
| Henderson & Pabis | $MR = 1.019\exp(-0.0112t)$ | 0.9915 | 0.0243 | 0.0077 |
| Two compartment | $MR = 0.5096\exp(-0.0112\,t) + 0.5096\exp(-0.0112t)$ | 0.9915 | 0.0264 | 0.0077 |
| Logarithmic | $MR = 0.949\ \exp(-0.0134t) + 0.0856$ | 0.9932 | 0.0226 | 0.0061 |

Table 4.10: Results of statistical analysis for three spouted bed configurations at 75 ˚C drying air temperature

| **Conventional bed** | | | | |
|---|---|---|---|---|
| **Model** | **Equation** | **$R^2$** | **RMSE** | **SSE** |
| Newton | $MR = \exp(-0.0314t)$ | 0.8961 | 0.0835 | 0.0697 |
| Page | $MR = \exp(-\ 0.1491t^{0.5723})$ | 0.9931 | 0.0227 | 0.0046 |
| Henderson & Pabis | $MR = 0.8917\exp(-0.0272t)$ | 0.9180 | 0.0782 | 0.0551 |
| Two compartment | $MR = 0.3258\exp(-0.0080t) + 0.6737\exp(-0.0766t)$ | 0.9992 | 0.0088 | 0.0005 |
| Logarithmic | $MR = 0.8218\exp(-0.0566t) + 0.1676$ | 0.9964 | 0.0174 | 0.0024 |
| **Spouted bed with porous draft tube** | | | | |
| **Model** | **Equation** | **$R^2$** | **RMSE** | **SSE** |
| Newton | $MR = \exp(-0.0181t)$ | 0.9616 | 0.0499 | 0.0349 |
| Page | $MR = \exp(-0.0491t^{0.7566})$ | 0.9926 | 0.0227 | 0.0067 |
| Henderson & Pabis | $MR = 0.906\exp(-0.0115t)$ | 0.9713 | 0.0404 | 0.0229 |
| Two compartment | $MR = 0.1602\exp(-0.0007t) + 0.840\exp(-0.0278t)$ | 0.9940 | 0.0002 | 0.0002 |
| Logarithmic | $MR = 0.8537\ \exp(-0.0273t) + 0.1458$ | 0.9940 | 0.0007 | 0.0002 |
| **Spouted bed with non- porous draft tube** | | | | |
| **Model** | **Equation** | **$R^2$** | **RMSE** | **SSE** |
| Newton | $MR = \exp - 0.0163t)$ | 0.9820 | 0.0389 | 0.0196 |
| Page | $MR = \exp(-0.0125t^{1.065})$ | 0.9833 | 0.0389 | 0.0182 |
| Henderson & Pabis | $MR = 1.033\exp(-0.0169t)$ | 0.9839 | 0.0383 | 0.0176 |
| Two compartment | $MR = 0.5164\exp(-0.0093t) + 0.5164\exp(-0.0169t)$ | 0.9839 | 0.0420 | 0.0176 |
| Logarithmic | $MR = 0.9927\ \exp(-0.0193t) + 0.0545$ | 0.9856 | 0.0378 | 0.0156 |

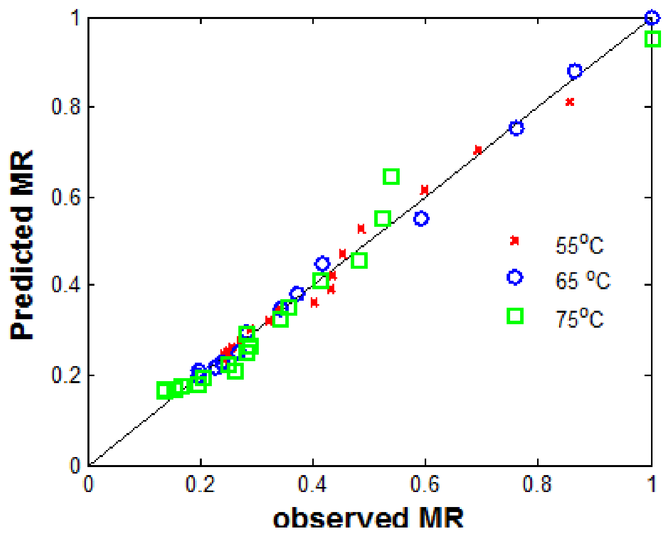



Figure 4. 21: A comparison between the observed moisture ratio and predicted moisture ratio of black pepper dried at different drying air temperatures in conventional spouted bed using Logarithmic model.

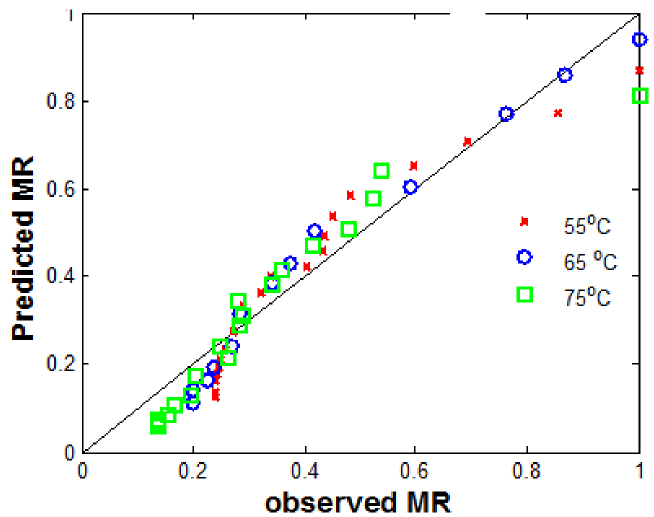



Figure 4. 22:A comparison between the observed moisture ratio and predicted moisture ratio of black pepper dried at different drying air temperatures in conventional spouted bed using Henderson and Pabis model.

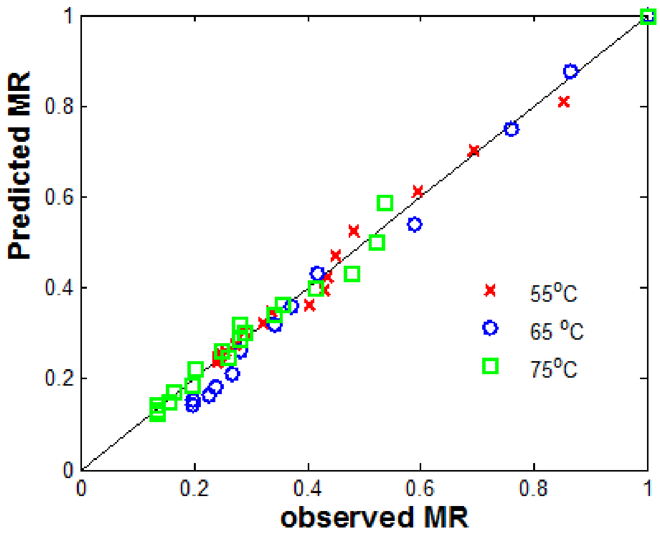



Figure 4. 23:A comparison between the observed moisture ratio and predicted moisture ratio of black pepper dried at different drying air temperatures in conventional spouted bed using Two Compartment model.

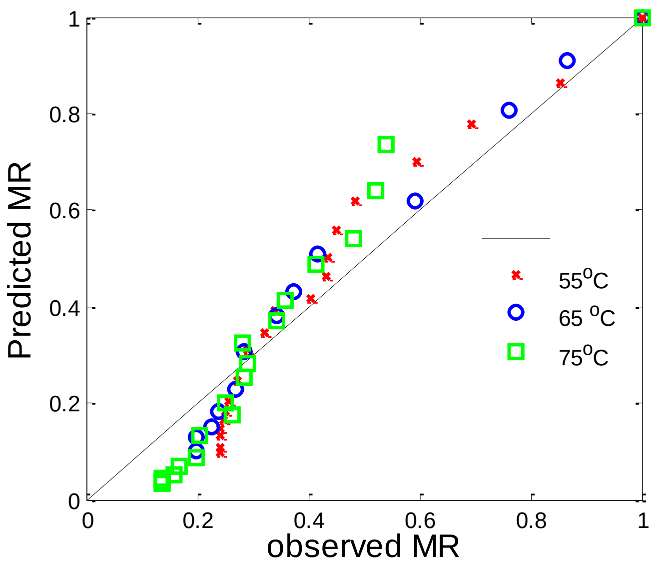



Figure 4. 24:A comparison between the observed moisture ratio and predicted moisture ratio of black pepper dried at different drying air temperatures in conventional spouted bed using Newton model.

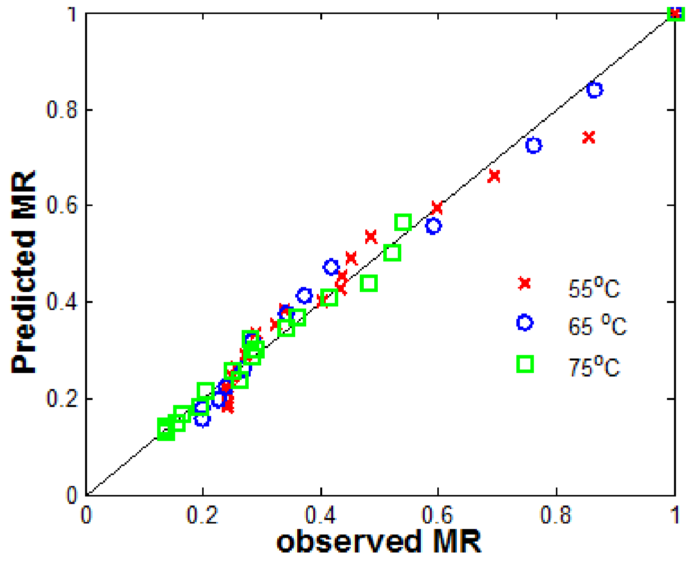



Figure 4. 25 : A comparison between the observed moisture ratio and predicted moisture ratio of black pepper dried at different drying air temperatures in conventional spouted bed using Page model.

Figure 4. 21 to Figure 4. 25 show the comparison between the observed moisture ratio and predicted moisture ratio of black pepper dried in conventional spouted bed using selected models. According to the results of statistical analyses shown in Table 4.8 to Table 4.10 and Figure 4. 21 to Figure 4. 25, selected thin layer models can describe the drying kinetics of wetted black pepper in three configurations satisfactorily.

Statistical analysis and the observed moisture ratio vs. predicted moisture ratio data laying around the straight line in Figure 4. 21 and Figure 4. 23 prove the Logarithmic model and the Two compartment model are the best fitting models for wetted black pepper drying in any of three configurations of spouted bed dryer.

However in work of Kalwar and Raghavan, Page model described the drying process of shelled corn in draft plates fitted two dimensional spouted bed with sufficient accuracy [33]. Jittanit et al. conducted drying experiments in a fluidized bed dryer and a spouted bed dryer using rewetted samples of paddy, wheat and maize. They fitted the drying kinetics data into four thin layer models and, Page model and Two Compartment model were found as the best fitted model [80].

**Chapter specific nomenclature**

$D_{eff}$ -effective moisture diffusivity ($m^2/s$)

$D_i$ - gas inlet diameter (m)

$D_o$ -pre exponential factor of Arrhenius equation

$D_T$ -diameter of draft tube (m)

$E_a$ -activation energy (kJ/mol)

H - Stagnant bed height (m)

$H_T$- tube height (m)

$L_H$ -entrainment height (m)

$L_T$ - total height of the draft tube

$t_{Ums}$ - drying time when air velocity is set to minimum spouting velocity

$t_{V1}$ - drying time when air velocity is set to $v_1$

$T_d$- drying air temperature at the inlet of the drying chamber (°C)

$U_{ms}$ -minimum spouting velocity (m/s)

**Abbreviations**

CSB - Conventional spouted bed

SBNPDT - Spouted bed equipped with non-porous draft tube

SBPDT - Spouted bed equipped with porous draft tube

$R^2$ - Coefficient of determination

RMSE - Root mean square error

SSE - Sum of square error

**Chapter 5**

# 5. HYDRODYNAMICS OF SPOUTING, DRYING KINETICS AND MATHEMATICAL MODELING OF DRYING OF RAW BLACK PEPPER IN CONVENTIONAL SPOUTED BED

This chapter presents the results of major experiments described under section 3.1.6.1, 3.1.6.2 and 3.1.6.4. All the experiments were conducted in conventional spouted bed with raw black pepper. Hydrodynamics of black pepper in the conventional spouted bed and drying kinetics of raw black pepper dried in the conventional spouted bed are discussed. Furthermore, results of mathematical modeling of drying kinetics of raw black pepper in conventional spouted bed dryer are presented and discussed.

## 5.1 Minimum spouting velocity

Spouting behavior of raw black pepper was studied. Measurements of Pressure drop across the bed versus air velocity were taken for four stagnant bed heights at ambient temperature.

The variation of pressure drop across the bed with increasing and decreasing air flow for 0.07 m, 0.14 m, 0.18 m and 0.22 m static bed heights of raw black pepper respectively are shown in Figure 5.1 to Figure 5.4. Curve ABCDE in Figure 5.1 shows the evolution of pressure drop across the bed with increasing air flow rate for a loosely packed bed. At low flow rates, pressure drop across the particle bed increased with increasing air velocity. Gradually the inner cavity converted to an internal spout. Further increase of air velocity made the pressure drop to reach a peak value at point B. This peak in the pressure drop was due to the energy required to disrupt the packing.

Height of internal spout increased and formed a fountain of particles above the packed bed. Then the pressure drop declined significantly with increase of the air velocity approaching the point C. Then the bed approached to the point of incipient spouting, internal cavity ruptured with slight increase in velocity caused sharp decrease in pressure drop to point D and lead to point of onset spouting such that steady spouting was established. As the air velocity was increased further, pressure drop remained constant as in DE.

Curve EDC′B′A in Figure 5.1 shows the variation of the pressure drop across the bed when the air flow rate was reduced. When the air velocity was gradually decreased in a stable spouted bed, the bed remained in the spouting state and the pressure drop remained constant until point C′. When the spout collapsed or with disappering of external spout pressure drop was suddnely increased to point B′ since particles get loosely packed and made an resistance to flow. Pressure drop at point B′ was a much lower pressure drop compared to peak value reported in flow rate ascending process. Point C′ was identified as the state of minimum spouting condition. Similar trend for conical spouted bed with heavy particles was also reported by Sari et al. [112]. Figure 5. 5(a) to Figure 5. 5(d) appear in similar scale, show the comparison of variation of pressure drop across the bed with increasing and decreasing air flow for above mentioned four diffrent stagnant bed heights of raw black pepper.

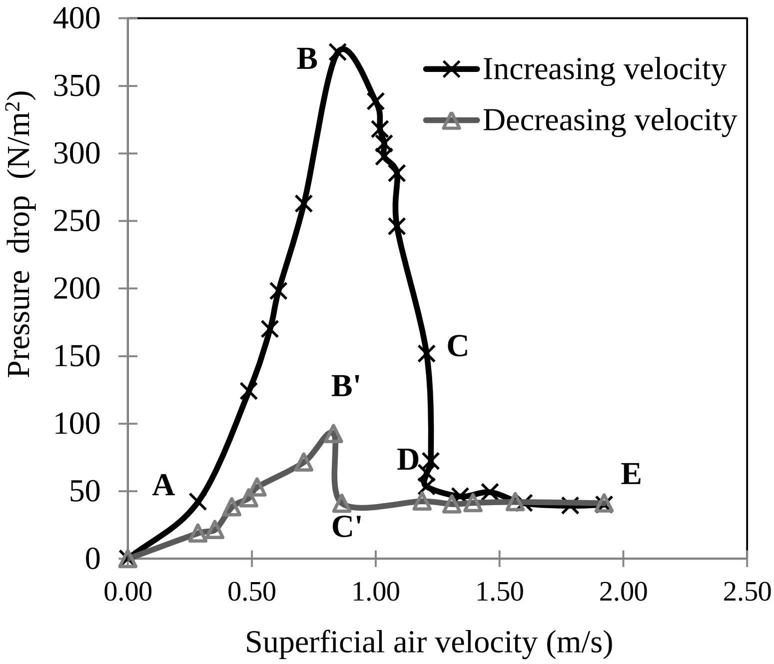



Figure 5.1: Pressure drop vs. superficial air velocity for 0.07 m static bed of raw black pepper at ambient temperature

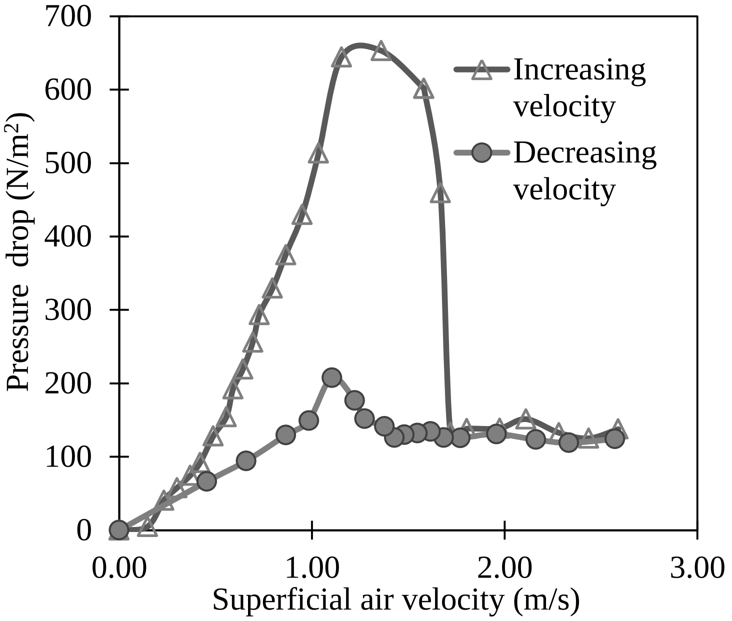



Figure 5.2: Pressure drop vs. superficial air velocity for 0.14 m static bed of raw black pepper at ambient temperature

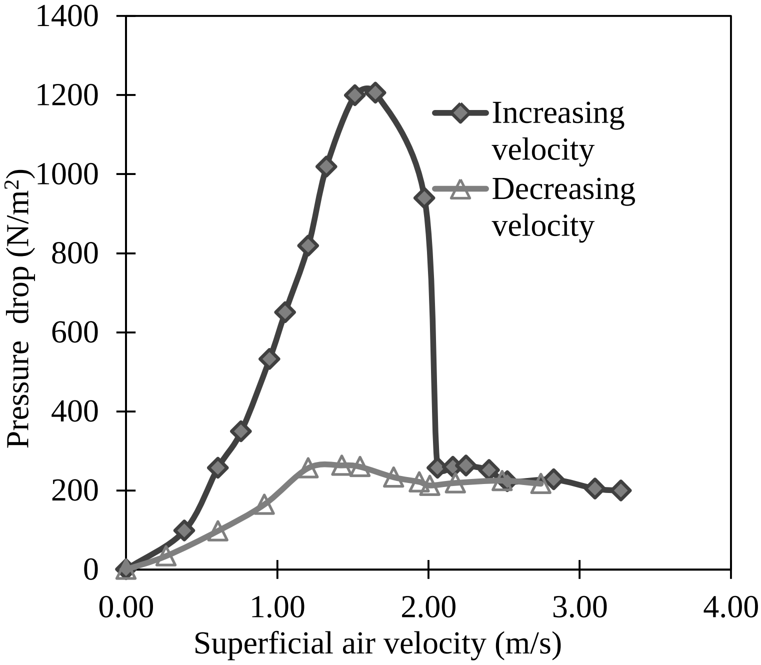



Figure 5.3:Pressure drop vs. superficial air velocity for 0.18 m static bed of raw black pepper at ambient temperature

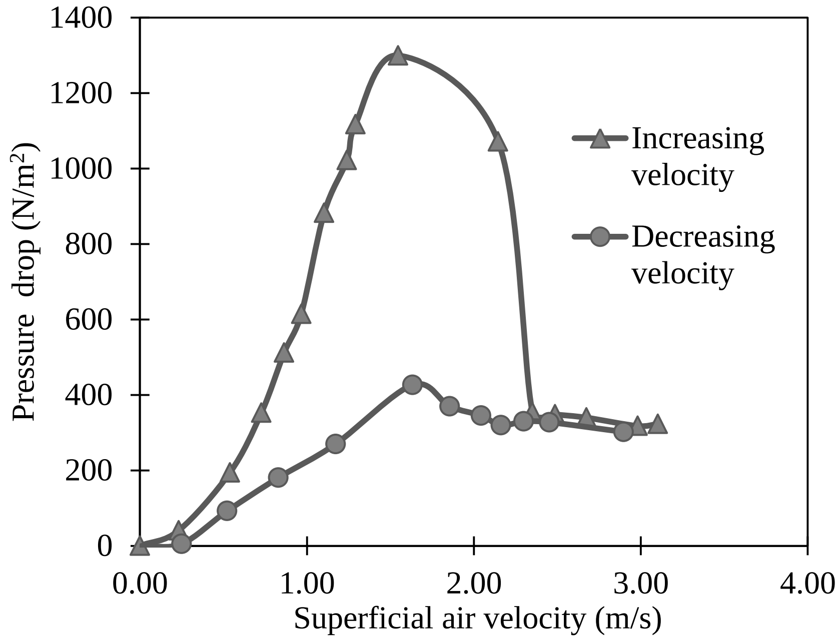



Figure 5.4: Pressure drop vs. superficial air velocity for 0.22 m static bed of raw black pepper at ambient temperature

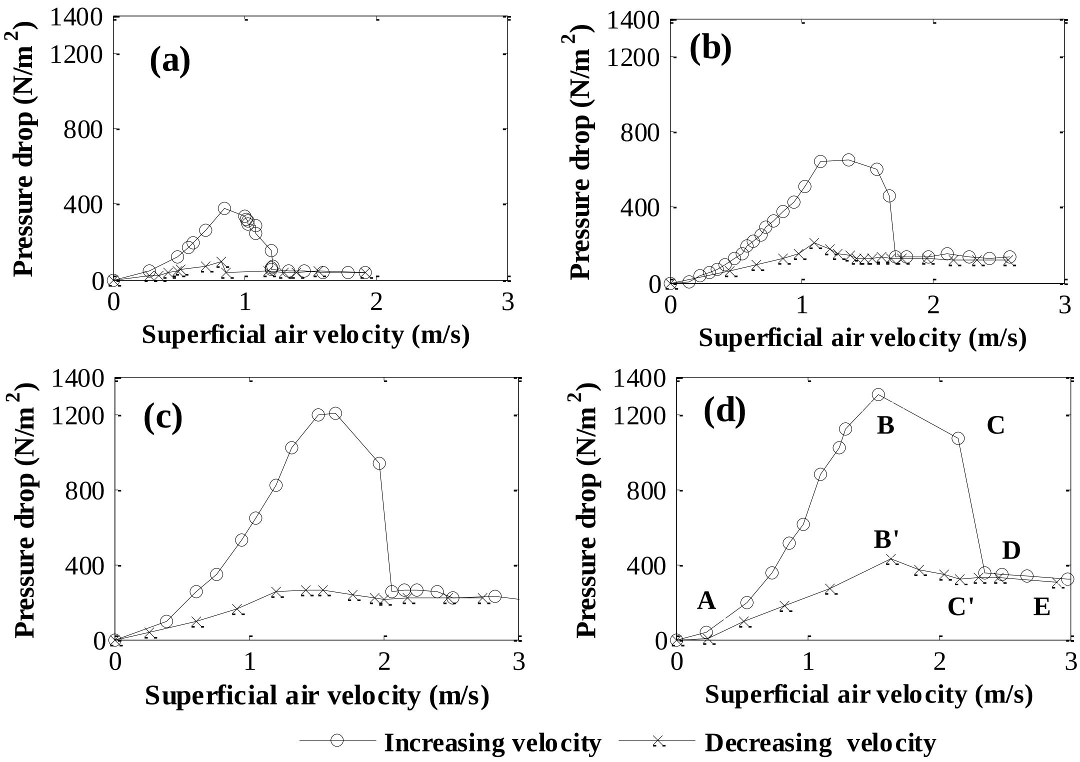



Figure 5. 5: Pressure drop vs. superficial air velocity for different static bed heights of raw black pepper at ambient temperature: (a) 0.07 m, (b) 0.14 m, (c) 0.18 m, (d) 0. 22 m

Similarly pressure drop versus air velocity plots were prepared for all the bed heights. Minimum spouting velocities for each bed height were determined and shown in Table 5.1. The results show that the minimum spouting velocity increases with increasing static bed heights since more energy is required to expand the deeper beds to attain loose state to disrupt the packing state [113]. This is in agreement with the results reported for hydrodynamics of silicon particles in draft tubes fitted spouted fluid bed by Zhang et al. [41].

Widely used Mathur and Gishler equation presented in Equation 2.8 and Wu *et al*. correlation shown in Equation 2.10 were used to compare the experimental values of minimum spouting velocity [13, 62]. Equation 5.1 shows the expression for determining maximum pressure drop in either particulate fluidization or spouting [13]. It was used to compare the experimental values of peak pressure drop and the results are shown in Table 5.1.

$$-\Delta P_M = H(\rho_p - \rho)(1 - \epsilon)g \qquad (5.1)$$

Figure 5.6 shows the predicted and experimental minimum spouting velocities. The experimentally determined values lie between the values predicted by two correlations given in Mathur and Gishler equation (Equation 2.8) and Wu *et al*. correlation (Equation 2.10). However the accuracy of the Mathur and Gishler equation is ±15% [37] and therefore experiment results approximately lies within this range.

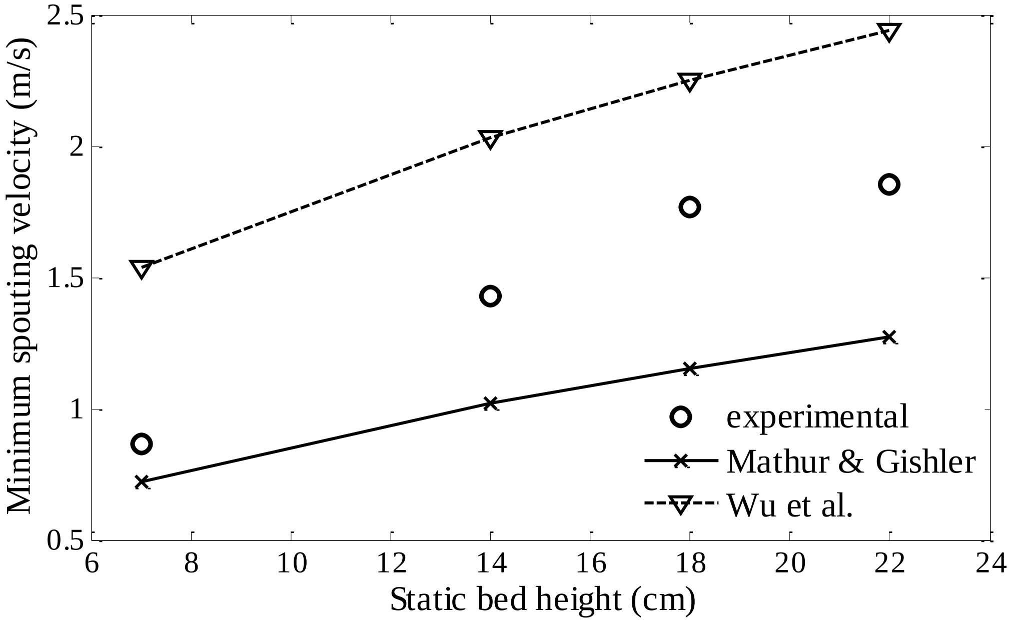



Figure 5.6: Minimum spouting velocity vs. static bed height

Minimum spouting velocity of raw black pepper for the conventional spouted bed vs static bed height were fitted to a power form of function using Matlab 2011. The relationship is given by Equation 5.2 with 0.97 of coefficient of determination ($R^2$). This is valid for ambient temperature.

$$U_{ms} = 5.26\ H^{0.67} \qquad (5.2)$$

Table 5.1: Experimental and predicted minimum spouting velocity for selected stagnant bed heights of raw black pepper

| **$H_o$ (m)** | **Experimental $U_{ms}$ (m/s)** | **Predicted $U_{ms}$(m/s)** | |
|---|---|---|---|
| | | **Mathur & Gishler equation** | **Wu at al. (m/s)** |
| 0.07 | 0.86 | 0.72 | 1.54 |
| 0.14 | 1.43 | 1.02 | 2.03 |
| 0.18 | 1.77 | 1.15 | 2.25 |
| 0.22 | 1.86 | 1.28 | 2.44 |

Table 5. 2- Experimental and predicted maximum pressure drop for selected stagnant bed heights of raw black pepper

| $H_o$ (m) | Experimental $\Delta P_M$ ($N/m^2$) | Predicted $\Delta P_M$ ($N/m^2$) |
|---|---|---|
| 0.07 | 374.78 | 289.38 |
| 0.14 | 653.06 | 578.76 |
| 0.18 | 1205.43 | 744.12 |
| 0.22 | 1300.00 | 909.48 |

All the experimentally determined $\Delta P_M$ values are underestimated by the predicted $\Delta P_M$ by Equation 5.1. The experimental results showed that the exponent of static bed height in power form of function shown in Equation 5.2 derived for current study is 0.67. However, exponent of static bed height in both Mathur and Gishler equation (Equation 2.8) and Wu et al. correlation (Equation 2.10) are 0.5 and 0.405 respectively. This difference is due to the use of different geometrical dimensions of spouted beds with varieties of material used to for investigations.

### 5.2 Drying kinetics

#### 5.2.1 Effect of drying air temperature

Drying experiments were conducted using 0.14 m of stagnant bed of raw black pepper at four different drying air temperatures; 45 ˚C, 55 ˚C, 65 ˚C and 75 ˚C. The superficial air velocity of 2.37 m/s was maintained for these experiments as explained in section 3.1.6.2. Data containing moisture content versus time obtained from experiments at different air temperatures were used to determine the effect of drying air temperature on drying kinetics. Figure 5. 7 and Figure 5.8 show the moisture content vs. time and the rate of change of moisture content vs. moisture content plotted at different drying air temperatures.

Figure 5. 7 shows that increase in the drying air temperature from 45 ˚C to 75 ˚C causes significant reduction of drying time confirming that the total drying time is reduced with the increase in drying air temperature. Serowick *et. al.* has obtained similar trend in their experiments on drying of semi-refined carrageenan in a spouted bed [114].

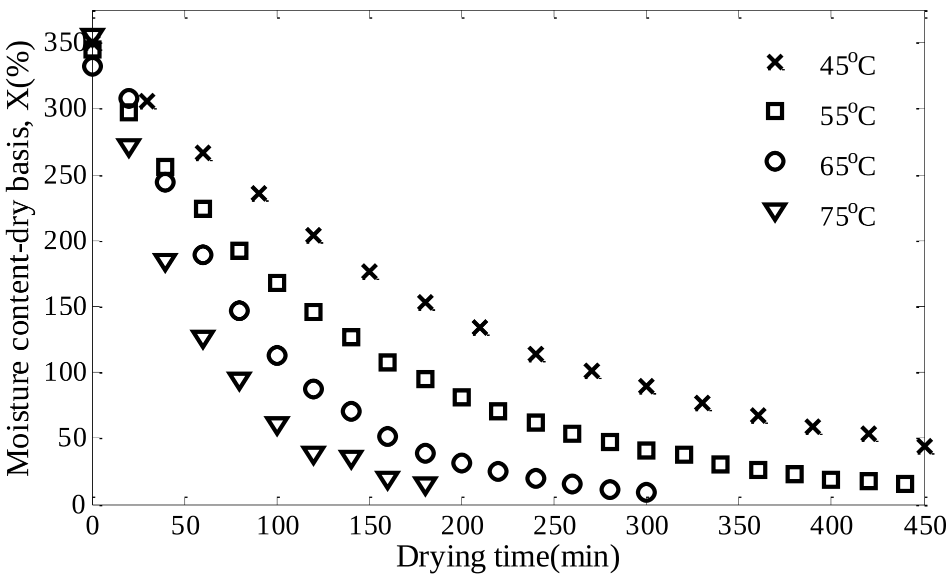



Figure 5. 7: Moisture content- dry basis vs. time of black pepper when dried in conventional spouted bed at different drying air temperatures. Experiment conditions: $D_i$=0.05 m, H =0.14 m, and air flow of 2.37 m/s

Black pepper drying rate curves in Figure 5.8 show only falling rate periods which is due to unsaturated surface drying [14]. As discussed in the literature many agricultural products have shown similar drying behaviour with the falling rate drying periods without appearing the constant rate period [82 , 31 , 115 , 108 , 116].

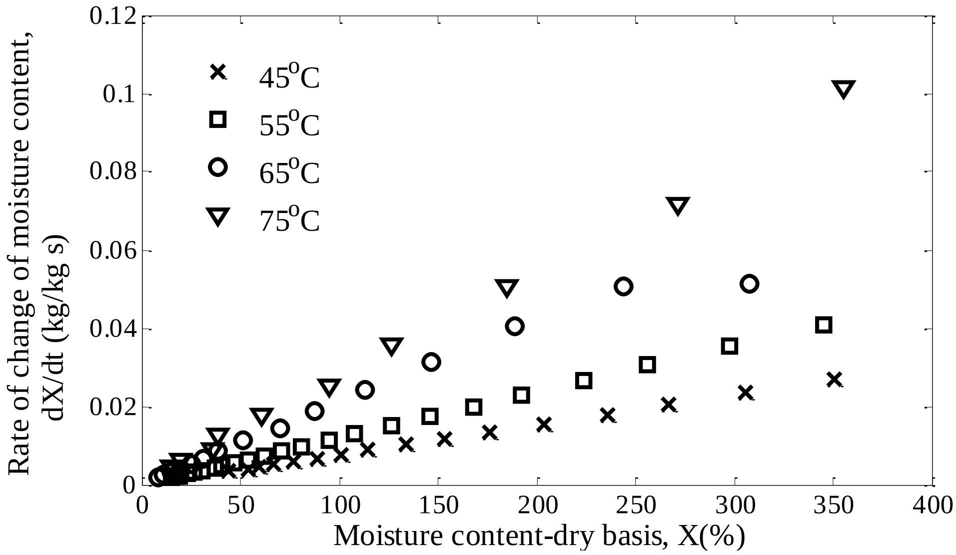



Figure 5.8: Rate of change of moisture content vs moisture content- dry basis of black pepper when dried in conventional spouted bed at different drying air temperatures; experiment conditions: $D_i$=0.05 m, H =0.14 m and air flow of 2.37 m/s

The highest drying rate was achieved while black pepper was dried at drying air temperature of 75 °C. At higher drying air temperatures, hot air provides higher external heat fluxes leading to higher moisture diffusivities and hence higher drying rate. Table 5.3 shows the air requirement for drying of raw black pepper in the conventional spouted bed at different drying air temperatures. In addition, Figure 5.9, Figure 5.10 and

Table 5.3 provide information on the drying time and volume of air required for drying of raw black pepper in conventional spouted bed dryer regarding the drying of 1 kg of raw black pepper, to achieve 1 kg of dried black pepper and to evaporate 1 kg of moisture in raw black pepper. As per the analysis of air requirement of different drying air temperatures, low amount of hot air is required at higher drying temperatures.

Despite the fact that rise in drying air temperature reduces the time of drying and the specific energy consumption of the process as described in section 5.3, the quality of the final product may get affected. Therefore, attention was paid to analyse the quality of the final product and presented in chapter 6.

Table 5.3: Drying time and volume of air required for raw black pepper when dried in conventional spouted bed at different drying air temperatures. Experiment conditions: $D_i$=0.05 m, H =0.14 m (bed weight = 1 kg), and air flow of 2.37 m/s

| **Description** | **Drying air temperature (°C)** | | | |
|---|---|---|---|---|
| | **45** | **55** | **65** | **75** |
| Drying time (min) | 650 | 439 | 260 | 181 |
| Volume of air sent throughout the drying period ($m^3$) | 1632.41 | 714.00 | 652.96 | 454.56 |
| Volume of air required to evaporate 1kg of moisture ($m^3$) | 2192.19 | 962.74 | 890.13 | 608.12 |
| Volume of air required to dry 1kg of raw black pepper ($m^3$) | 1632.41 | 714.00 | 652.96 | 454.56 |
| Volume of air required to have 1kg of dried black pepper after drying of raw black pepper ($m^3$) | 6392.78 | 2763.54 | 2450.69 | 1800.22 |
| Average moisture removal rate (g/s) | 0.019 | 0.028 | 0.047 | 0.069 |

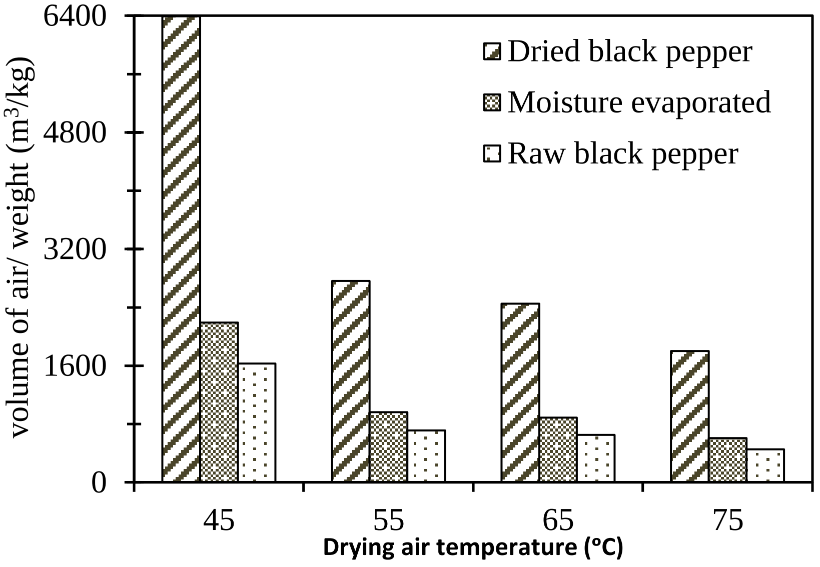



Figure 5.9: Volume of air required for raw black pepper when dried in conventional spouted bed at different drying air temperatures. Experiment conditions: $D_i$=0.05 m, H =0.14 m, and air flow of 2.37 m/s

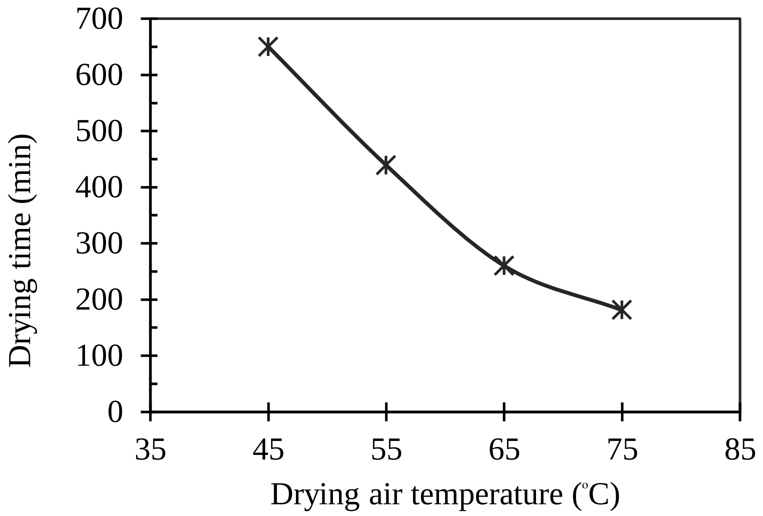



Figure 5.10: Drying time for black pepper when dried in conventional spouted bed at different drying air temperatures. Experiment conditions: $D_i$=0.05 m, H =0.14 m, and air flow of 2.37 m/s

### 5.2.2 Effect of bed height

Figure 5.11 and Figure 5.12 show the effect of bed height on the drying kinetics of black pepper in the conventional spouted bed. Figure 5.11 shows that time required for a given moisture reduction increases with the bed height. The time required to reach a moisture content of 15 % dry basis are 225 min, 260 min, 330 min and 335 min in the 0.07 m, 0.14 m, 0.18 m and 0.20 m beds respectively. Figure 5.12 indicates that rate of change of moisture content decreases with increasing bed height showing that deeper beds require longer drying time for moisture removal than the shallow bed. In spouted bed dryers, intensive heating and evaporation takes place in the spout region while particles are tempered in the annulus region. Since the particles in the deeper beds have longer residence time in the annulus region, rate of change of moisture content of deep bed is lower than that of shallow beds. According to Law and Mujumdar, this behaviour will appear only up to a certain bed height beyond which the bed height will not have any effect on the drying rate [108].

Table 5.4, Figure 5.13 and Figure 5.14 show the drying time and air requirement for drying of raw black pepper at different bed heights. However, average of moisture evaporated per unit time at 0.07 m, 0.14 m and 0.20 m static bed heights are 0.033 g/s, 0.047 g/s, 0.056 g/s and 0.066 g/ s respectively. This result indicates despite the rate of change of moisture content (dX/dt) decreases with the increasing bed height; the average weight of moisture evaporated per unit time is increased. In addition, volume of air required to dry 1 kg of raw black pepper or to get 1kg of dried black pepper is decreased with increasing static bed height of the dryer. This is due to the fact that at higher static bed heights of spouted bed, a larger fraction of thermal energy of hot air is utilized for drying operation without sending out through the dryer outlet. Therefore it is economical to run spouted bed dryers with deeper bed heights or closer to their maximum spoutable heights.

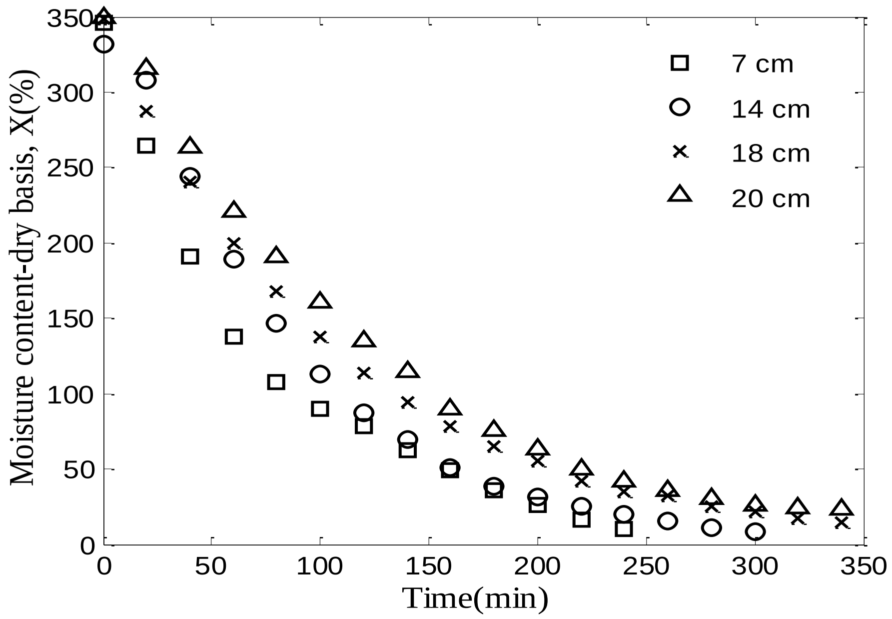



Figure 5.11: Moisture content (% dry basis) versus time of black pepper when dried in conventional spouted bed at different static bed heights; Experiment conditions: $D_i$ =0.05 m, $T_d$=65 °C and air flow of 2.37 m/s

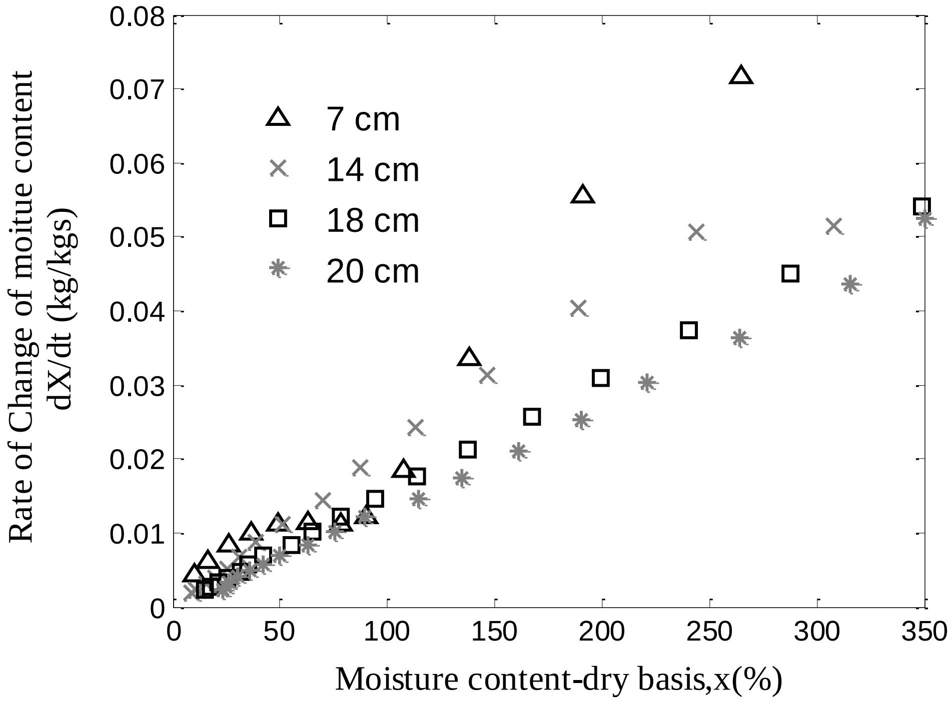



Figure 5.12: Rate of change of moisture content, dx/dt versus moisture content (% dry basis) of black pepper when dried in conventional spouted bed at different static bed heights;experiment conditions: $D_i$ =0.05 m, $T_d$=65 °C and air flow of 2.37 m/s

Table 5.4: Volume of air required for raw black pepper when dried in conventional spouted bed at different static bed heights; experiment conditions: $D_i$ =0.05 m, $T_d$=65 °C and air flow of 2.37 m/s

| Description | Static bed height (m) | | | |
|---|---|---|---|---|
| | **0.07** | **0.14** | **0.18** | **0.2** |
| Drying time (min) | 225 | 260 | 330 | 340 |
| Volume of air sent throughout the drying period ($m^3$) | 562.55 | 652.96 | 828.76 | 841.32 |
| Volume of air required to evaporate 1kg of moisture ($m^3$) | 1263.75 | 890.13 | 742.8 | 637.22 |
| Volume of air required to dry 1kg of raw black pepper ($m^3$) | 937.59 | 652.96 | 552.51 | 474.38 |
| Volume of air required to have 1kg of dried black pepper after drying of raw black pepper ($m^3$) | 3632.84 | 2450.69 | 2156.74 | 1856.25 |
| Average moisture removal rate (g/s) | 0.033 | 0.047 | 0.056 | 0.066 |

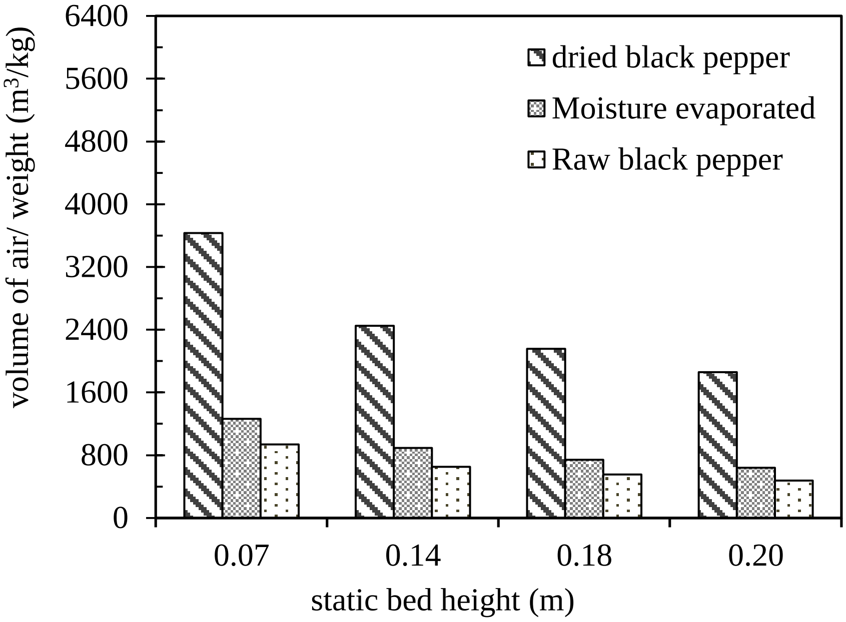



Figure 5.13 :Volume of air required for raw black pepper when dried in conventional spouted bed at different static bed heights; experiment conditions: $D_i$ =0.05 m, $T_d$=65 °C and air flow of 2.37 m/s

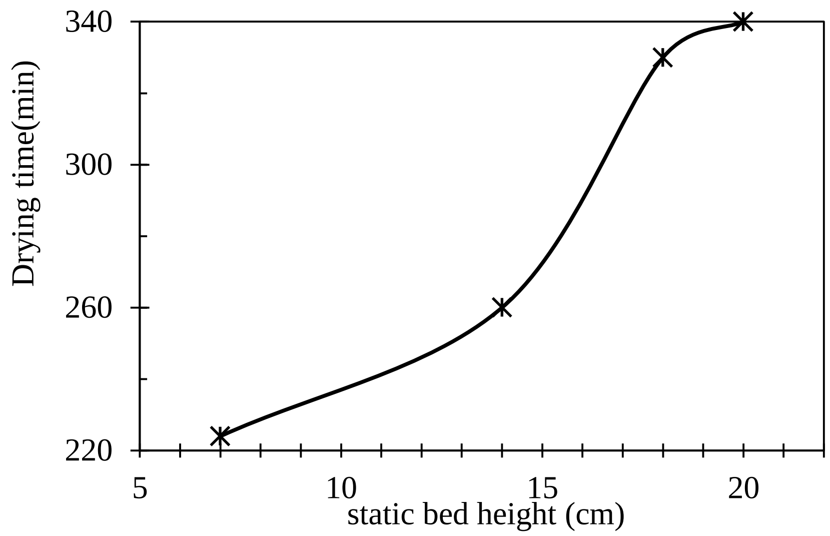


Figure 5.14: Drying time of raw black pepper when dried in conventional spouted bed at different static bed heights; experiment conditions: $D_i$ =0.05 m, $T_d$=65 $^oC$ and air flow of 2.37 m/s

### 5.2.3 Effect of air flow rate

Effect of airflow rate on drying kinetics of black pepper in conventional spouted bed was analyzed. Air velocity was set at 1.6 m/s, 1.97 m/s and 2.37 m/s. Figure 5.15 and Figure 5.16 show the moisture content as a function of time and rate of change of moisture content as a function of moisture content plotted at different air velocities.

Table 5.5, Figure 5.17 and Figure 5.18 show the air requirement for drying of raw black pepper in the conventional spouted bed for different air velocities.

Significant decrease in drying time and increase in drying rate were observed when air velocity changes from 1.6 m/s (closer to minimum spouting velocity) to 1.97 m/s. However, further increase of air velocity up to 2.37 m/s does not show significant change in drying rate or time. Low volume of air is also required for drying at low air velocities. Therefore, it is suitable to adjust the airflow rate just above the minimum spouting velocity to cause stable spouting operation considering the energy and cost involved.

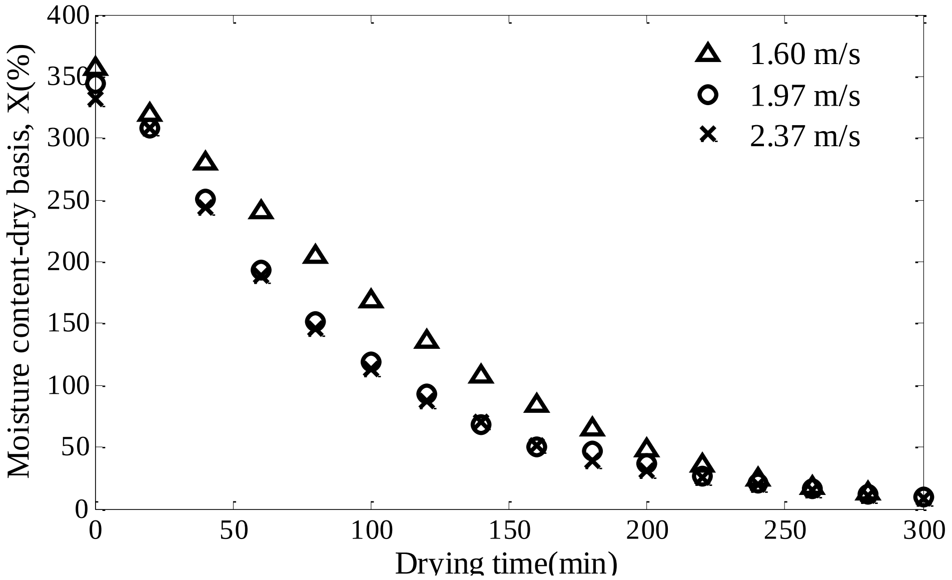



Figure 5.15: Moisture content (% dry basis) vs. time of black pepper when dried in conventional spouted bed dryer at different superficial air velocities; Experiment conditions: $D_i$=0.05 m, $T_d$=65 $^{\circ}$C and H=0.14 m

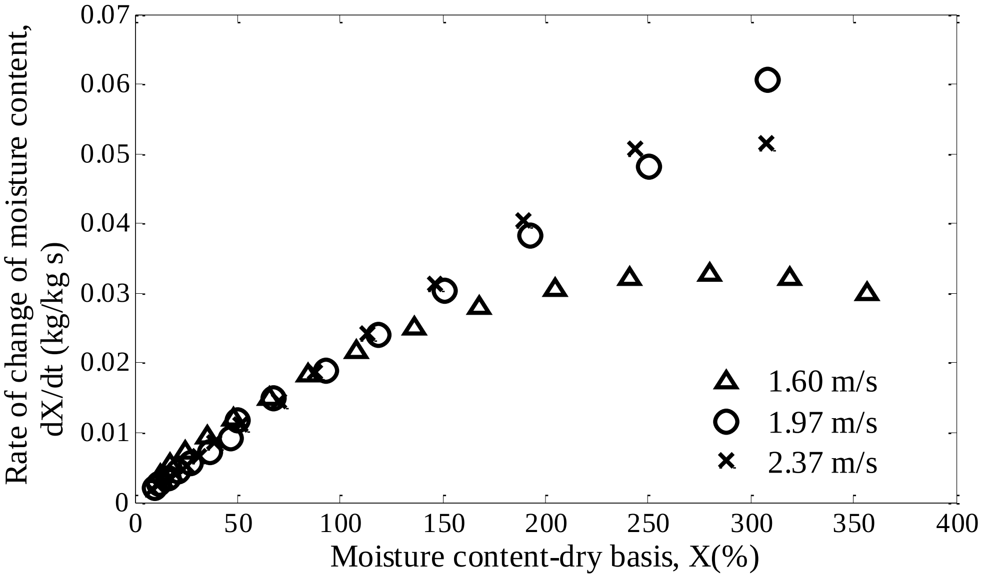



Figure 5.16: Rate of change of moisture content vs. moisture content- dry basis of black pepper when dried in conventional spouted bed at different superificial air velocities; Experiment conditions: $D_i$=0.05 m, $T_d$=65 $^{\circ}$C and H=0.14 m

Table 5.5 : Drying time and volume of air required for raw black pepper when dried in conventional spouted bed dryer at different superficial air velocities; Experiment conditions: $D_i$=0.05 m, $T_d$=65 °C and H=0.14 m

| **Description** | **Superficial air velocity (m/s)** | | |
|---|---|---|---|
| | 2.37 | 1.97 | 1.60 |
| Drying time (min) | 260 | 266 | 270 |
| Volume of air sent throughout the drying period ($m^3$) | 652.96 | 557.16 | 457.89 |
| Volume of air required to evaporate 1kg of moisture ($m^3$) | 890.13 | 751.70 | 612.15 |
| Volume of air required to dry 1kg of raw black pepper ($m^3$) | 652.96 | 557.16 | 457.89 |
| Volume of air required to have 1kg of dried black pepper after drying of raw black pepper ($m^3$) | 2450.69 | 2152.80 | 1816.99 |
| Average moisture removal rate (g/s) | 0.047 | 0.046 | 0.046 |

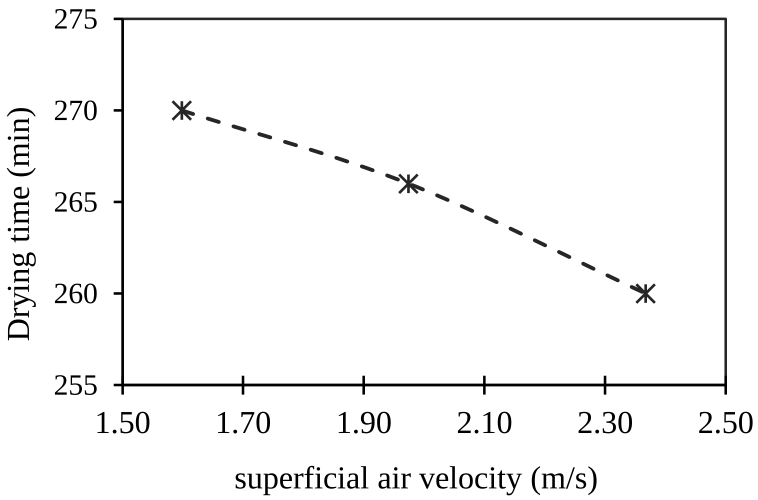



Figure 5.17: Drying time of raw black pepper when dried in conventional spouted bed dryer at different superficial air velocities; Experiment conditions: $D_i$=0.05 m, $T_d$=65 °C and H=0.14 m

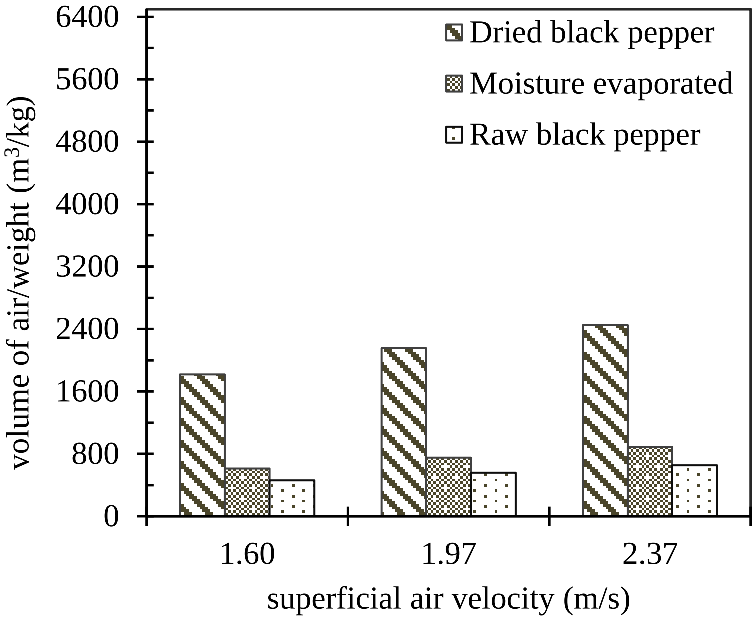



Figure 5.18 : Volume of air required for raw black pepper when dried in conventional spouted bed dryer at different superficial air velocities; Experiment conditions: $D_i$=0.05 m, $T_d$=65 °C and H=0.14 m

However, airflow with superficial velocity of 2.37 m/s was used for the experiments conducted to analyze the effect of drying temperature and bed height as described in section 3.2.1 and 3.2.2. Air velocity of 2.37 m/s was selected to have stable spouting operation with all possible bed heights. Since 2.37 m/s was below the terminal velocity for the shortest bed height; 0.07 m used and it was also above the minimum spouting velocity of maximum spoutable bed height; 0.25 m of the spouted bed column used for the current investigation.

### 5.2.4 Summary on effect of operational variables

Drying air temperature, airflow rate and static bed height have effect on rate of change of moisture content from black pepper. Decreasing the bed height or increasing the air temperature, higher drying rates can be obtained.

High moisture content of black pepper particles provides large driving force for mass transfer at the initial stage of drying. Higher concentration gradient from surface to deeper parts of the particle creates low internal resistance for diffusion of moisture [14]. Therefore, initially drying rates are high as shown in Figure 5.8, Figure 5.12 and Figure 5.16. Further, at initial stage of drying when the moisture content is high, the drying rates at given moisture content show a significant difference with the above operational parameters; temperature, bed height and air flow rate. However, the drying curves overlaps at later stages of drying showing less effect of the above parameters.

Particle has high internal resistance to moisture transfer when the material being dried reaches to low moisture content. Usually high internal moisture resistance is observed at the end of the falling rate period [108]. Therefore, when the drying is progressed, the drying rate gradually falls showing that more energy is required for diffusion of moisture.

## 5.3 Specific energy consumption

Specific Energy Consumption (SEC) defined as in Chapter 2, were calculated based on the Equation 2.8 and the results are presented in Table 5.6 and Figure 5.19. Maximum SEC values of 54.43 MJ/kg, 38.03 MJ/kg and 26.17 MJ/kg were obtained at 55 $^{\circ}$C drying temperature for 0.07 m, 0.14 m and 0.20 m stagnant beds respectively. Then SEC decreased gradually with temperature due to inverse effect of decrease in drying time [21].

Table 5.6 shows that the SEC decreased gradually with increasing static bed height of black pepper in the conventional spouted bed for a particular drying air temperature at selected air velocity. This phenomenon recalls fact that utilization of a larger fraction of thermal energy of hot air at higher static bed heights of the spouted bed as discussed in section 5.2.2.

Figure 5.19 shows that SEC increases with increasing air velocity due to the increase in energy required to heat up higher flow rates of ambient air to drying temperature and the loss of more energy with exhaust air leaving the dryer

Table 5.6: Specific energy consumption for drying of black pepper at different drying temperaures (air velocity 2.37 m/s)

| **Static bed height H (m)** | **Drying temperature $T_d$ ($^{\circ}$C)** | **SEC** | |
|---|---|---|---|
| | | **(MJ/kg of moisture evaporated)** | **(kWh/kg of water removed)** |
| 0.07 | 45 | 33.98 | 9.44 |
| | 55 | 54.43 | 15.12 |
| | 65 | 43.06 | 11.96 |
| | 75 | 54.29 | 15.08 |
| 0.14 | 45 | 32.22 | 8.95 |
| | 55 | 38.03 | 10.56 |
| | 65 | 29.80 | 8.28 |
| | 75 | 26.51 | 7.36 |
| 0.20 | 45 | 21.69 | 6.03 |
| | 55 | 26.17 | 7.27 |
| | 65 | 22.66 | 6.29 |
| | 75 | 16.62 | 4.62 |

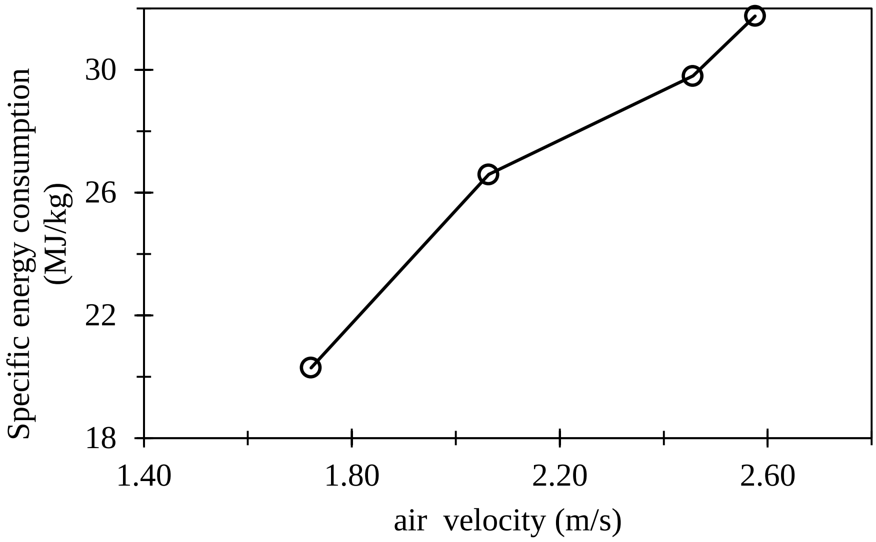



Figure 5.19: Specific energy consumption vs. air velocity for black pepper dried in conventional spouted bed at different superficial air velocities; Experiment conditions: $D_i$ =0.05 m, $T_d$=65 °C and H=0.14 m

### 5.4 Effective moisture diffusivity of raw pepper drying in conventional spouted bed

During drying of particles, moisture diffuses from interior of the particles to the particle surface and moisture transfer to the particle air interface. Effective diffusivity refers to overall transport coefficient that takes into account all the method of moisture transporting from interior to the surface of the particle namely molecular diffusion, liquid diffusion, vapour diffusion, etc. When the drying process has a falling rate period, mass transfer from particles to gas is controlled internally by internal movement of moisture [13].

Data containing moisture content versus time collected from the drying experiments conducted at four different drying air temperatures: 45 °C, 55 °C, 65 °C and 75 °C were converted to moisture ratio values using Equation 2.4. Plots of Logarithmic of moisture ratio (Ln MR) as a function of time were plotted for different drying air temperatures as shown in Figure 5.20. Effective diffusivity ($D_{eff}$) of black pepper at different drying air temperatures were calculated using the gradient of the plots as per the Equation 2.6 and presented in Table 5.7. According to the results, $D_{eff}$ of black pepper depends on drying temperature. In addition, $D_{eff}$ increased with increasing temperature.

Effective diffusivity ($D_{eff}$) values were ranged from $6.05\times 10^{-11}$ $m^2/s$ to $2.03\times 10^{-10}$ $m^2/s$ for the temperatures under investigation and the results are in the same order of magnitude as the results obtained for other agricultural crops such as coffee and peanuts [117].

As shown in Table 5.7, effective diffusivity ($D_{eff}$) of black pepper increases with increasing drying temperatures. Usually with increasing drying temperatures, drying rates or moisture removal rate is increased. Because at high drying temperature, drying air provides high external heat fluxes leading to higher moisture diffusivities and hence higher drying rate [108].

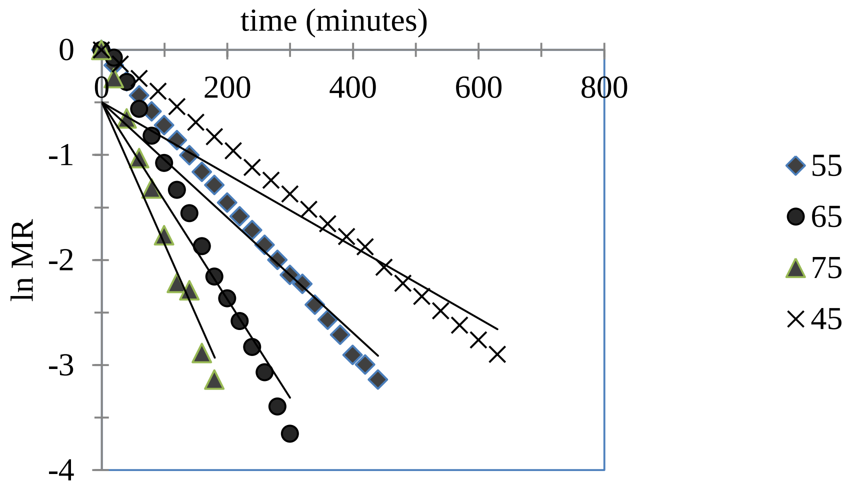



Figure 5.20: Ln (MR) vs time of raw black pepper dried in conventional spouted bed dryer

Natural logarithm of effective diffusivity ($D_{eff}$) vs. reciprocal of absolute drying temperature ($1/T_d$) were plotted and shown in Figure 5.21. The pre-exponential factor ($D_0$) and the activation energy for the raw black pepper dried at conventional spouted bed were calculated using Arrhenius type relationship given in Equation 2.7 and found to be $3.68\times10^{-4}$ $m^2/s$ and 42.41 kJ/mol respectively. This result corresponds well with those given in the literature for drying of different foods: between 18- 42 kJ/mol for corn [21]; between 19 -22 kJ/mol for red apple [109]; and between 49-54 kJ/mol for grapes [16].

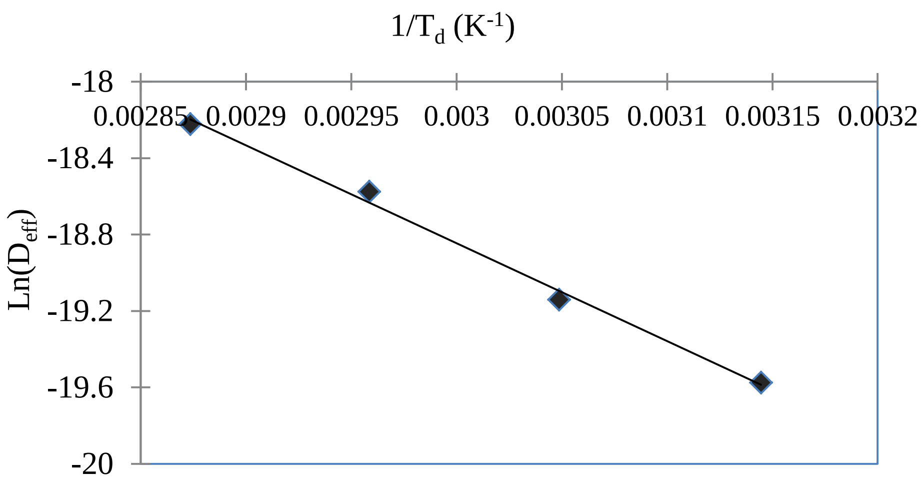



Figure 5.21: Ln (effective diffusivity) vs 1/temperature for raw black pepper dried in conventional spouted bed dryer

Table 5.7 : Effective moisture diffusivity of raw black pepper dried in conventional spouted bed dryer at different temperatures

| **Drying temperature $T_d$ (°C)** | **Effective diffusivity $D_{eff}$ ($m^2/s$)** | **$R^2$ of the plot** |
|---|---|---|
| 45 | $4.00 \times 10^{-11}$ | 0.9141 |
| 55 | $6.28 \times 10^{-11}$ | 0.9304 |
| 65 | $1.07 \times 10^{-10}$ | 0.9138 |
| 75 | $1.55 \times 10^{-10}$ | 0.9151 |

## 5.6 Mathematical modeling of drying kinetics

Drying experiments were conducted for four different stagnant bed heights of raw black pepper at four different drying air temperatures as described in section 3.1.6.4. Moisture content of drying material was recorded at selected time intervals and moisture content was normalized to moisture ratio.

Five thin layer drying models namely Newton, Page, Henderson and Pabis, Two compartment and Logarithmic model were used to fit the drying behaviour of black pepper drying in the conventional spouted bed. RMSE, SSE and coefficient of determination ($R^2$) were calculated to identify the best model which describes the thin layer drying behaviour.

RMSE value closer to zero or very low indicates that the model has a smaller random error component, and that the fit will be more useful for prediction. Just as with RMSE value, SSE value closer to 0 shows model is useful for prediction. $R^2$ can take on any value between 0 and 1, with a value closer to 1 indicating that a greater proportion of variance is accounted for by the model.

Five thin layer drying models developed for black pepper for each drying temperature and initial stagnant bed height in spouted bed dryer are shown in Table 5.8 to Table 5. 12. Statistical parameters $R^2$, RMSE and SSE which measure goodness of the fit were also presented together with the developed thin layer drying models. According to the statistical analysis, all the models were found to be satisfactorily described the drying behaviour of black pepper dried in spouted bed.

Table 5.8: Newton model developed for black pepper drying in conventional spouted bed for various stagnant bed heights and drying air temperatures at 2.37 m/s of air velocity

| **$T_d$ (°C)** | **H (m)** | **Newton model** $\boldsymbol{MR = \exp(-kt)}$ | **$R^2$** | **RMSE** | **SSE** |
|---|---|---|---|---|---|
| 45 | 14 | $MR = \exp(-0.0091t)$ | 0.9980 | 0.0133 | 0.0030 |
| | 18 | $MR = \exp(-0.0101t)$ | 0.9983 | 0.0126 | 0.0017 |
| | 20 | $MR = \exp(-0.0041t)$ | 0.9971 | 0.0154 | 0.0062 |
| | 22 | $MR = \exp(-0.0038t)$ | 0.9965 | 0.0162 | 0.0078 |
| 55 | 14 | $MR = \exp(-0.0066\ t)$ | 0.9902 | 0.0296 | 0.0193 |
| | 18 | $MR = \exp(-0.0052t)$ | 0.9937 | 0.0229 | 0.0110 |
| | 20 | $MR = \exp(-0.0064t)$ | 0.9939 | 0.0231 | 0.0091 |
| | 22 | $MR = \exp(-0.0057t)$ | 0.9958 | 0.0184 | 0.0102 |
| 65 | 7 | $MR = \exp(-0.0131t)$ | 0.9960 | 0.0191 | 0.0044 |
| | 14 | $MR = \exp(-0.0106t)$ | 0.9938 | 0.02271 | 0.0088 |
| | 18 | $MR = \exp(-0.0091t)$ | 0.9980 | 0.0133 | 0.0030 |
| | 20 | $MR = \exp(-0.0101t)$ | 0.9983 | 0.0126 | 0.0017 |
| | 22 | $MR = \exp(-0.0052t)$ | 0.9956 | 0.0199 | 0.0075 |
| 75 | 14 | $MR = \exp(-0.0175t)$ | 0.9975 | 0.0161 | 0.0023 |
| | 18 | $MR = \exp(-0.0137t)$ | 0.9957 | 0.0204 | 0.0050 |
| | 20 | $MR = \exp(-0.01404t)$ | 0.9956 | 0.0215 | 0.0046 |
| | 22 | $MR = \exp(-0.0091t)$ | 0.9985 | 0.0114 | 0.0022 |

Table 5.8 summarizes the statistical analysis of Newton model developed for black pepper drying in conventional spouted bed for various stagnant bed heights and drying air temperatures at 2.37 m/s of air velocity. According to Table 5.8, $R^2$, RMSE and SSE values ranged from 0.9902 to 0.9985, 0.0114 to 0.0296 and 0.0017 to 0.0193 respectively.

Table 5.9: Page's model developed for black pepper drying in conventional spouted bed for various stagnant bed heights and drying air temperatures at 2.37 m/s of air velocity

| $T_d$ (°C) | H (m) | Page model $MR = \exp(-k\,t^n)$ | $R^2$ | RMSE | SSE |
|---|---|---|---|---|---|
| 45 | 14 | $MR = \exp(-0.0091t^1)$ | 0.9980 | 0.0133 | 0.0030 |
| | 18 | $MR = \exp(-0.0100t^{0.9900})$ | 0.9983 | 0.0132 | 0.0017 |
| | 20 | $MR = \exp(-0.0040t^1)$ | 0.9971 | 0.0154 | 0.0062 |
| | 22 | $MR = \exp(-0.0045t^{0.9701})$ | 0.9968 | 0.0157 | 0.0071 |
| 55 | 14 | $MR = \exp(-0.0066t^1)$ | 0.9902 | 0.0296 | 0.0193 |
| | 18 | $MR = \exp(-0.0052t^1)$ | 0.9937 | 0.0229 | 0.0110 |
| | 20 | $MR = \exp(-0.0064t^1)$ | 0.9939 | 0.0231 | 0.0091 |
| | 22 | $MR = \exp(-0.0057t^1)$ | 0.9958 | 0.0184 | 0.0102 |
| 65 | 7 | $MR = \exp(-0.0130\ t^{0.9993})$ | 0.9960 | 0.0199 | 0.0044 |
| | 14 | $MR = \exp(-0.01061\ \ t^1)$ | 0.9939 | 0.0233 | 0.0087 |
| | 18 | $MR = \exp(-0.0091t^1)$ | 0.9980 | 0.0133 | 0.0030 |
| | 20 | $MR = \exp(-0.0101t^{0.9900})$ | 0.9983 | 0.0132 | 0.0017 |
| | 22 | $MR = \exp(-0.0057t^1)$ | 0.9956 | 0.0199 | 0.0075 |
| 75 | 14 | $MR = \exp(-0.0175t^1)$ | 0.9978 | 0.0162 | 0.0021 |
| | 18 | $MR = \exp(-0.0175t^1)$ | 0.9957 | 0.0204 | 0.0050 |
| | 20 | $MR = \exp(-0.0141t^1)$ | 0.9956 | 0.0215 | 0.0046 |
| | 22 | $MR = \exp(-0.0091\ t^1)$ | 0.9985 | 0.0114 | 0.0022 |

Table 5.9 shows the statistical analysis of Page model developed for black pepper drying in conventional spouted bed for various stagnant bed heights and drying air temperatures at 2.37 m/s of air velocity. $R^2$, RMSE and SSE values ranged from 0.9902 to 0.9985, 0.0114 to 0.0296 and 0.0017 to 0.0193 respectively.

Table 5.10: Henderson and Pabis model developed for black pepper drying in conventional spouted bed for various stagnant bed heights and drying air temperatures at 2.37 m/s of air velocity

| **$T_d$ (°C)** | **H (cm)** | **Henderson and Pabis model** $MR = a\exp(-kt)$ | **$R^2$** | **RMSE** | **SSE** |
|---|---|---|---|---|---|
| 45 | 14 | $MR = 1.021\exp(-0.0093t)$ | 0.9985 | 0.0117 | 0.0022 |
| | 18 | $MR = 0.9964\exp(-0.0100t)$ | 0.9983 | 0.0131 | 0.0017 |
| | 20 | $MR = 1.02\exp(-0.0041t)$ | 0.9979 | 0.0135 | 0.0045 |
| | 22 | $MR = 0.9939\exp(-0.0037t)$ | 0.9965 | 0.0163 | 0.0077 |
| 55 | 14 | $MR = 1.046\exp(-0.0069t)$ | 0.9928 | 0.0260 | 0.0142 |
| | 18 | $MR = 1.017\exp(-0.0053t)$ | 0.9941 | 0.0228 | 0.0104 |
| | 20 | $MR = 1.016\exp(-0.0065t)$ | 0.9942 | 0.0232 | 0.0086 |
| | 22 | $MR = 1.014\exp(-0.0058t)$ | 0.9960 | 0.0182 | 0.0097 |
| 65 | 7 | $MR = 1.005\exp(-0.0130t)$ | 0.9960 | 0.0182 | 0.0097 |
| | 14 | $MR = 1.007\exp(-0.0107t)$ | 0.9939 | 0.0233 | 0.0087 |
| | 18 | $MR = 1.021\exp(-0.0093t)$ | 0.9985 | 0.0117 | 0.0022 |
| | 20 | $MR = 0.9964\exp(-0.0099t)$ | 0.9983 | 0.0131 | 0.0017 |
| | 22 | $MR = 1.038\exp(-0.0053t)$ | 0.9974 | 0.0156 | 0.0044 |
| 75 | 14 | $MR = 1.014\exp(-0.0177t)$ | 0.9978 | 0.0162 | 0.0021 |
| | 18 | $MR = 1.015\exp(-0.0139t)$ | 0.9960 | 0.0206 | 0.0047 |
| | 20 | $MR = 1.028\exp(-0.0144t)$ | 0.9967 | 0.0196 | 0.0035 |
| | 22 | $MR = 1.011\exp(-0.0093t)$ | 0.9987 | 0.0111 | 0.0020 |

Table 5.10 shows the statistical analysis of Henderson and Pabis model developed for black pepper drying in conventional spouted bed for various stagnant bed heights and drying temperatures at 2.37 m/s of air velocity. $R^2$, RMSE and SSE values were ranged from 0.9928 to 0.9985, 0.0111 to 0.0260 and 0.0017 to 0.0142 respectively.

Table 5. 11: Two compartment model developed for black pepper drying in conventional spouted bed for various stagnant bed heights and drying air temperatures at 2.37 m/s of air velocity

| $T_d$ (°C) | H (cm) | **Two compartment model** $MR = a\exp(-k_1 t) + b\exp(-k_2 t)$ | $R^2$ | RMSE | SSE |
|---|---|---|---|---|---|
| 45 | 14 | $MR = 0.4825\exp(-0.0093t) + 0.5377\exp(-0.0093t)$ | 0.9985 | 0.0125 | 0.0022 |
| | 18 | $MR = 0.512\exp(-0.0101t) + 0.4843\exp(-0.0099t)$ | 0.9983 | 0.0147 | 0.0017 |
| | 20 | $MR = -1.432\exp(-0.0040t) + .457\exp(-0.0041t)$ | 0.9979 | 0.0140 | 0.0045 |
| | 22 | $MR = 0.05509\exp(-0.0037t) + 0.9390\exp(-0037t)$ | 0.9965 | 0.0169 | 0.0077 |
| 55 | 14 | $MR = 0.5646\exp(-0.0070t) + .4818\exp(-0.0069t)$ | 0.9928 | 0.0273 | 0.0142 |
| | 18 | $MR = 0.7296\exp(-0.0053t) + .2876\exp(-0.0053t)$ | 0.9941 | 0.0240 | 0.0104 |
| | 20 | $MR = 0.1765\exp(-0.0065t) + 0.8394\exp(-.0065t)$ | 0.9942 | 0.0248 | 0.0086 |
| | 22 | $MR = -0.06805\exp(-0.0058t) + 1.081\exp(-.0058t)$ | 0.9960 | 0.0189 | 0.0097 |
| 65 | 7 | $MR = 0.5024\exp(-0.0131t) + 0.5024\exp(-0.0131t)$ | 0.9961 | 0.0220 | 0.0043 |
| | 14 | $MR = 0.0065\exp(0.0044t) + 1.011\exp(-0.0113t)$ | 0.9955 | 0.0214 | 0.0064 |
| | 18 | $MR = 0.4825\exp(-0.0093t) + 0.5377\exp(-0.0093t)$ | 0.9985 | 0.0125 | 0.0022 |
| | 20 | $MR = 0.512\exp(-0.0101t) + 0.4843\exp(-0.0099t)$ | 0.9983 | 0.0147 | 0.0017 |
| | 22 | $MR = -0.0026\exp(-0.0054t) + 1.04\exp(-0.0053t)$ | 0.9974 | 0.0165 | 0.0044 |
| 75 | 14 | $MR = -0.069\exp(-0.0174t) + 1.08\exp(-0.0176t)$ | 0.9978 | 0.0187 | 0.0021 |
| | 18 | $MR = 0.3968\exp(-0.0139t) + 0.6177\exp(-0.0139t)$ | 0.9960 | 0.0227 | 0.0047 |
| | 20 | $MR = 0.5207\exp(-0.0144t) + 0.5069\exp(-0.0144t)$ | 0.9967 | 0.0222 | 0.0035 |
| | 22 | $MR = 0.4774\exp(-0.0094t) + 0.532\exp(-0.0091t)$ | 0.9987 | 0.0119 | 0.0020 |

Table 5. 11 shows the statistical analysis of Two Compartment model developed for black pepper drying in conventional spouted bed for various stagnant bed heights and drying temperatures at 2.37 m/s of air velocity. $R^2$, RMSE and SSE values ranged from 0.9928 to 0.9987, 0.0119 to 0.0273 and 0.0009 to 0.0142 respectively.

Table 5. 12: Logarithmic model developed for black pepper drying in conventional spouted bed for various stagnant bed heights and drying air temperatures at 2.37 m/s of air velocity

| $T_d$ (°C) | $H_o$ (cm) | Logarithmic model $MR = a\, exp(-kt) + b$ | $R^2$ | RMSE | SSE |
|---|---|---|---|---|---|
| 45 | 14 | $MR = 1.027\ exp(-0.0091\, t) - 0.0107$ | 0.9987 | 0.0116 | 0.0020 |
| | 18 | $MR = 0.9979 exp(-0.0099\, t) - 0.0023$ | 0.9970 | 0.0162 | 0.0055 |
| | 20 | $MR = 1.027\ exp(-0.0041\ t) - 0.0028$ | 0.9979 | 0.0137 | 0.0045 |
| | 22 | $MR = 0.9854\, exp(-0.0040\ t) + 0.0184$ | 0.9971 | 0.0152 | 0.0065 |
| 55 | 14 | $MR = 1.07\ exp(-0.0064\, t) - 0.0367$ | 0.9940 | 0.0242 | 0.0117 |
| | 18 | $MR = 1.018\ exp(-0.0053t) - 0.0011$ | 0.9941 | 0.0234 | 0.0104 |
| | 20 | $MR = 1.022\ exp(-\ 0.0063\, t) - 0.0088$ | 0.9943 | 0.0237 | 0.0085 |
| | 22 | $MR = 1.033\ exp(-0.0053t) - 0.0342$ | 0.9976 | 0.0143 | 0.0058 |
| 65 | 7 | $MR = 1.003\ exp(-0.0131t) - 0.0022$ | 0.9961 | 0.0208 | 0.0043 |
| | 14 | $MR = 0.9979 exp(-0.0099\, t) - 0.0023$ | 0.9983 | 0.0138 | 0.0017 |
| | 18 | $MR =\ 0.9925 exp(-0.0116t) + 0.0271$ | 0.9954 | 0.0209 | 0.0066 |
| | 20 | $MR = 1.027\, exp(-0.0091\, t) - 0.0107$ | 0.9987 | 0.0116 | 0.0020 |
| | 22 | $MR = 1.054\, exp(-0.0050t - 0.0242$ | 0.9980 | 0.0142 | 0.0034 |
| 75 | 14 | $MR =\ 1.017\, exp(-0.0175\ t) - 0.0045$ | 0.9978 | 0.0172 | 0.0021 |
| | 18 | $MR = 1.019\ exp(-0.0136\, t) - 0.0065$ | 0.9960 | 0.0214 | 0.0046 |
| | 20 | $MR = 1.072 exp(-\ 0.0125\, t) - 0.0591$ | 0.9992 | 0.0104 | 0.0009 |
| | 22 | $MR = 1.018\ exp(-0.0089t) - 0.0113$ | 0.9988 | 0.0108 | 0.0018 |

According to the statistical analysis of Logarithmic model developed, $R^2$, RMSE and SSE values ranged from 0.9940 to 0.9992 , 0.0104 to 0.0242 and 0.0117 to 0.0009.

Drying rate constant , k value for Newton models are in the range of 0.003-0.018 per minute, 0.003-0.017 per minute for k value of both Logarithmic model and Henderson & Pabis model. Value of constant ‘a’ in the Henderson and Pabis model is varied between 0.99- 1.04 which imply constant ‘a’ is approximately equal to 1. Values of constant, n, in the Page model are approximately equal to the one. This can be compared with the Newton model and the Henderson and Pabis model where ‘A’ term is not appearing, which denotes the constant ‘a’ is equal to the one. In addition ‘a’ values of Logarithmic model also fluctuate in 0.98 to 1.07 where it is approximately equal to one. Further, the very low parameter ‘b’ values which fluctuate in -0.05 to 0.02 shows that the effect of the second term in the Logarithmic model is less significant. The above comparison of the parameters shows the similarity of the four models namely Newton, Page, Hendeson & Pabis and Logarithmic equations valid for drying of black pepper in spouted bed. A Similar trend has been shown for the microwave drying of black pepper also [118].

Also $k_1$ and $k_2$ values of Two Compartment models are almost similar for many runs while summation of drying constants ‘a’ and ‘b’ of every run is approximately equal to the one also.

Considering the statistical analysis as mentioned in Table 5.8 to Table 5. 12, Logarithmic models was appeared to be the best fitting model due to highest $R^2$ and lowest RMSE and SSE values. In addition, it has been appeared as the best model for many runs. Figure 5.22 to Figure 5.24 show that good relationship between observed moisture ratio with predicted moisture ratio from Logarithmic model of black pepper in conventional spouted bed dryer at different drying air temperatures for selected three bed heights.

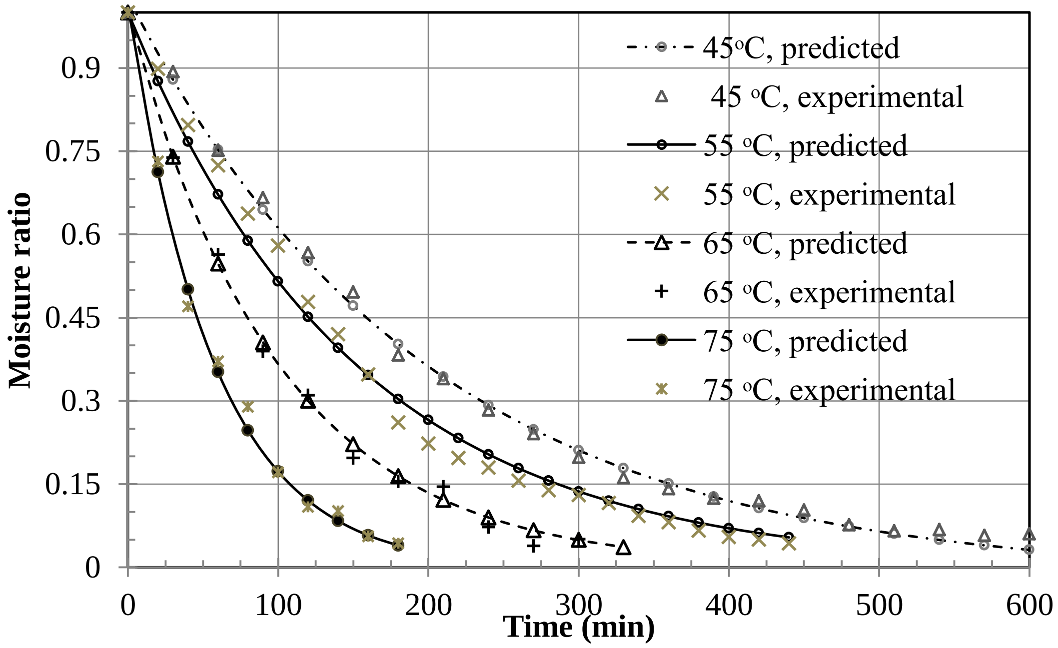



Figure 5.22: A comparison between the experimental moisture ratio and predicted moisture ratio (using Logarithmic model) of black pepper dried in various temperatures at static 0.14 m bed height

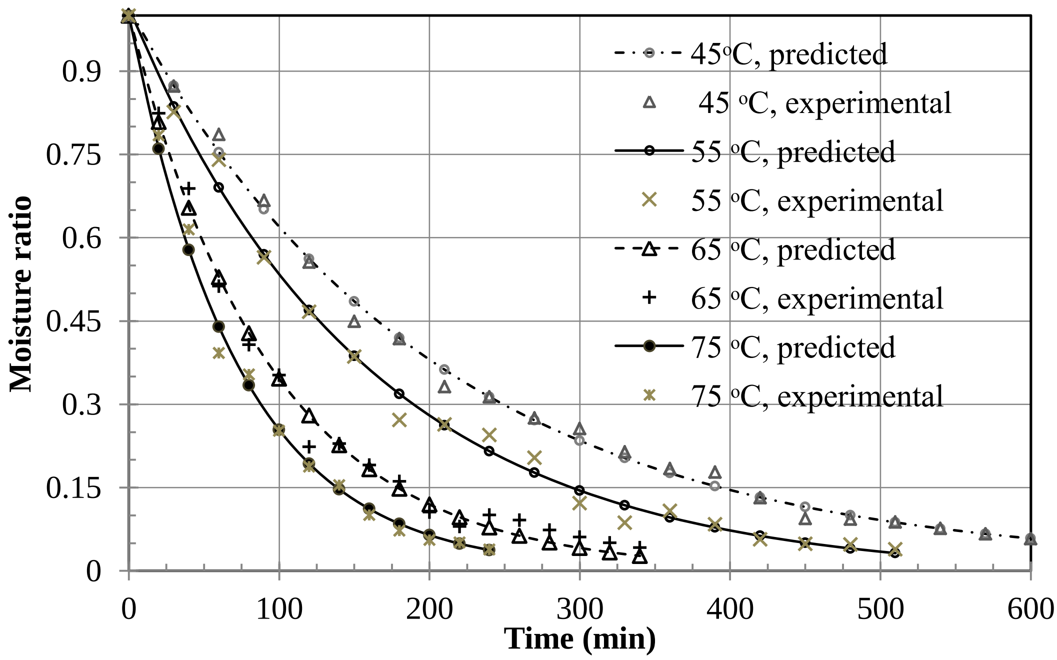



Figure 5.23: A comparison between the experimental moisture ratio and predicted moisture ratio (using Logarithmic model) of black pepper dried in various temperatures at static 0.10 m bed height

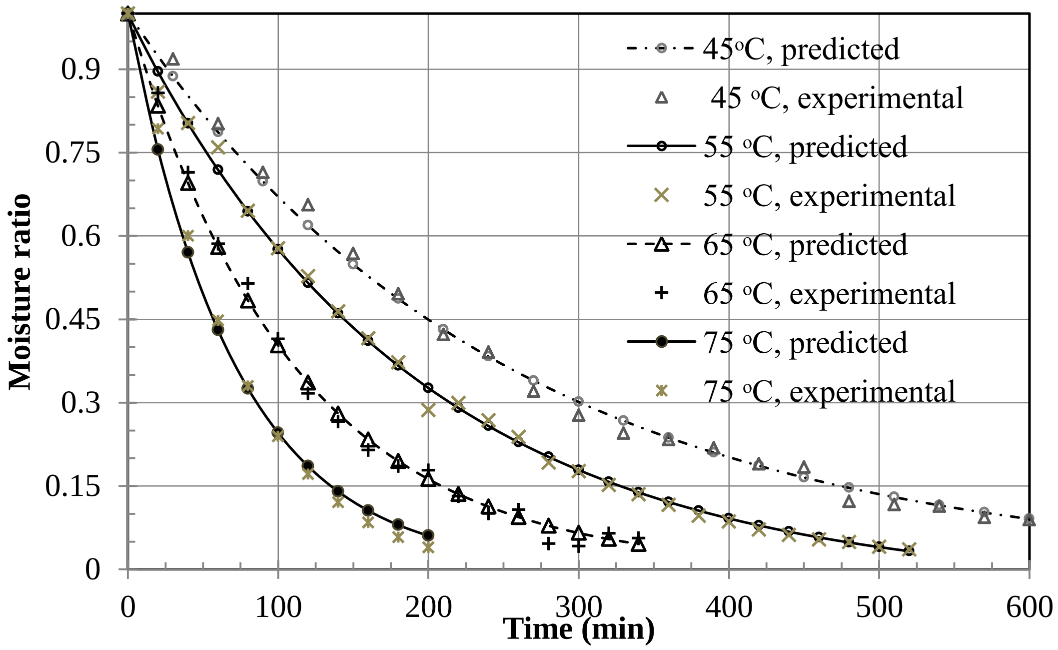



Figure 5.24: A comparison between the experimental moisture ratio and predicted moisture ratio (using Logarithmic model) of black pepper dried in various temperatures at static 0.20 m bed height

The developed models shown in Table 5.8 to Table 5. 12 can be used for the specified drying conditions only. Therefore, four additional models were introduced for black pepper drying in conventional spouted bed by correlating drying constants and coefficients of Logarithmic model shown in Table 5. 12 to stagnant bed height only at specified temperatures; 45 °C, 55 °C, 65 °C, and 75 °C. The optimal results of the models for black pepper drying from 45-75 °C are given in Table 5. 13. The model constants and coefficients are as follows:

Logarithmic model is derived from the Henderson and Pabis model, which related to the first term of the analytical solution of the diffusion equation. Logarithmic model can describe the black pepper drying process in spouted bed for 45-75 °C drying temperatures as a function of initial stagnant bed height. Modified equations for spouted bed drying black pepper are shown Table 5. 14.

Table 5. 13: The results of the multiple regressions on the coefficients and constants of the logarithmic model for the effects of the stagnant bed height

| $T_d$ (°C) | coefficient | equation | $R^2$ |
|---|---|---|---|
| 45 | a | $1.0720 + 0.5630H - 1.8660\ H^2$ | 0.6780 |
| | k | $0.0021 + 0.0441\ H - 0.1650\ H^2$ | 0.8499 |
| | b | $-0.0750 + 0.4097\ H$ | 0.7723 |
| 55 | a | $1.442 - 4.0191\ H + 9.5455\ H^2$ | 0.8818 |
| | k | $0.0031 + 0.0475\ H - 0.175\ H^2$ | 0.7655 |
| | b | $-0.2944 + 2.7289\ H - 6.3441\ H^2$ | 0.9999 |
| 65 | a | $1.452 - 5.790\ H + 18.15\ H^2$ | 0.9649 |
| | k | $-0.05885 + 0.8442\ H - 2.519\ H^2$ | 0.9967 |
| | b | $0.5728 + 6.913\ H - 20.19\ H^2$ | 0.7965 |
| 75 | a | $0.9864 + 0.35H - 0.9375\ H^2$ | 0.9900 |
| | k | $0.0318 - 0.1010\ H$ | 0.9647 |
| | b | $0.0079 - 0.0852H$ | 0.9462 |

Table 5. 14: Modified Logarithmic model for black pepper drying for 45 °C - 75 °C

| $T_d$ (°C) | Modified Logarithmic model | $R^2$ | Equation No |
|---|---|---|---|
| 45 | $MR = (1.0720 + 0.5630\ H - 1.866\ H^2) \exp(0.0021 + 0.0441\ H - 0.1650\ H^2)\ t + (-0.075 + 0.4097\ H)$ | 0.8897 | 5.3 |
| 55 | $MR = (1.442 - 4.0191\ H + 9.5455\ H^2) \exp(0.0031 + 0.0475\ H - 0.1750 H^2) t + (-0.2944 + 2.7289\ H - 6.3441\ H^2)$ | 0.9935 | 5.4 |
| 65 | $MR = (1.4520 - 5.79H + 18.15\ H^2) \exp((-0.05885 + 0.8442\ H - 2.519\ H^2)\ t + (0.5728 + 6.913\ H - 20.19\ H^2)$ | 0.9960 | 5.5 |
| 75 | $MR = (0.9864 + 0.3500H - 0.9375\ H^2) \exp((0.0318 - 0.1010\ H) t) + (0.0079 - 0.0852H)$ | 0.9893 | 5.6 |

Equations 5.3 to 5.6 in Table 5. 14 are the modified Logarithmic model. They can be used to estimate the drying time of black pepper in a spouted bed dryer for given moisture reduction. It shows that those models satisfactorily represented the drying of black pepper in the ranges of 45-75 °C air temperature, 0.14 -0.22 m stagnant bed heights and in 2.37 m/s air velocity.

Figure 5.25 to Figure 5.28 show that these models shown in Equations 5.3 to 5.6 are in good agreement with the experimental results under all drying conditions. Figure 5.29 to Figure 5.32 show comparison of experimental moisture ratio and the predicted moisture ratio estimated using developed models (Equations 5.3 to 5.6).
When comparing the experimental moisture ratio values with the predicted values estimated using developed models at any particular drying condition, the values lay around a straight line for black pepper. This means that the modified model is valid at drying air temperatures of 45-75 °C and velocities 2.37 $ms^{-1}$.

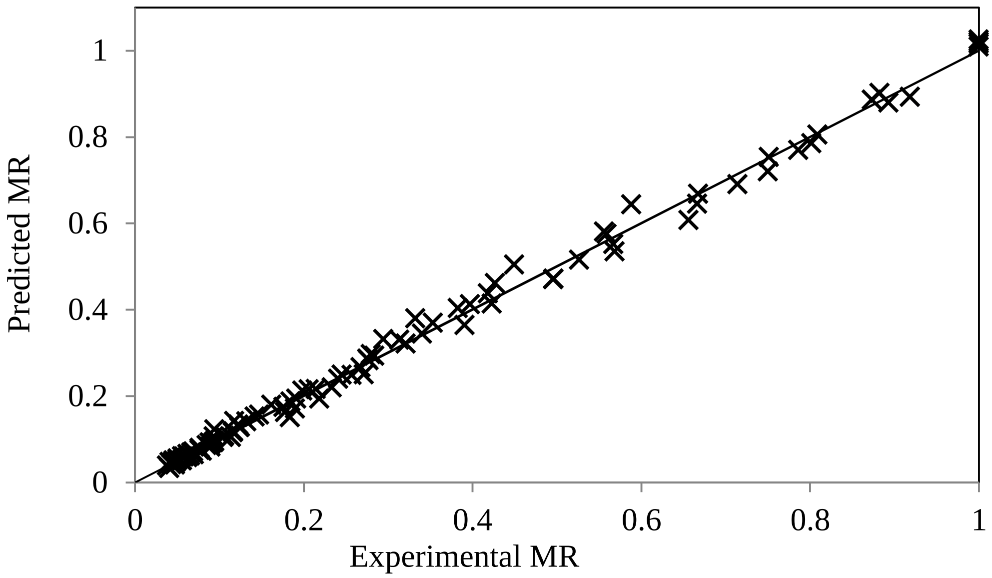



Figure 5.25: A comparison between the experimental moisture ratio and predicted moisture ratio of black pepper dried in 45 °C

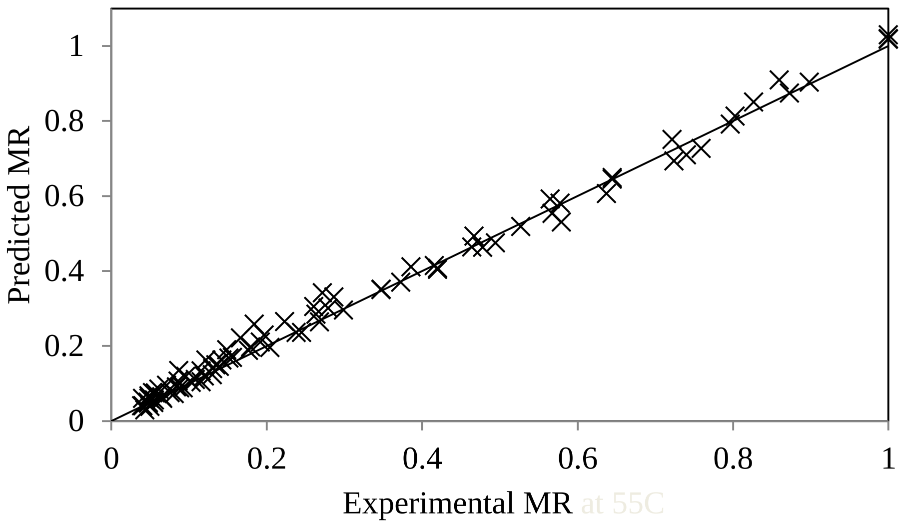



Figure 5.26: A comparison between the experimental moisture ratio and predicted moisture ratio of black pepper dried in 55 °C

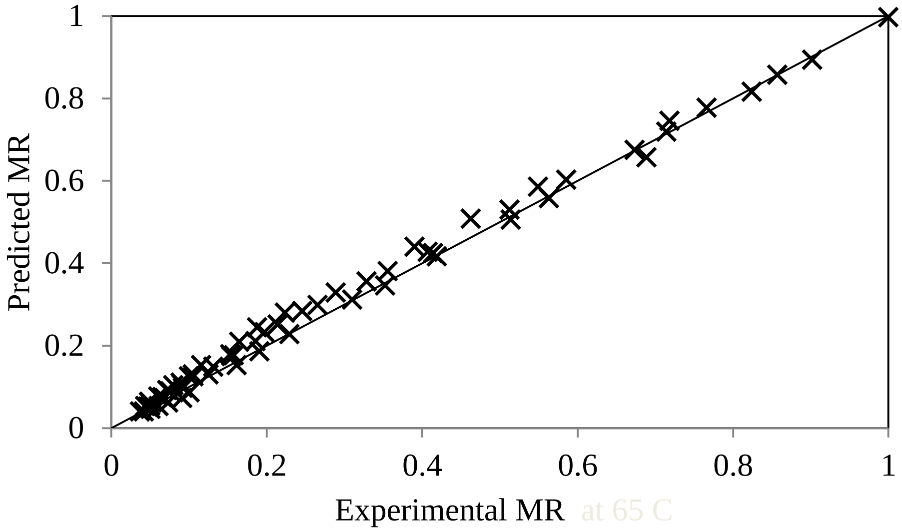



Figure 5.27: A comparison between the experimental moisture ratio and predicted moisture ratio of black pepper dried in 65 °C

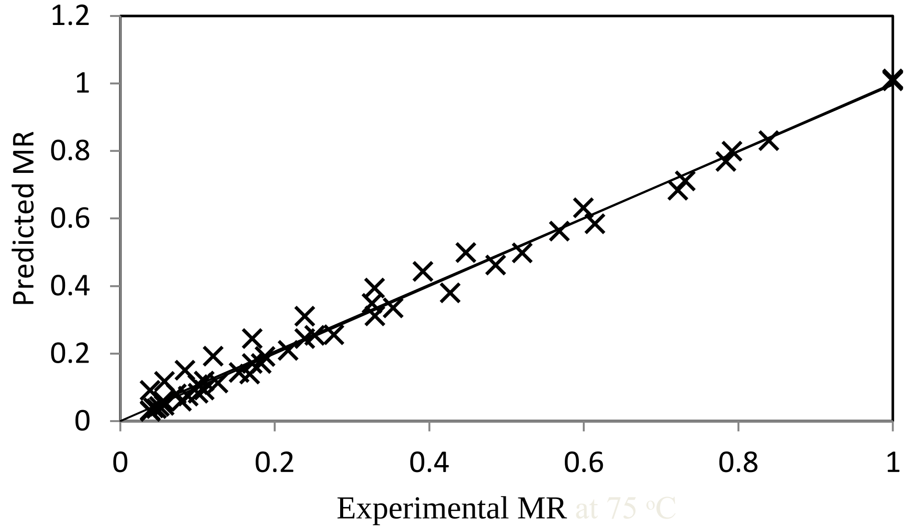



Figure 5.28: A comparison between the experimental moisture ratio and predicted moisture ratio of black pepper dried in 75 °C

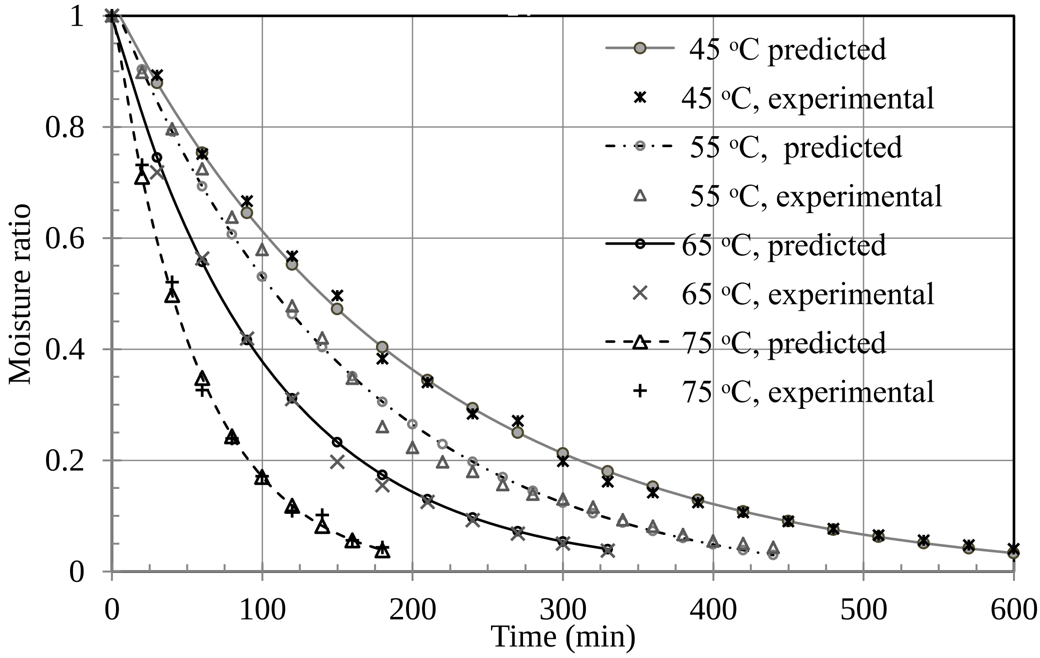



Figure 5.29: A comparison between the experimental moisture ratio and predicted moisture ratio of black pepper dried in various temperatures at static 0.14 m bed height

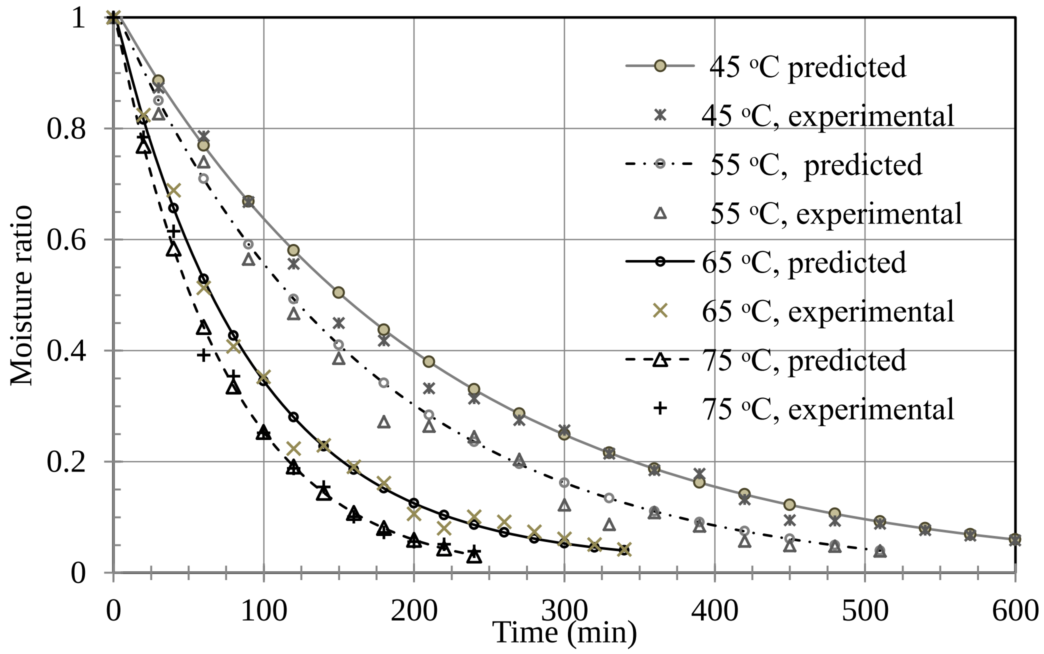



Figure 5.30: A comparison between the experimental moisture ratio and predicted moisture ratio of black pepper dried in various temperatures at static 0.18 m bed height

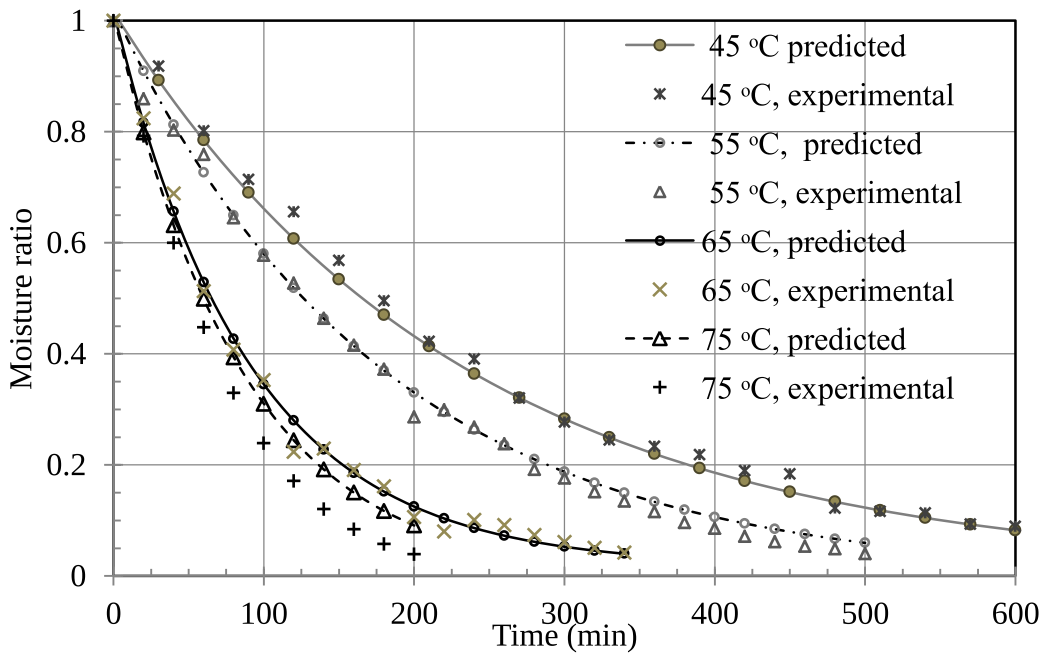



Figure 5.31: A comparison between the experimental moisture ratio and predicted moisture ratio of black pepper dried in various temperatures at static 0.20 m bed height

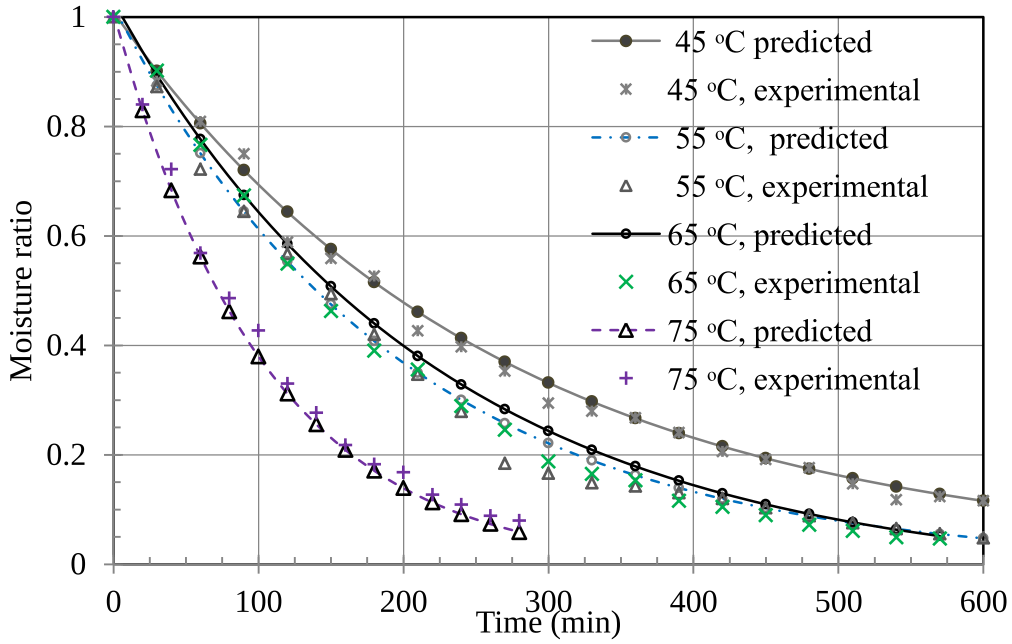



Figure 5.32: A comparison between the experimental moisture ratio and predicted moisture ratio of black pepper dried in various temperatures at static 0.22 m bed height

**Chapter specific nomenclature**

$D_{eff}$ -effective moisture diffusivity ($m^2/s$)

$D_i$ - gas inlet diameter (m)

$D_o$ -pre exponential factor of Arrhenius equation

$E_a$ -activation energy (kJ/mol)

$H_o$ -static bed height (m)

$T_d$ - drying air temperature at the inlet of the drying chamber (°C)

$U_{ms}$ -minimum spouting velocity (m/s)

X - moisture content ( kg moisture/ kg dry solid)

$\Delta P_M$ - Peak pressure drop ($N/m^2$)

**Abbreviations**

MR - Moisture ratio

$R^2$ - Coefficient of determination

RMSE - Root mean square error

SEC - Specific energy consumption

SSE - Sum of square  error

**Chapter 6**

# 6. ANALYSIS OF QUALITY OF BLACK PEPPER

This chapter presents the investigations on the essential oil derived from black pepper dried at different drying conditions. This investigation consists of the extraction and analysis of essential oil using GC-MS technique and essential oil yield.

Thermal operations can cause degradation and evaporation of some compounds. Hence, a percentage of certain compounds, which are responsible to generate aroma and pungency of black pepper can be loss during the drying process. Main pungent component of black pepper is non-volatile but most of the aroma compounds in black pepper are volatile [5]. Loss of pungent component is negligible compared to aroma compounds in black pepper during a thermal operation. Therefore, our investigation is focussed to analyse the volatile components of black pepper dried in the conventional spouted bed. As a result of this analysis, optimum drying conditions will be identified for black pepper drying in conventional spouted bed to achieve maximum yield of essential oil with consistent quality.

## 6.1 Analysis of black pepper essential oil

Essential oil extracted from black pepper dried at five different drying conditions were analysed using Gas Chromatography Mass Spectrometry technique. Five different drying conditions are sun drying and spouted bed dying at 45 $^{\circ}$C, 55 $^{\circ}$C, 65 $^{\circ}$C and 75 $^{\circ}$C drying air temperatures with minimum spouting conditions. Section 3.1.6.5 gives more information on the preparation of essential oil. Twenty chromatograms of black pepper essential oil were studied as each experiment was replicated. Appendix D shows the chromatograms of 20 black pepper essential oil samples with their gas chromatography data sheets.

Approximately 230 components were identified in the essential oil extracted from the black pepper dried under sun radiation and spouted bed dryer. Mean composition of each components at different drying conditions are listed in Table 1 in Appendix E. The analysis of components shows that the black pepper oil comprised mainly monoterpenes and sesquiterpenes. 13-66% of total oil was monoterpenes while 24-47% of total oil was sesquiterpenes. Table 6.1 presents a quantitative analysis of terpenes presents in essential oil extracted from black pepper dried under different drying conditions. Moreover, Table 2 in Appendix E presents the percentage of specific constituents in terpenes in essential oil extracted from black pepper dried at different drying conditions. In addition, Figure 6.1 shows the mean percentage of components in black pepper oil.

Oxygenated terpenes are the minor constituents consisting average percentage of 13-23% of total oil for all five different drying conditions. Terpenes and terpene oxide are present up to 97-99.9% of total oil while remaining components are in trace amounts.

Table 6.2 lists out the concentration and the formula of the ten most abundant components of black pepper essential oil which were Caryophyllene (14.79 %), D limonene(13.72 %), Caryophyllene oxide(11.53 %), α-Copaene (8.19 %), (1R)- α -Pinene(6.98 %), α-Pinene(6.85 %), α-Cubebene (6.43 %), L-β-Pinene(5.71 %), Sabinene(5.61 %) and δ3-p-Menthene(4.83 %) under this investigation.

Abundant sesquiterpene present in black pepper essential oil was found to be caryophyllene and this factor has been also confirmed by Parthasarathy et. al. [119]. D limonene is the abundant monoterpene present in black pepper essential oil under our investigation however many literature reports that α-pinene and β pinene as the dominant monoterpene components in black pepper essential oil [95, 96] .

Table 6.1: Constituents of essential oil extracted from black pepper dried under different drying conditions

| Sample No | % percentage of components | | | | |
|---|---|---|---|---|---|
| | **Drying condition** | **monoterpene** | **oxygeneted monoterpene** | **sesquiterpene** | **oxygenated sesquterpene** |
| 1 | Sun dried | 41.79 | 15.12 | 30.89 | 5.60 |
| 2 | Sun dried | 50.56 | 7.22 | 32.69 | 4.56 |
| 3 | Sun dried | 37.11 | 14.02 | 24.36 | 8.17 |
| 4 | Sun dried | 71.47 | 1.48 | 25.15 | 1.79 |
| 5 | 45 °C | 43.22 | 6.48 | 37.90 | 5.64 |
| 6 | 45 °C | 66.27 | 1.95 | 27.78 | 1.19 |
| 7 | 45 °C | 13.33 | 16.08 | 24.73 | 39.03 |
| 8 | 45 °C | 50.76 | 1.29 | 39.16 | 7.37 |
| 9 | 55 °C | 24.95 | 15.32 | 27.51 | 9.59 |
| 10 | 55 °C | 40.49 | 10.63 | 33.38 | 4.91 |
| 11 | 55 °C | 48.59 | 6.06 | 38.84 | 5.26 |
| 12 | 55 °C | 42.14 | 9.69 | 32.53 | 7.00 |
| 13 | 65 °C | 49.96 | 1.63 | 34.69 | 11.13 |
| 14 | 65 °C | 43.82 | 9.25 | 37.30 | 3.74 |
| 15 | 65 °C | 49.64 | 7.78 | 32.73 | 6.48 |
| 16 | 65 °C | 46.56 | 5.96 | 36.82 | 4.97 |
| 17 | 75°C | 50.26 | 2.51 | 42.80 | 2.58 |
| 18 | 75 °C | 42.75 | 7.77 | 39.20 | 2.59 |
| 19 | 75 °C | 55.81 | 1.30 | 41.40 | 1.38 |
| 20 | 75 °C | 27.89 | 11.82 | 46.94 | 10.15 |

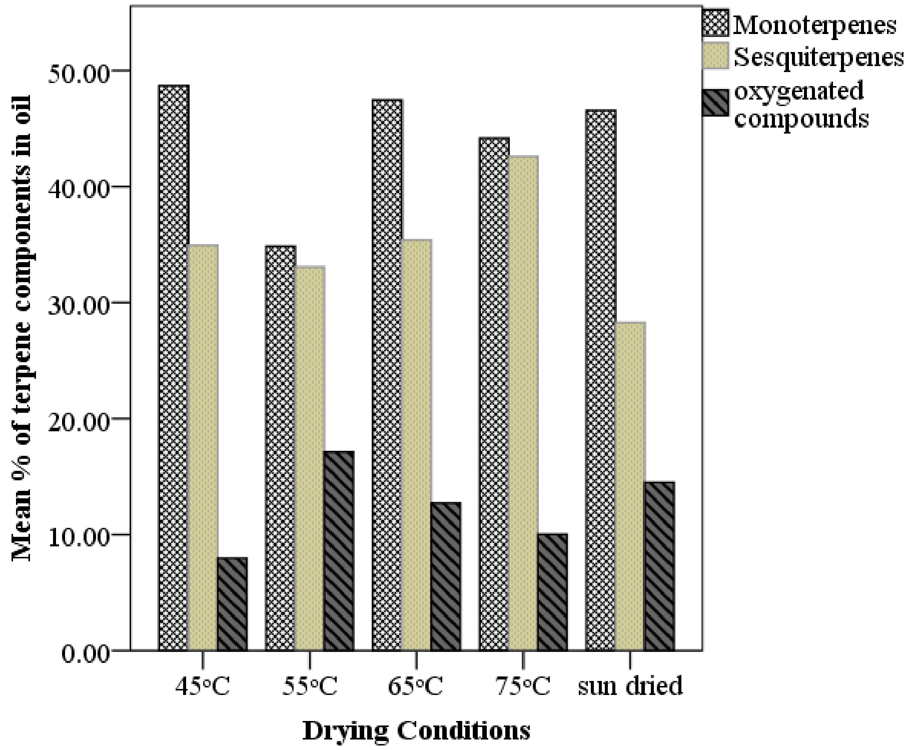



Figure 6.1: Percentage of mean sesquiterpenes, monoterpenes and oxygenated compounds in Black pepper essential oil at different drying conditions

Table 6.2: Ten Most Abundant Components of Black Pepper Essential Oil

| **Component** | **Concentration % (w/w)** | **Formula** [120] |
|---|---|---|
| Caryophyllene | 14.79 | $C_{15}H_{24}$ |
| D limonene | 13.72 | $C_{10}H_{16}$ |
| Caryophyllene oxide | 11.53 | $C_{15}H_{24}O$ |
| α-Copaene | 8.19 | $C_{15}H_{24}$ |
| (1R)- α -Pinene | 6.98 | $C_{10}H_{16}$ |
| α-Pinene | 6.85 | $C_{10}H_{16}$ |
| α-Cubebene | 6.43 | $C_{15}H_{24}$ |
| L-β-Pinene | 5.71 | $C_{10}H_{16}$ |
| Sabinene | 5.61 | $C_{10}H_{16}$ |
| δ3-p-Menthene | 4.83 | $C_{10}H_{16}$ |

Average percentage of sesquiterpene compounds have increased from 32% to 43% of total oil when temperature was increased from 45 °C to 75 °C as shown in Figure 6.1. Sesquiterpenes have higher molecular weights and they are larger molecules compared to the monoterpenes. Therefore, sesquiterpenes' ability to leach or transfer from black pepper particle to water is low compared to monoterpene [115]. Further, their boiling points are high and volatility is less than those of monoterpenes. Therefore they are not able to vaporize easily through distillation processes as monoterpenes [121]. Hence, average percentage of monoterpene is always higher than the percentage of sesquiterpene in the extracted essential oil at every drying condition.

Moreover, raising the drying air temperature causes the rupture of cells and increases the permeability of the skin and give more ability to release high percentage of sesquiterpenes during extraction process [122].

According, Figure 6.1 the percentage of oxygenated compounds present in the essential oil is highest at 55 °C. The residence time in the dryer and the rate of oxidation reaction of terpenes are some of the factors, which affect the percentage of oxygenated compounds available in black pepper essential oil. Usually the rate of reaction is substantially low at lower temperatures. Further low temperature drying processes have longer residence times as described in Chapter 5 thus providing more time for oxidization and vice versa. Depending on these two factors, essential oil derived from black pepper dried at 55 °C drying air temperature shows higher percentage of oxygenated compounds compared to those of other drying conditions. Table 3 and Table 4 in Appendix E show more information about the ten most components in black pepper essential oil.

### 6.2 Analysis of variance

One way analysis of variance (ANOVA) test in IBM SPSS Statistics 20 were conducted to evaluate the significance of the differences among the essential oil extracted from black pepper dried at different drying conditions.

One way ANOVA test was used to compare the following components at five different drying conditions:

- Monoterpene concentration
- Sesquiterpene concentration
- oxygenated terpenes concentration
- Caryophyllene concentration
- essential oil yield

Five different drying conditions and mean of above mentioned components of essential oil were considered as the independent variable and dependent variables respectively. Then null hypothesis ($H_o$) and alternative hypothesis ($H_1$) were defined as follows:

$$H_o: \mu_{45} = \mu_{55} = \mu_{65} = \mu_{75} = \mu_{\text{sun dried}}$$

$$H_1: \mu_{45} \neq \mu_{55} \neq \mu_{65} \neq \mu_{75} \neq \mu_{\text{sun dried}}$$

Where, $\mu$ represents the mean of the selected component. $\mu_{45}$ represents the mean of selected component of essential oil extracted from black pepper dried at 45 $^{\circ}$C drying temperature. Confident interval was set as 0.05. If the significance level is less than 0.05, then there are statistical significant differences between group hence null hypothesis is rejected and alternative hypothesis is accepted.

According to the statistical analysis of the sesquiterpene concentration values obtained by black pepper dried at five different conditions showed that the variation of sesquiterpene concentration was significant. As per ANOVA test, p-value was 0.007. However, a significant level for monoterpene analysis was greater than 5% of confidence level, and thus variation of concentration of monoterpenes was not significant for all the drying air temperatures under investigation. Furthermore, variation of oxygenated terpenes concentration was not significant with variation of drying air temperature. Table 5 in Appendix E presents the results of analysis of variance for comparative study of sesquiterpenes, monoterpenes and oxygenated terpenes with drying conditions.

## 6.3 Effect of drying condition on Caryophyllene concentration

Caryophyllene also known as beta-Caryophyllene is the primary sesquiterpene contributing to the spiciness of black pepper. It is also the major constituent of cloves [123]. Effect of drying condition on concentration of caryophellene is studied. Figure 6.2 shows the percentage of caryophyllene and caryophyllene oxide in essential oil derived from black pepper dried at different conditions. The results show that the quality of each samples of black pepper dried in sun and at 45 °C drying air temperature were not consistent. The intensity of solar radiation is an uncontrollable factor and intensive sunlight affects the quality of the pepper. Furthermore, at low drying air temperatures, residence time in the dryer is lengthy which gives more opportunity to oxidize and isomerise the components in essential oil.

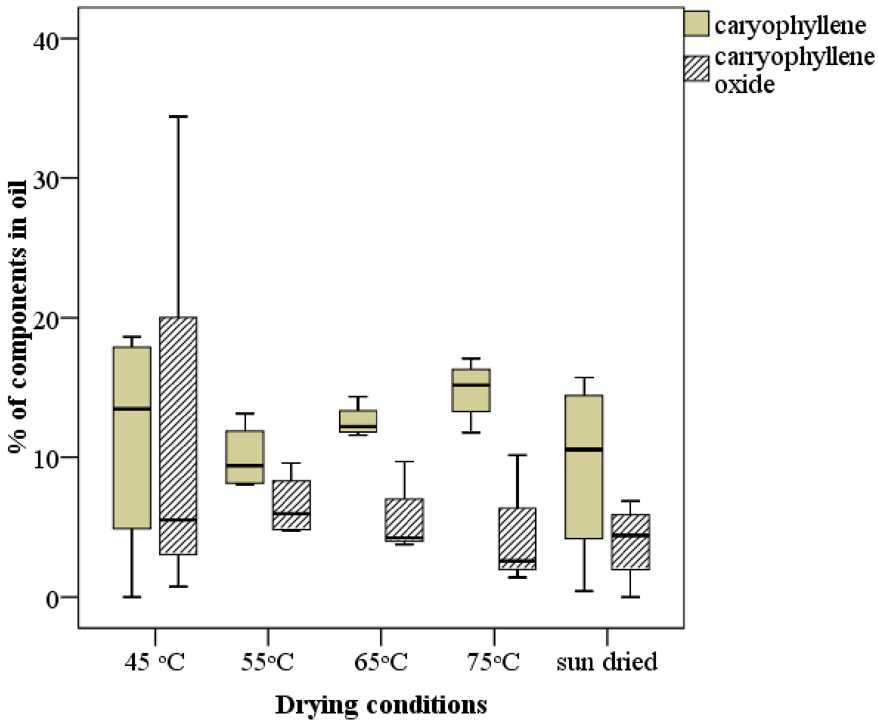



Figure 6.2: Percentage of Caryophyllene and percentage of caryophyllen oxide vs. drying conditions

As shown in Figure 6.2, the percentage of Caryophyllene was strongly increased when drying air temperature is raised from 55 °C to 75 °C. Percentage of Caryophyllene is moderately high at 45°C drying air temperature despite the fact that the value is not consistent within the investigations. However, the percentage of caryophyllene is consistent at 65°C drying air temperature. Moreover, analysis of variance for concentration of caryophyllene among drying air temperatures was not significant. In addition to the Caryophyllene, there were alpha Caryophyllene, Caryophyllene oxide and other isomers and oxides derived from caryophyllene. It was non-significant because isomerization and oxidation of terpenes may take place during the drying process. Similar observations have been discussed for thyme and rosemary by Piga et al. [124]. Table 6 in Appendix E presents the results of analysis of variance for Caryophyllene concentration with drying conditions.

### 6.4 Effect of drying condition on essential oil yield

The oil yield was calculated as volume of oil extracted per weight of dried black pepper used. According to Figure 6.3, average oil yield was increased from 0.0099 mL/g to 0.0174 mL/g when drying air temperature increased from 45 °C to 65 °C. Then the average oil yield was reduced to 0.0104 mL/g at 75 °C drying temperature. The oil yield for sun-dried black pepper is recorded as 0.0101 mL/g.

SLSI standards does not remark about volatile oil content of black pepper, but other associations such as ESA and ASTA stated that minimum content of volatile matter should be 2 % v/w. To benchmark the globally recognized black pepper quality, variation of essential oil yield with drying conditions is shown Table 9 in Appendix A where oil yield is presented as a percentage of millilitre of oil extracted per gram (V/W %) of black pepper used.

Analysis of variance was conducted for variation of oil yield with drying conditions and results are presented in Table 7 in Appendix E. According to the ANOVA test, effect of drying temperature on the essential oil yield was statistically significant under investigation. The p-value was 0.046. Therefore, optimum drying air temperature to obtain the highest oil yield was selected as 65 °C.

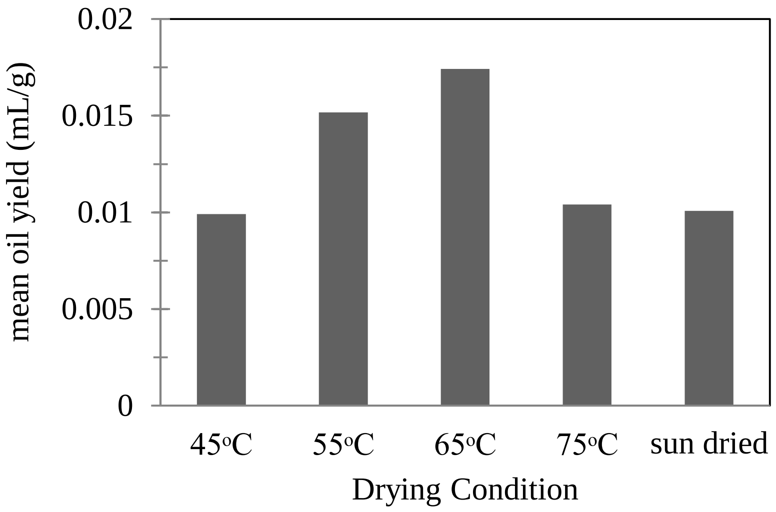



Figure 6.3: Mean oil yield vs. drying conditions

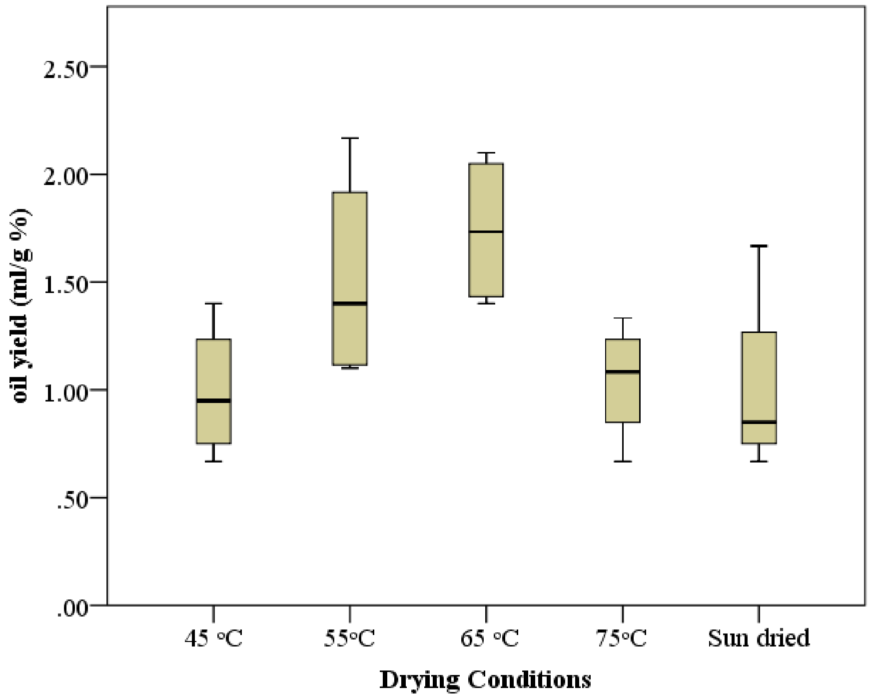



Figure 6.4:-Black pepper essential oil yield vs. drying conditions

Furthermore, 65 °C drying air temperature provides consistent quality essential oil with high percentage of caryophyllene and 65 °C can be selected as the optimum temperature to dry black pepper in the conventional spouted bed dryer without degrading large amount of volatile components.

**Chapter specific nomenclature**

$H_1$ - alternative hypothesis

$H_o$ - null hypothesis

$\mu$ - mean of the selected component

**Abbreviations**

ANOVA - analysis of variance

ASTA - American Spice Trade Association

ESA - Europe Spice Association

GC-MS - Gas Chromatography Mass Spectrometry

**Chapter 7**

# 7. NON DIMENSIONAL MODEL

This chapter describes the modelling of heat transfer characteristics of black pepper dried in conventional spouted bed dryer in unsteady state. Heat transfer coefficients for different operational conditions were determined from the experimental results. Important non-dimensional numbers were identified by dimensionless analysis according to the Buckingham pi theorem [104]. A non-dimensional model was developed for heat transfer process by non-linear multiple regression. Model development, comparison of experimentally determined heat transfer coefficient and Nusselt number with predicted values from existing correlations and the correlation developed in this work are presented in this chapter.

## 7.1 Dimensional analysis for heat transfer process

As described in section 3.2.2, the dimensional matrix was formed for selected important variables of the heat transfer process of black pepper drying in conventional spouted bed. Table 7.1 shows the dimensional matrix related to heat transfer process.

Table 7.1: Dimensional matrix of the fundamental dimensions related to heat transfer process

| | U | H | $d_p$ | $\mu_g$ | $k_g$ | $T_{gi}$ | $T_{gi}$-$T_{gi,w}$ | ρ | $h_p$ |
|---|---|---|---|---|---|---|---|---|---|
| M | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 0 |
| L | 1 | 1 | 1 | -1 | -1 | 0 | 0 | -3 | -2 |
| t | -1 | 0 | 0 | -1 | -1 | 0 | 0 | 0 | 1 |
| Q | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 1 |
| T | 0 | 0 | 0 | 0 | -1 | 1 | 1 | 0 | -1 |

Where

$d_p$ - particle diameter (m)

H - Static bed height (m)

$h_p$ - overall heat transfer coefficient fluid to particle($W/m^2K$)

$k_g$ -Air thermal conductivity (W/mK)

L, M, Q, T, t - Dimensions of length, mass, heat, temperature and time respectively

$T_{gi}$- inlet gas temperature ($^{\circ}C$)

$T_{gi,w}$ - gas inlet wet bulb temperature ($^{\circ}C$)

U - Superficial air velocity (m/s)

ρ - Density of fluid/air ($kg/m^3$)

$\mu_g$ - viscosity of air (kg/ms)

Number of variables involved (n′) is 9 and the rank of the dimensional matrix (r′) is 5. According to Buckingham pi theorem, number of independent dimensionless groups 'i′' is equal to n′-r′ [104].

Thus, $i'=n'-r'$

$i'=4$

Then four dimensionless parameters namely *pi* groups are symbolized as $\pi_1$, $\pi_2$, $\pi_3$ and $\pi_4$. Group of *r′* number of variables were chosen as core group which consisted of those variables that would be appeared in each *pi* group and other variables were named as non-core group. Usually several fundamental dimensions are included in the variables of core group than the variables of non-core group. Nevertheless thermal conductivity of air was excluded from the core group arbitrarily to isolate its effect [104].

Core group of variables: $h_p$, ρ, $\mu_g$, $T_{gi}$, $d_p$,

Non- core group of variables: U, H, $k_g$, $T_{gi}$-$T_{gi,w}$

Each *pi* group includes variables in core group and one of non-core group. In order to become each dimensionless, variable are raised to certain exponents such as:

$$\pi_1 = {h_p}^a \rho^b {\mu_g}^c {d_p}^d {T_{gi}}^e U$$

$$\pi_2 = {h_p}^f \rho^g {\mu_g}^h {d_p}^i {T_{gi}}^j H$$

$$\pi_3 = {h_p}^k \rho^l {\mu_g}^m {d_p}^n {T_{gi}}^p k_g$$

$$\pi_4 = {h_p}^q \rho^r {\mu_g}^s {d_p}^u {T_{gi}}^w \Delta T$$

Each *pi* group was arranged using dimensions then each *pi* group was considered independently to evaluate the exponent of as follows:

For $\pi_1$ $\quad 0 = \left(\frac{Q}{L^2 tT}\right)^a \left(\frac{M}{L^3}\right)^b \left(\frac{M}{Lt}\right)^c (L)^d (T)^e \left(\frac{L}{t}\right)$

Exponent of each fundamental dimension in both sides of the expression are equated.

For L $\quad 0 = -2a - 3b - c + d + 1$

For M $\quad 0 = b + c$

For t $\quad 0 = -a - c - 1$

For T $\quad 0 = -a + e$

For Q $\quad 0 = a$

From these $\quad a = 0;\ b = 1;\ c = -1;\ d = 1;\ e = 0$

Thus first dimensionless group is

$$\pi_1 = \frac{U \rho d_p}{\mu_g} = Re$$

Similarly

For $\pi_2$ $\quad 0 = \left(\frac{Q}{L^2 tT}\right)^f \left(\frac{M}{L^3}\right)^g \left(\frac{M}{Lt}\right)^h (L)^i (T)^j L$

For L $\quad 0 = -2f - 3g - h$ + i +1

For M $\quad 0 = g + h$

For t $\quad 0 = -f - h$

For T $0 = -f + j$

For Q $0 = f$

From these $f = 0; g = 0;\ h = 0;\ i = -1;\ j = 0$

Thus second dimensionless group is

$$\pi_2 = \frac{H}{d_p} = \left(\frac{static\ bed\ height}{particle\ diamter}\right)$$

Similarly

For $\pi_3$ $0 = \left(\frac{Q}{L^2 tT}\right)^k \left(\frac{M}{L^3}\right)^l \left(\frac{M}{Lt}\right)^m (L)^n (T)^p \left(\frac{Q}{LtT}\right)$

similarly

For L $0 = -2k - 3l - m + n - 1$

For M $0 = l + \mathrm{m}$

For t $0 = -k - m - 1$

For T $0 = -k + p - 1$

For Q $0 = k + 1$

From these $k = -1;\ l = 0;\ m = 0;\ n = -1$

Thus third dimensionless group is

$$\pi_3 = \frac{k_g}{h_p d_p} = \frac{1}{Nu}$$

Nu- Nusselt number

For $\pi_4$ $0 = \left(\frac{Q}{L^2 tT}\right)^q \left(\frac{M}{L^3}\right)^r \left(\frac{M}{Lt}\right)^s (L)^u (T)^w T$

Similarly

For L $0 = -2q - 3r - s + u$

For M $0 = r + s$

For t $0 = -q - s$

For T $0 = -q + w + 1$

For Q $0 = q$

From these $w = -1; u = 0;\ r = 0; q = 0; s = 0$

Thus fourth dimensionless group is

$$\pi_4 = \frac{T_{gi} - T_{gi,w}}{T_{gi}} = Gu$$

Gu- Gukhman number

The results of the dimensional analysis of heat transfer process of black pepper drying in spouted bed dryer indicate that a possible relation correlating the important variable is of the form of:

$$Nu = f\left(Re, Gu, \frac{H}{d_p}\right)$$

**7.2 Experimental results**

Drying experiments were conducted as described in section 3.1.6.3. 48 experiments were conducted. Heat transfer coefficients ($h_p$) for 48 experiments with different operating conditions were obtained by solving Equation 3.13. Heat transfer coefficients thus calculated and their operating conditions are presented in Table 7.2.

The analysis of heat transfer indicates that over the operating conditions studied, heat transfer coefficient ($h_p$) for black pepper drying in conventional spouted bed ranges from 35-68 W/m$^2$K. Dimensionless parameter Nusselt (Nu) number was calculated and the particle Nu number for the black pepper drying in conventional spouted bed ranges from 6.69 to 11.8. Dimensionless numbers, heat transfer coefficients and their operating conditions are presented in Table 1 in Appendix F.

Table 7.2: Operating conditions, heat transfer coefficient for black pepper dried in conventional spouted bed

| **Operating conditions** | | | **$h_p$ ( $W/m^2K$ )** |
|---|---|---|---|
| **H (cm)** | **$T_{gi}$ ( $^{\circ}C$)** | **U (m/s)** | |
| 14 | 45 | 2.37 | 49.00 |
| 14 | 55 | 2.37 | 45.00 |
| 14 | 65 | 2.37 | 54.67 |
| 14 | 75 | 2.37 | 57.24 |
| 14 | 65 | 1.60 | 51.69 |
| 14 | 65 | 1.97 | 59.09 |
| 7 | 65 | 2.37 | 65.93 |
| 18 | 65 | 2.37 | 51.09 |
| 20 | 65 | 2.37 | 46.96 |
| 20 | 75 | 2.37 | 47.90 |
| 20 | 55 | 2.37 | 47.16 |
| 22 | 75 | 2.37 | 45.64 |
| 20 | 45 | 2.37 | 40.80 |
| 14 | 45 | 2.37 | 51.09 |
| 18 | 45 | 2.37 | 53.82 |
| 18 | 55 | 2.37 | 43.50 |
| 18 | 55 | 2.37 | 53.68 |
| 14 | 45 | 1.60 | 47.09 |
| 14 | 60 | 2.37 | 57.50 |
| 18 | 75 | 2.37 | 56.29 |
| 18 | 75 | 1.60 | 53.51 |
| 22 | 55 | 2.37 | 45.28 |
| 22 | 45 | 2.37 | 40.86 |

Table 7.2. (Continued)

| Operating conditions | | | $h_p$ ( $W/m^2K$ ) |
|---|---|---|---|
| H (cm) | $T_{gi}$ ( °C) | U (m/s) | |
| 22 | 60 | 1.60 | 40.18 |
| 14 | 35.3 | 2.37 | 34.50 |
| 24 | 75 | 2.37 | 52.40 |
| 24 | 65 | 2.37 | 48.37 |
| 22 | 65 | 1.60 | 44.86 |
| 24 | 65 | 2.57 | 48.95 |
| 24 | 55 | 2.57 | 47.27 |
| 24 | 55 | 2.37 | 47.91 |
| 7 | 65 | 1.60 | 65.10 |
| 7 | 75 | 2.37 | 67.18 |
| 7 | 45 | 2.06 | 58.14 |
| 7 | 55 | 2.33 | 63.93 |
| 7 | 55 | 1.72 | 61.80 |
| 7 | 65 | 1.72 | 63.14 |
| 7 | 65 | 2.54 | 67.60 |
| 7 | 75 | 2.49 | 69.47 |
| 7 | 65 | 2.06 | 67.75 |
| 14 | 60 | 1.60 | 51.49 |
| 14 | 60 | 2.54 | 54.99 |
| 14 | 65 | 2.59 | 56.80 |
| 7 | 36 | 1.68 | 49.64 |
| 7 | 40 | 2.15 | 57.13 |
| 14 | 40 | 2.20 | 45.60 |
| 18 | 65 | 2.49 | 57.65 |
| 18 | 65 | 2.06 | 48.91 |

### 7.3 Correlation for heat transfer process.

Important non dimensional numbers were identified for the heat transfer process of black pepper drying in the conventional spouted bed using dimensional analysis as shown in section 7.1. Non-dimensional numbers were Nusselt (Nu), Reynolds (Re), Gukhman (Gu) and ratio of static bed height to particle diameter $\left(\frac{H}{d_p}\right)$. Heat transfer coefficient represented by Nu with Re, Gu and ratio of static bed height to particle diameter$\left(\frac{H}{d_p}\right)$ was correlated to a power form of function as shown in Equation 7.1 using statistical software IBM SPSS Statistics 20.

$$Nu = a'Re^{b'}Gu^{c'}\left(\frac{H}{d_p}\right)^{d'} \qquad (7.1)$$

The values of the constant '$a'$' and exponents '$b'$', '$c'$' and '$d'$' were determined by the method of multiple non-linear regression of experimental results and the equation thus determined is shown in Equation 7.2

$$\mathrm{Nu} = 12.057\mathrm{Re}^{0.137}\mathrm{Gu}^{0.180}\left(\frac{\mathrm{H}}{\mathrm{d_p}}\right)^{-0.293} \qquad (7.2)$$

The correlation for heat transfer is yielded with 0.791 of coefficient of determination ($R^2$) with significance level 0.000 and valid for the following conditions.

$400 \leq Re \leq 750$

$0.1 \leq Gu \leq 0.6$

$13 \leq H/d_p \leq 47$

The correlation is valid for a geometrically similar system of conventional spouted bed. Geometric similarity exists between the prototype (scale up spouted bed) and the model (spouted bed used for the investigation), if both of them are identical in shape but different only in size. In addition, ratio of all the linear dimensions should be equal [13 ,104]. Geometric similarity of the prototype can be described as follows:

- Ratio of column diameter ($D_c$) to gas inlet diameter ($D_i$) of the conventional spouted bed is equal to three.
- Cone angle of the spouted bed base is $60^{\circ}$.
- Ratio of column height (height of cylindrical section of the spouted bed column) to column diameter is 100/15.

Detailed information on statistical analysis is shown in Appendix G and information on dimensionless numbers and correlations for determining density, viscosity and thermal conductivity of air are stated in Appendix H.

The heat transfer coefficient; $h_p$ was varied over the range of values studied from 35-68 $W/m^2K$ under the investigation. In addition, Nu number varied with 6.5 to 11.8. However Prachayawarakorn et al. found that heat transfer coefficient for spout region varied from 57 to 123 $W/m^2K$ while heat transfer coefficient of downcomer(annulus) zone varied in between 19 and 32 $W/m^2K$ in two dimensional spouted bed of paddy [39]. The reasons for these contradictory results are the difference of material being dried; paddy and black pepper while this study analyses the heat transfer process considering the whole bed including spout, annulus and fountain regions in a conventional spouted bed.

The comparison of experimental heat transfer coefficient and predicted heat transfer coefficient from Equation 7.2 is shown in Figure 7.1. Response surfaces of predicted Nu number as a function of Gu number and $H/d_p$ at three different Re numbers are shown in Figure 7.2. Figure 7.3 shows the validity of correlated equation (Equation 7.2) and comparison of experimental Nu number values with predicted Nu number from some of existing correlations. Table 2.3 of Chapter 2 shows the existing correlations for heat transfer process of spouted bed drying. Both Figure 7.1 and Figure 7.3 show that predicted values from the developed correlation vs. experimental values data are lying around the straight line. It is seen that experimental heat transfer coefficient and experimental Nu number are in good agreement with predicted values of the developed correlation.

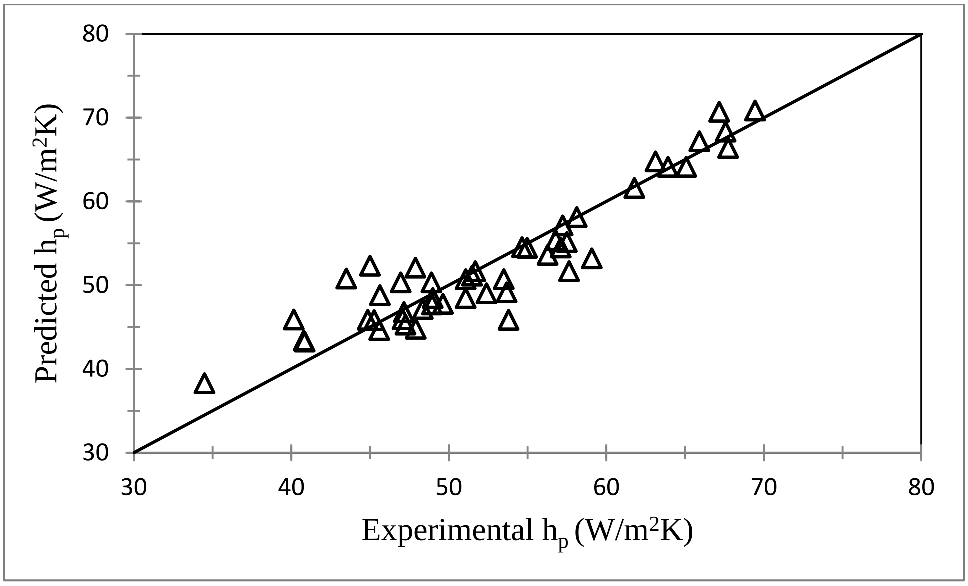



Figure 7.1: Comparison of experimented heat transfer coefficient with predicted heat transfer coefficient

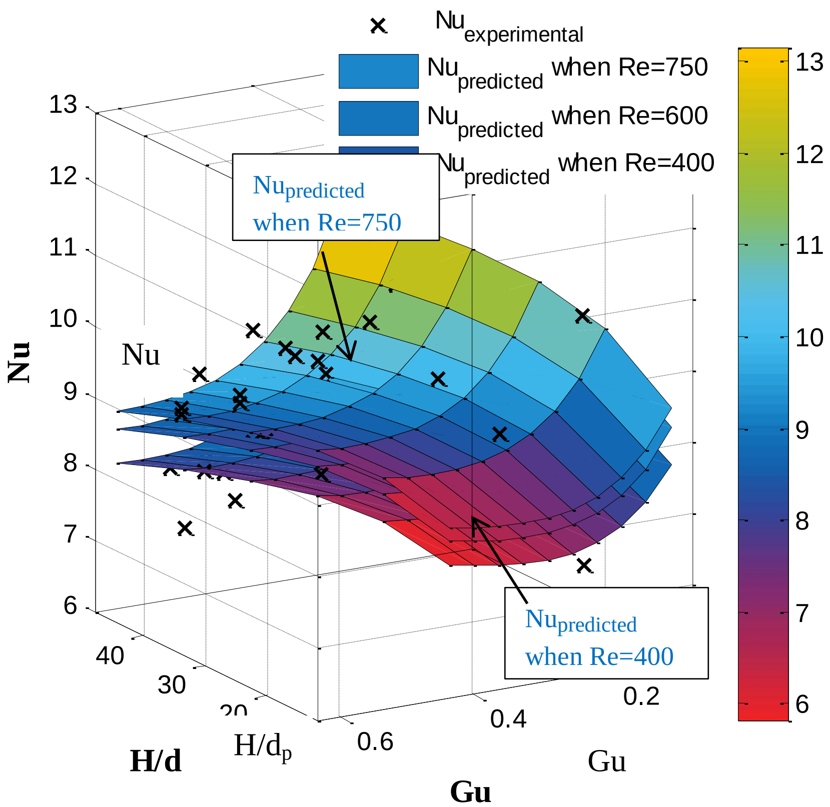



Figure 7.2: Comparison of experimented Nu with response surfaces of predicted Nu as a function of Gu and H/$d_p$ at three different Re numbers

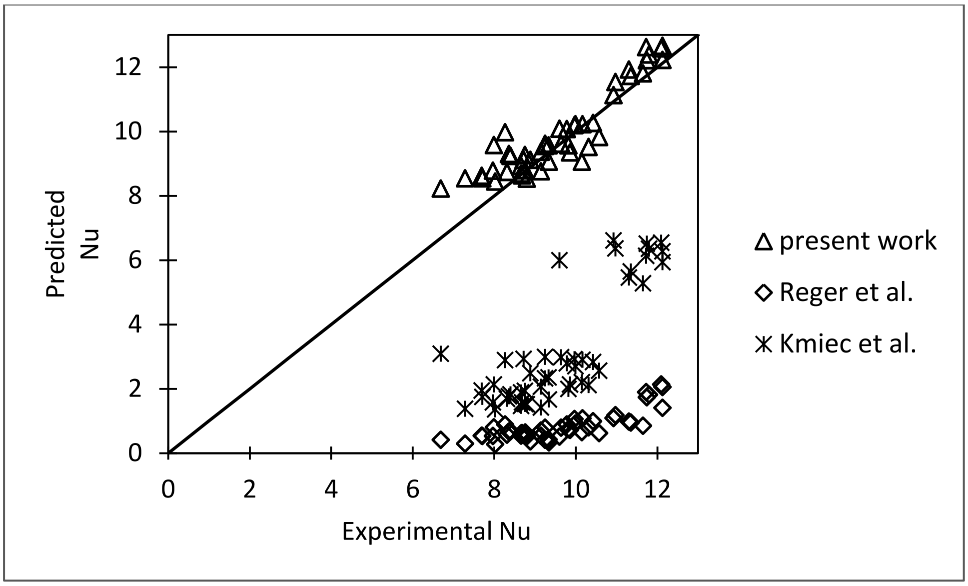



Figure 7.3: Comparison of experimental Nu with predicted Nu using existing correlations and present work

Existing correlations for evaluation of heat and mass transfer coefficients have been developed considering a particular system of properties such as contactor geometry, geometry of the material being dried (spherical, rectangular slabs) and the characteristics of the fluid being used for heat and mass transfer. In addition, many existing correlations were developed considering a particular material at steady state drying process or constant rate drying periods. Therefore, predicted values from correlations derived by works of Reger et al. and Kmiec et al. are considerably below the experimental values [125,27].

### 7.4 Effect of operational conditions on heat transfer

The Nu number represents the effectiveness of heat transfer processes. The Nu number is the ratio of heat transferred by convection to the heat transferred by conduction. The Nu number is an important parameter in heat transfer systems for determining the mode of heat transfer and estimating heat transfer coefficient using non dimensional correlations. A System having Nu number equals to unity, interprets that the fluid is stationary and heat is transferred by conduction only. If Nu number is greater than 1 indicates that the fluid motion enhances the heat transfer by convection. Moreover, Nu number is increased with increasing heat transfer coefficients.

Figure 7.4 and Figure 7.5 present the effect of drying temperature on heat transfer coefficient and Nu number. The trend of Nusselt number and heat transfer coefficient as a function of Re number or Gu number is presented in Figure 7. 6, Figure 7. 7 and Figure 7.10. The values of heat transfer coefficient and Nu number are increased with increasing drying temperature due to increase of driving forces for heat transfer. Temperature difference is the driving force for heat transfer.

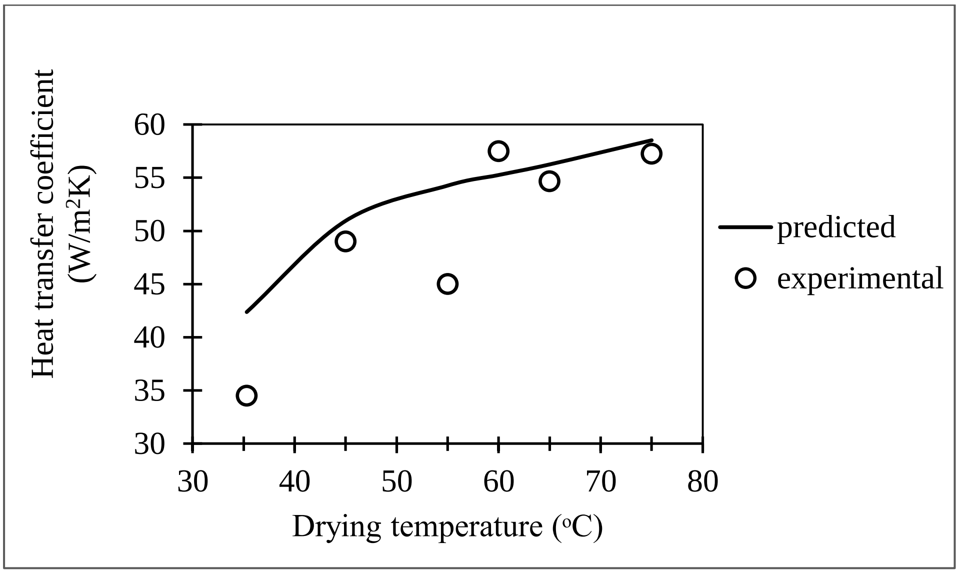



Figure 7.4: Effect of drying temperature on heat transfer coefficient for black pepper dried in conventional spouted bed at different drying temperatures; Experiment conditions: $D_i$=0.05 m, H=0.14 m and U=2.37 m/s

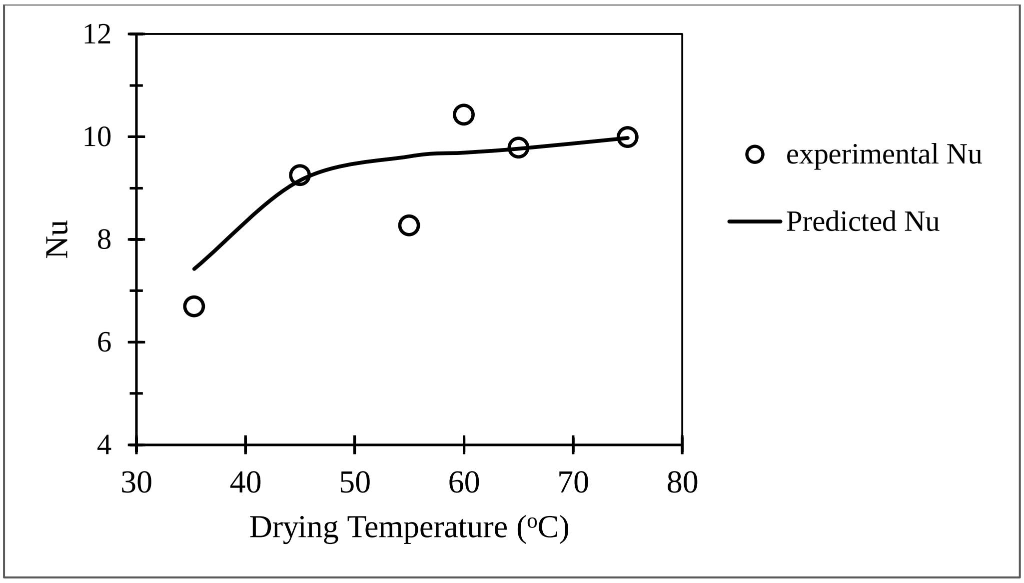



Figure 7.5: Nusselt number as a function of drying temperature for black pepper dried in conventional spouted bed at different drying temperatures; Experiment conditions: $D_i$=0.05 m, H=0.14 m and U=2.37 m/s

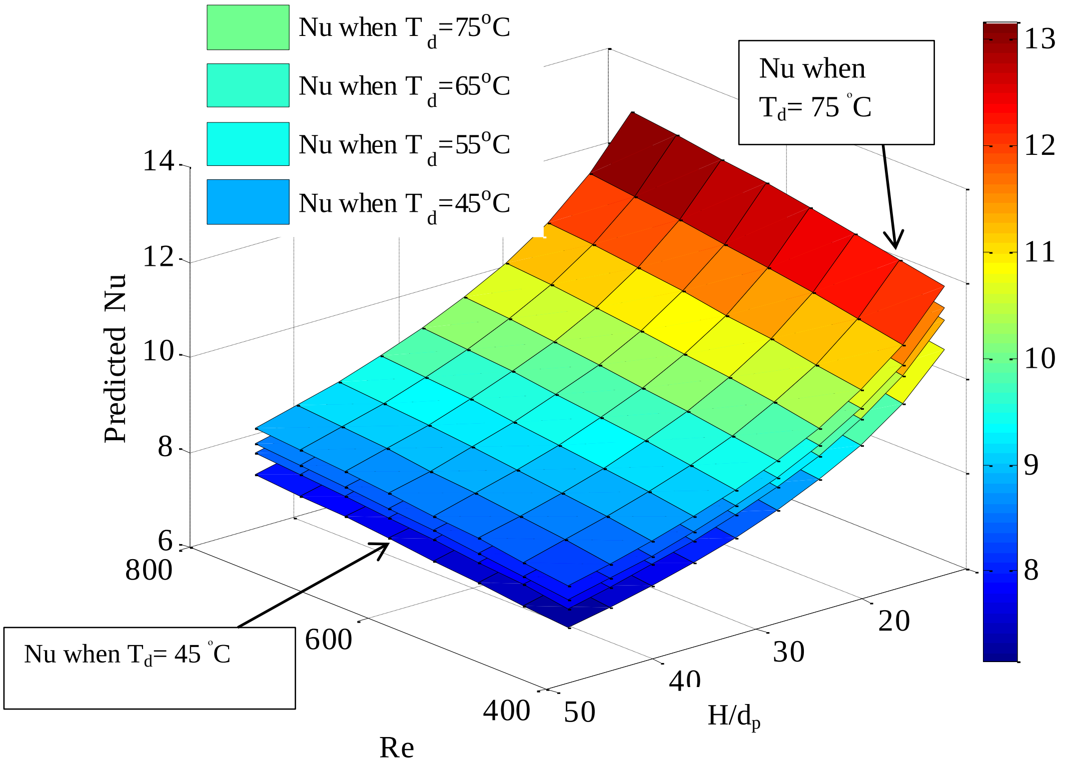



Figure 7. 6: Response surfaces for predicted Nu number as a function of Re number and $H/d_p$ at different drying air temperatures

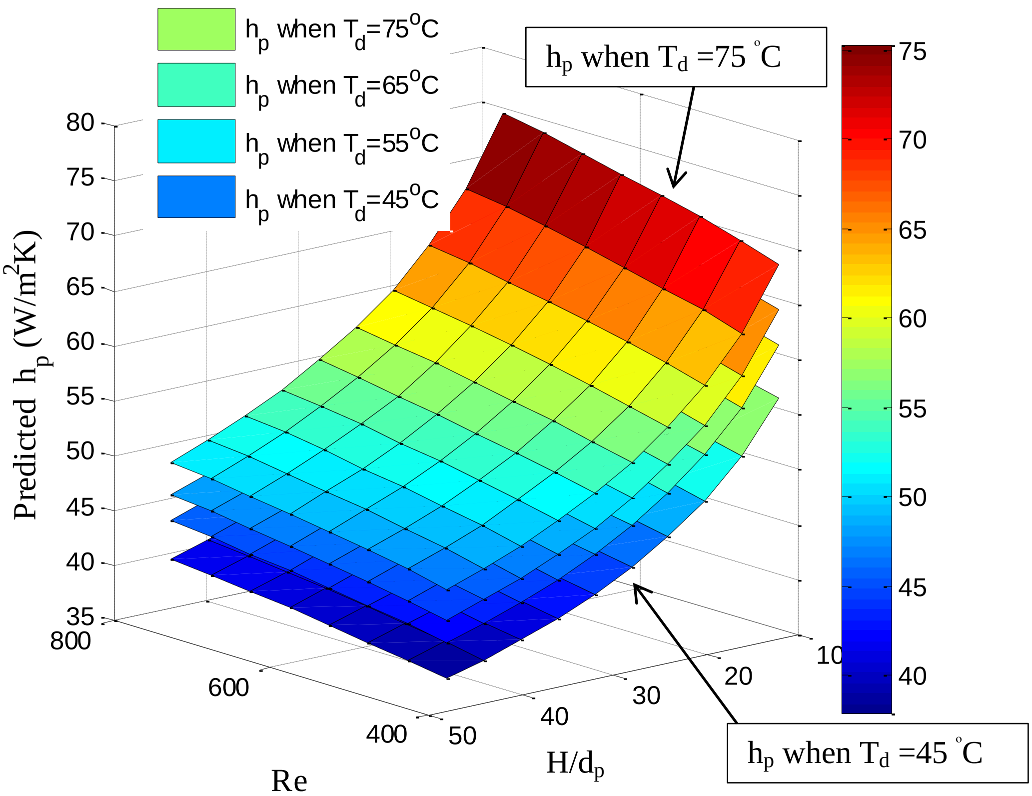



Figure 7. 7: Response surfaces for predicted heat transfer coefficient as a function of Re and $H/d_p$ at different drying air temperatures

Figures 7.8 to 7.13 present the effect of static bed height and superficial air velocity on the both heat transfer coefficient and Nu number. The value of heat transfer coefficient and Nu number increased with drying temperature and air velocity but decreased with increasing static bed height.

According to Figure 7.8 and Figure 7.9, heat transfer coefficient or Nu number has a higher value at the lower static beds. Exponent of $(H/d_p)$ is negative for the correlation (Equation 7.2) developed for heat transfer processes. Same phenomenal is shown in existing correlations as shown in Table 2.3 of Chapter 2. Figure 7.10 shows the response surface for predicted Nu number as a function of Gu and Re number at different static bed heights.

Low static beds create greater turbulence while spouting, due to the low number of particles in the bed compared to those of deeper beds. Then this greater turbulence caused inside the dryer decreases the gas film thermal resistance around the particle surface, leading to achieve higher heat transfer coefficients [39].

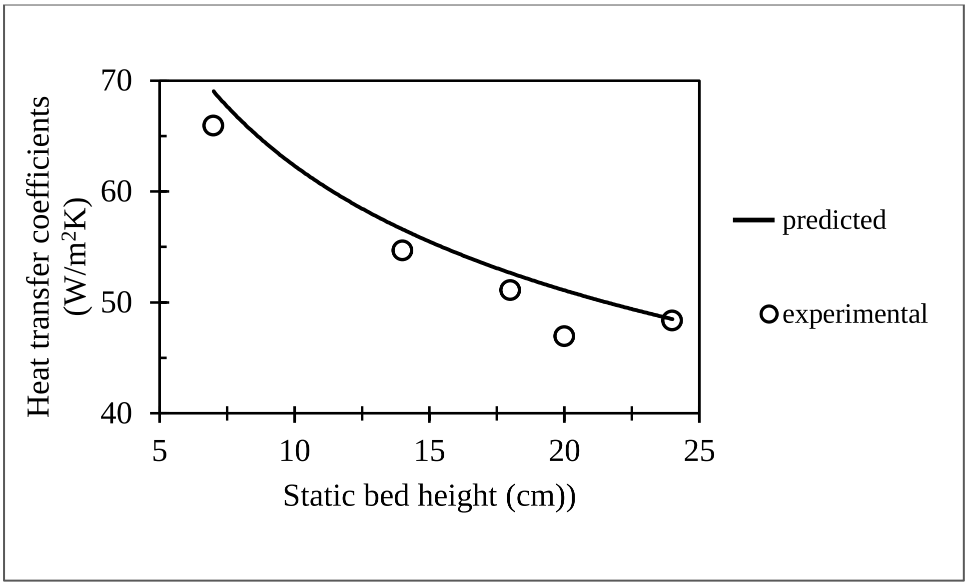



Figure 7.8: Effect of static bed height on heat transfer coefficient for black pepper dried in conventional spouted bed of different bed heights; Experiment conditions: $D_i$=0.05 m, $T_{gi}$=65 °C and U=2.37 m/s

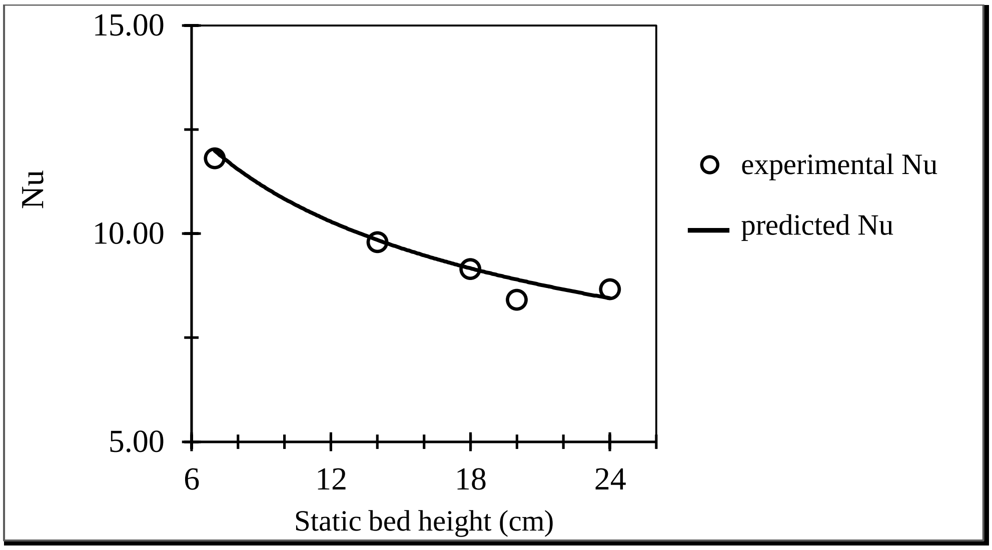



Figure 7.9: Nusselt number as a function of static bed height for black pepper dried in conventional spouted bed of different bed heights; Experiment conditions: $D_i$=0.05 m, $T_{gi}$=65 °C and U=2.37 m/s

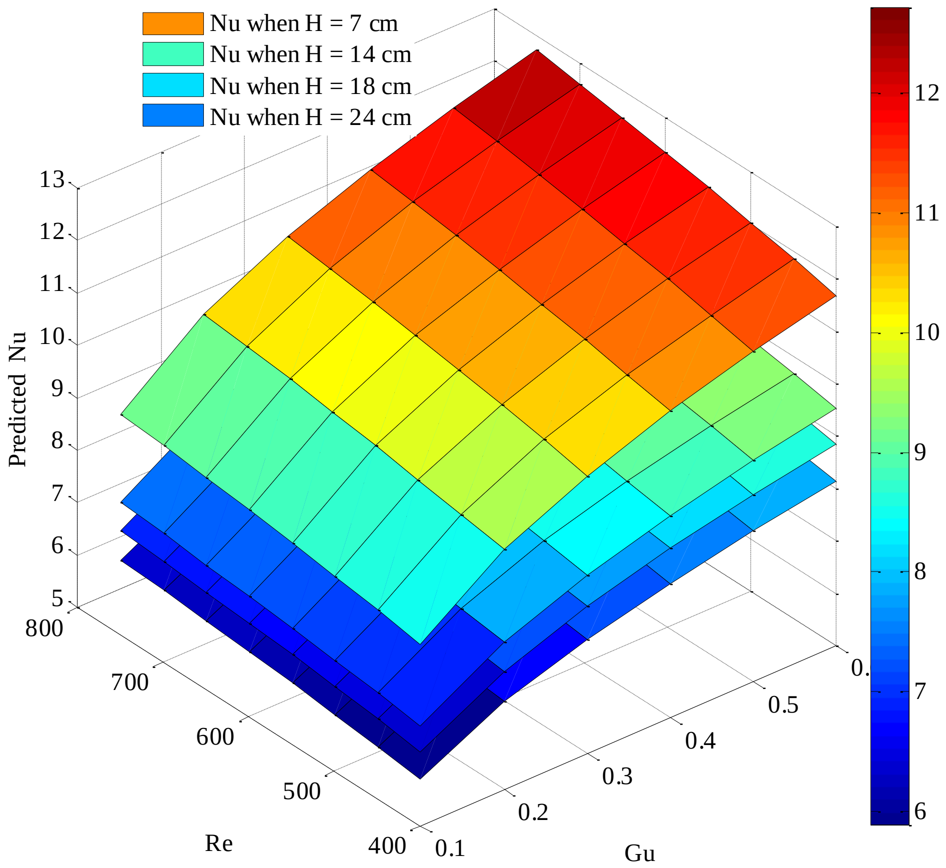



Figure 7.10: Response surfaces for predicted Nu number as a function of Gu number and Re number at different static bed heights

The behaviour of the heat transfer coefficient was dependent on air velocity. The values of heat transfer coefficient and Nu number were increased with increasing air velocity as shown in Figures 7.11-7.13. This factor is also interpreted in the correlations developed in present work as shown in Equation 7.2.

However, exponent of Re number in existing correlations; Equation 2.15 to Equation 2.21 (in Table 2.3 of Chapter 2) are more than twice as high as that in the correlation developed for heat transfer by this work; Equation 7.2. This is due to the fact that those correlations were developed for either steady state or constant rate drying processes. Exponent of external parameters are usually high for constant rate drying processes since external parameters such as air velocity, drying temperature, static bed height normally controls the rate of surface evaporation.

Figure 7. 6, Figure 7.10 and Figure 7.13 show that Nu number is increased with increasing Re number and Gu number and decreasing ratio of static bed height to particle diameter. It implies that as a result of an increase in drying air temperature and air velocity and a decrease in bed height, heat and mass transfer between air and the solid particle are increased. However the Re number is less effective than the other two parameters; Gu number and ratio of static bed height to particle diameter on Nusselt number as shown in Figure 7. 6 and Figure 7.10. This is due to the fact that shallow static beds have great turbulence during the spouting operation and higher values of air temperature can cause large driving force for heat transfer while the air velocity or Re number is low. Accordingly use of higher air velocity in a spouted bed dryer is not a wise solution considering the energy and the cost involved.

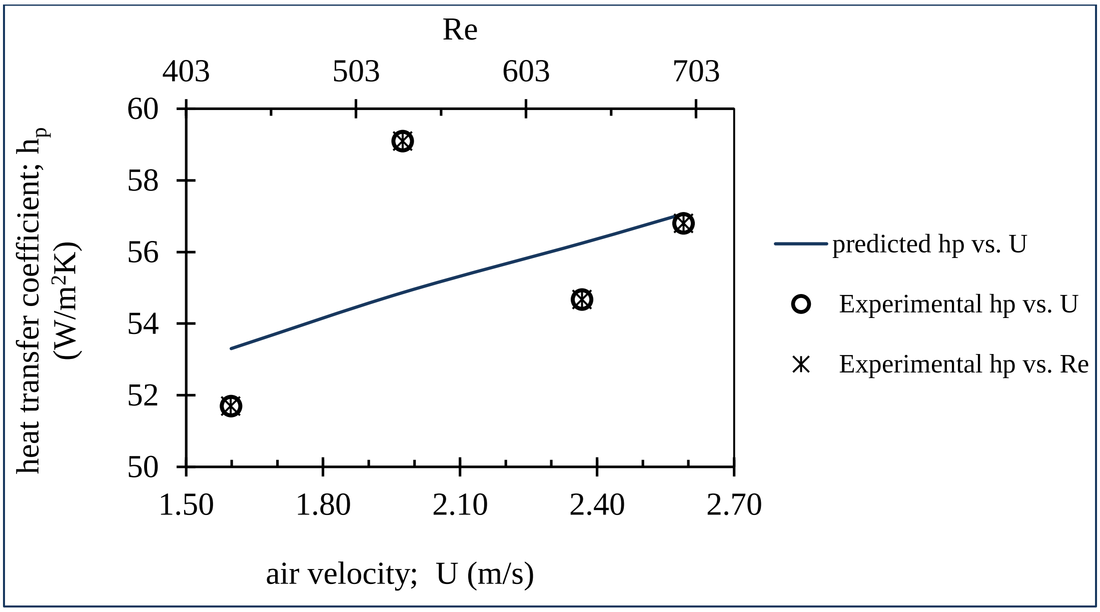



Figure 7.11- Effect of air velocity and Re number on heat transfer coefficient for black pepper dried in conventional spouted bed at different superficial air velocities; Experiment conditions: $D_i$=0.05 m, $T_{gi}$=65 °C and H=0.14 m

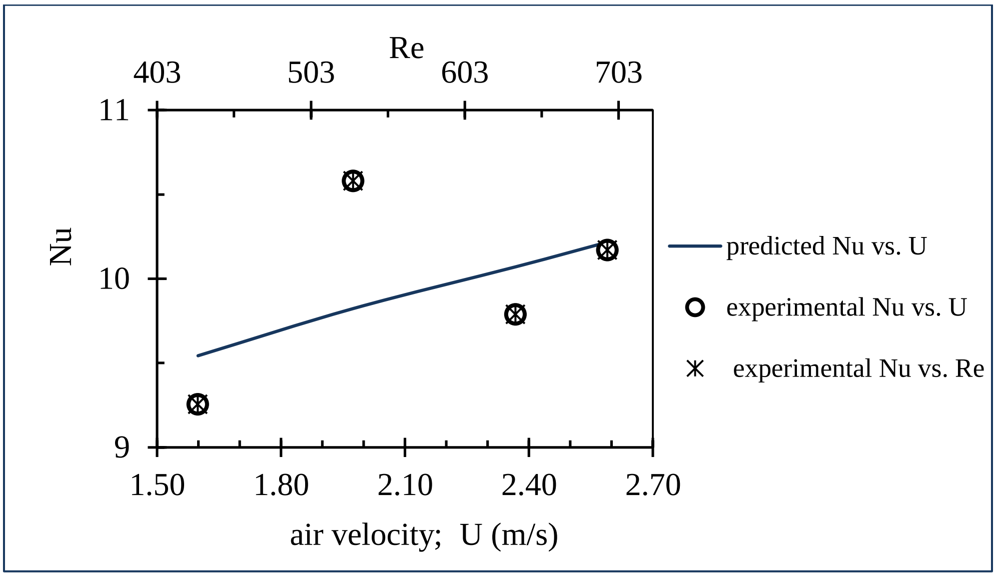



Figure 7.12-: Nusselt number as a function of Reynolds number and air velocity for black pepper dried in conventional spouted bed at different superficial air velocities; Experiment conditions: $D_i$=0.05 m, $T_{gi}$=65 °C and H=0. 14 m

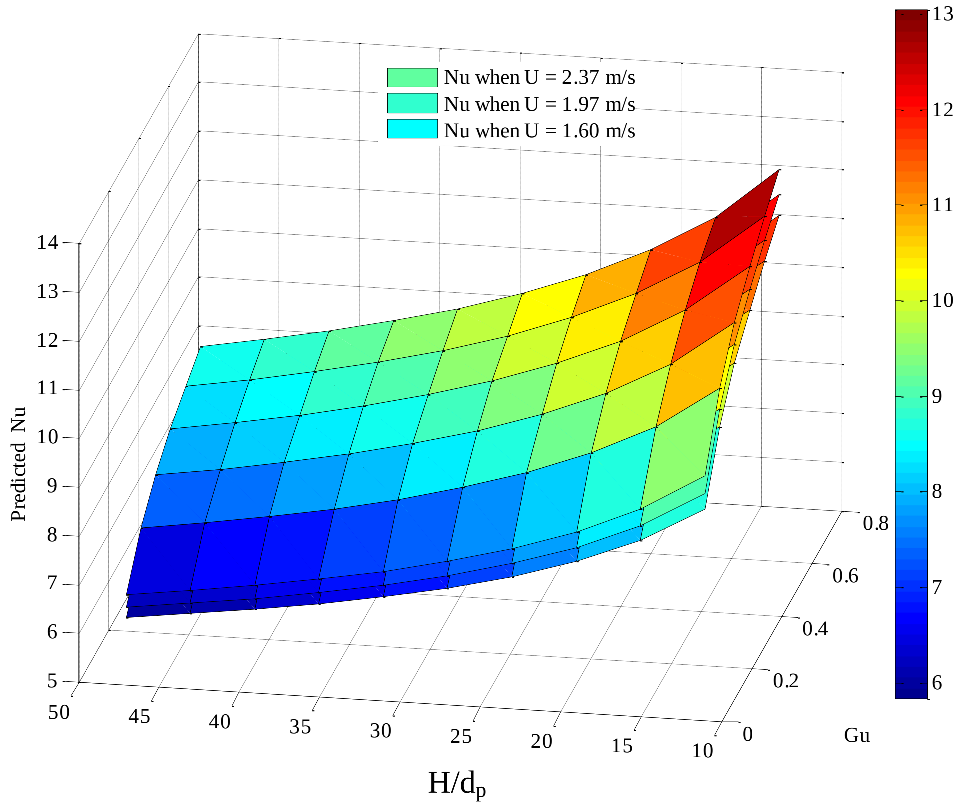



Figure 7.13: Response surfaces for predicted Nu number as a function of Gu number and $H/d_p$ at different air velocities.

**Chapter specific nomenclature**

a, b, c, d, e, f, g, h, i, j, k, l, m, n, p, q, r, s, t, u, w, a′, b′, c′, d′ – constants

$d_p$- particle diameter (m)

Gu- Gukhman number

H- Static bed height (m)

$h_p$ – overall heat transfer coefficient fluid to particle($W/m^2K$)

i′- number of independent dimensionless groups

$k_g$ -Air thermal conductivity (W/mK)

L, M, Q, T, t - Dimensions of length, mass, heat, temperature and time respectively

n′ -Number of variables involved

Nu- Nusselt number

r′-rank of the dimensional matrix

Re- Reynolds number

$T_{gi}$- inlet gas temperature or drying air temperature ($^{\circ}C$)

$T_{gi,w}$- gas inlet wet bulb temperature ($^{\circ}C$)

U- Superficial air velocity (m/s)

ρ - Density of fluid/air ($kg/m^3$)

$\mu_g$- viscosity of air (kg/ms)

**Chapter 8**

# 8. CONCLUSION & RECOMMENDATIONS FOR FUTURE WORK

## 8.1 Conclusion

Heat and mass transfer in drying of black pepper in an unsteady state spouted bed dryer was analysed. Experiments were conducted using wetted black pepper and raw black pepper.

Wetted black pepper was used for conducting preliminary experiments in three different spouted bed configurations namely conventional spouted bed, spouted bed equipped with non-porous draft tube and spouted bed equipped with porous draft tube. Spouted bed equipped with non-porous draft tube had the lowest value of minimum spouting velocity followed by the spouted bed equipped with porous draft tube while the conventional spouted bed had the highest minimum spouting velocity for a given bed heights.

Conventional spouted bed required shorter drying time, higher drying rate and higher moisture diffusivity compared to those of spouted beds equipped with draft tubes. Therefore, the conventional spouted bed dryer was identified as the optimum configuration of spouted bed among the spouted bed equipped with draft tubes to continue drying experiments with raw black pepper to achieve the objective of this research.

Main experiments were conducted using raw black pepper in the conventional spouted bed dryer. Minimum spouting velocity of conventional spouted bed was varied from 0.86-1.86 m/s for 0.07-0.22 m stagnant bed height of raw black pepper. Minimum spouting velocity of black pepper particles were increased with increasing static bed height.

Data of minimum spouting velocity of raw black pepper in the conventional spouted bed versus static bed height was correlated to a power form of function and the relationship has 0.97 of coefficient of determination. Equation 5.2 recalls the function of minimum spouting velocity of raw black pepper in the conventional spouted bed versus static bed height.

$$U_{ms} = 5.26\ H^{0.67}$$

The higher values of drying rates were achieved when the dryer was operated with moderately high temperatures, high airflow rates and shallow beds. Drying kinetic data of raw pepper drying in the conventional spouted bed dominates falling rate periods.

Effective moisture diffusivity of black pepper increased with increasing drying temperature. The highest effective moisture diffusivity of $1.55 \times 10^{-10}$ $m^2/s$ was obtained at a hot air temperature of 75 °C. Activation energy for drying of raw black pepper in conventional spouted bed was 42.41 kJ/kmol.

Kinetic data obtained from experiments were fitted to five thin layer drying models namely Newton, Page, Henderson and Pabis, Two compartments, and Logarithmic models. According to the statistical analysis, Logarithmic model show the best results for the drying behaviour of black pepper in conventional spouted bed dryer due to highest coefficient of determination and lowest root mean square error and sum of square error values. In addition, four models were developed for black pepper drying in the conventional spouted bed by correlating drying constants and coefficients of Logarithmic model to stagnant bed height only at specified temperatures; 45 °C, 55 °C, 65 °C, and 75 °C. Developed models can be used to estimate the drying time of black pepper in the conventional spouted bed dryer for given moisture reduction in the ranges of 0.14 -0.22 m stagnant bed heights and in 2.37 m/s air velocity at specified drying air temperatures.
Specific Energy Consumption (SEC) defined as the amount thermal energy supplied to evaporate 1 kg of moisture in drying of black pepper was calculated. SEC values were varied from 16 - 55 MJ/kg of moisture evaporated for stagnant bed height varied from 7 cm to 20 cm at the range of drying air temperature of 45 °C to 75 °C.

SEC increased with increasing air velocity and decreased gradually with increasing static bed height .

The analysis of components in black pepper essential oil shows that the black pepper essential oil comprised mainly monoterpenes and sesquiterpenes. 13-66% of total oil was monoterpenes while 24-47% of total oil was sesquiterpenes. The most abundant sesquiterpene component was Caryophyllene (14.79 %) while most abundant monoterpene was D limonene (13.72 %). Average percentage of sesquiterpene compounds have increased from 32% to 43% of total oil when drying air temperature was increased from 55 $^{\circ}$C to 75 $^{\circ}$C. Variation of sesquiterpene concentration in black pepper essential oil was significant while variations of monoterpene, oxygenated terpenes and caryophyllene concentration were non-significant in black pepper essential oil with drying air temperature.

Average oil yield was varied from 0.0099 mL/g to 0.0174 mL/g when drying air temperature increased from 45 $^{\circ}$C to 65 $^{\circ}$C. Then the average oil yield was reduced to 0.0104 mL/g at 75 $^{\circ}$C drying temperature. The variation of oil yield is statistically significant with drying air temperatures from 45 $^{\circ}$C to 75 $^{\circ}$C. 65 $^{\circ}$C drying air temperature provides consistent quality essential oil with high percentage of caryophyllene and 65 $^{\circ}$C is selected as the optimum temperature to dry black pepper in the conventional spouted bed dryer to achieve higher yield of essential oil without degrading large amount of volatile components.

Therefore black pepper dried at 65 $^{\circ}$C temperature in spouted bed dryer is suitable to use in perfumery industry since it had highest percentage of sesquiterpenes and minimum loss of volatile components compared to other drying temperatures.

Heat transfer coefficient was varied from 35-68 W/m$^2$ for different drying conditions of unsteady state drying of black pepper from initial moisture content to final moisture content of 15% dry basis.

Significant dimensionless numbers were Nusselt, Reynolds, Gukhman and ratio of static bed height to particle diameter according to analysis of the Buckingham pi theorem . A correlations was developed for heat transfer as a function of dimensionless groups with 0.791 of coefficient of determination and 0.000 of significance level. The correlation is valid for a system of conventional spouted bed geometric similar to the unit under investigation. Equation 7.2 recalls the developed correlation.

$$Nu = 12.057Re^{0.137}Gu^{0.180}\left(\frac{H}{d_p}\right)^{-0.293}$$

Heat transfer coefficients predicted from the developed correlation show a good agreement with the experimentally determined heat transfer coefficients.

## 8.2 Recommendations for future work

This research outcome provides recommendations for conventional spouted bed dryer for black pepper drying. Furthermore investigations can be carried out to improve the usability of two dimensional(slot -rectangular) spouted bed and two dimensional spouted bed with porous draft plates for black pepper or any other type of agricultural product. Oleoresins of black pepper consists mainly pungent components which can be used in food industry. Work presented in Chapter 6 can be extended to find the optimum drying conditions to achieve consistent quality black pepper with higher yield of either essential oil or the oleoresins.

Then a CFD model can be developed to simulate and describe the drying behaviour and the hydrodynamics of the unsteady state drying process of spouted bed dryer.

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# APPENDIX A

Table 1 : Brief description of widely used dryers

| Type | Description |
|---|---|
| Tray dryer (direct contact) | • Operated in batch mode.<br>• The material which may be lumpy solid or a pasty solid is spread uniformly on a metal tray.<br>• Hot air is re-circulated by a fan over and parallel to the surface of the trays.<br>• After drying, the cabinet is opened and the trays are replaced with a new batch of trays. |
| Flash dyer (Convective/ pneumatic/) | • Wet material is dispersed in to a stream of hot air which conveys through a duct.<br>• Drying takes place during short time in a drying duct.<br>• Therefore pneumatic driers are suitable for removal of surface moisture, only.<br>• Ability to handle in continuous operation.<br>• Flash dryers are suitable for agricultural products such as tea, coir, fish products, dairy products starch and etc. |
| Rotary dryer (Direct/ indirect) | • Consists of a hollow cylinder which is rotated and usually slightly inclined toward the outlet.<br>• The wet granular solids are fed at the high end and move through the shell as it rotates.<br>• The heating is by direct contact with hot gases in counter current or co-current flow.<br>• In some cases the heating is by indirect contact through the heated wall of the cylinder.<br>• The lifting flights extending from the cylinder wall lift the solid and allow to fall and simultaneous by pushing to the outlet. |

Table 1 Continued

| | |
|---|---|
| | • Rotary dryers are suitable for powders, granules, flakes, pastes, Slurries and etc. |
| Fluidized bed | • Usually Fluidized bed dryer consist of a shell of cylindrical or rectangular cross section.<br>• A grid is provided in the column over which the wet material is rests. In this type of dryer, the drying gas is passed through the bed of solids at a velocity sufficient to keep the bed in a fluidized state.<br>• Mixing and heat transfer are very rapid in this type of dryers.<br>• The dryer can be operated in batch or continuous mode.<br>• Ability to operate in batch mode and continuous mode.<br>• Fluidized bed dryer are suitable for granular and crystalline materials, pharmaceutical product, sludge, tea and etc. |
| Spouted bed dryer | • Hot gas is introduced vertically upward into the solid bed through a small opening which is located at the center of the base of the vessel.<br>• They are suitable to handle coarse particles such as grains, pastes, slurries and etc. |
| Spray dryer | • Liquid to be dried is atomized and introduced to a drying chamber.<br>• Air fed through the filler and heater enters at the top of the drying chamber flowing down co-current with the droplets being dried.<br>• The moisture evaporates and the dried product is collected to the bottom of the drier.<br>• They are suitable for dairy product, dye stuff, coffee, tea, yeast and etc. |
| Drum dryer (indirect dryer) | • A drum dryer consists of a heated metal roll on the outside of which a thin layer of liquid or slurry is evaporated to dryness.<br>• The final dry solid is scraped off the roll which is revolving slowly. |

Table 1 Continued

| | |
|---|---|
| | • Drum drier may be either a single drum, double drum, twin drum or vacuum double drum<br>• Drum driers are suitable for drying slurries, pastes and sludge. |
| Continuous tunnel dryer | • The solids are placed on trays or trucks which move continuously through a tunnel with hot gas passes over the surface of each tray.<br>• The air flow is either perpendicular to the material flow, co-current or counter-current. (However in practice it will be a combination). |

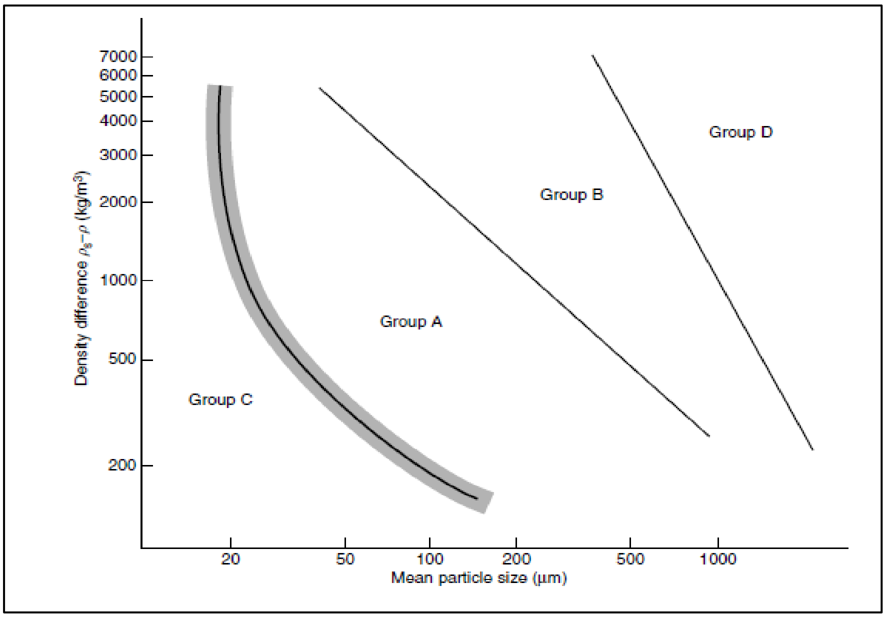


Figure 1: Powder classification diagram for fluidization by air at ambient conditions [12]

Table 2: Categorization of powders in relation of fluidization characteristics [12]

| Group | Typical particle size ($\mu$m) | Fluidization/Powder Characteristics | Examples of materials |
|---|---|---|---|
| A | 30-100 | Particulate expansion of bed will take place over significant velocity range.<br>Small particle size and low density (density < 1400 kg/m$^3$) | Cracker catalyst |
| B | 100-800 | Bubbling occurs at velocity > minimum fluidization velocity.<br>Most bubbles have velocities greater than interstitial gas velocity. No evidence of maximum bubble size. | sand |
| C | 20 | Fine cohesive powders, difficult to fluidize and readily form channels. | Flour<br>Fine silica |
| D | 1000 | All but largest bubble rise at velocities less than interstitial gas velocity. Can be made to form spouted beds. Particle large and dense | Wheat<br>Metal shot |

Table 3: Some of the key characteristics of gas spouted and gas fluidized bed dryers

| Type | Advantages | Limitations |
|---|---|---|
| Spouted bed | • Reduced pressure drop<br>• Relatively lower gas flow rate<br>• Prevention of particle segregation<br>• Possibility of handling coarse particles [56]<br>• Produce material circulation<br>• Producing excellent solid gas contact<br>• Possibility of using high temperatures.<br>• Fast drying rates and uniform | • Complex mechanism of particle movement and difficulty in control of cyclic pattern<br>• Limitation of scale up considering the size and the bed height<br>• Lack of data available for the design and applications [9]<br>• Low thermal efficiency [28] |
| Fluidized bed | • High rate of moisture removal<br>• High thermal efficiency<br>• Easy material transport inside dryer<br>• Ease of control<br>• Low maintenance cost [126]] | • High pressure drop<br>• High electrical power consumption<br>• Poor fluidization quality of some particulate products such as bubbling or slugging.<br>• Non uniform product quality of some materials<br>• entrainment of fine particles [126]<br>• Attrition or pulveriazation of particles<br>• Agglomeration of fine particles may occur in high temperature operations or with sticky particles,<br>• Erosion of vessel , internals and pipes<br>• A very noticeable gas flow rate is required to reach fluidization of large particles.-<br>• To confer the system adequate mixing and avoid dead zone, the gas rate should be doubled tripled with respect to the minimum fluidization velocity [56] |

Table 4: Characteristics of the conventional spouted bed versus spouted bed with draft tubes

| Type of bed | Advantages | Limitations | Applications |
|---|---|---|---|
| Conventional spouted bed | • Simple grid design<br>• Regular solid circulation<br>• Good solid mixing for coarse solids<br>• Low pressure drop<br>• Good fluidization for sticky or lumpy solid [45] | • Limitation of geometry and operation<br>• Limitation on bed height<br>• Somewhat narrower range of particle size<br>• Poor spouting for finer particles [45] | • Drying of grains and suspensions<br>• Coating of particles<br>• Granulation of particles<br>• Coal gasification<br>• Chemical product [45] |
| Spouted bed equipped with non-porous draft tube (SBNPDT) | • Greater operation flexibility<br>• low gas flow and pressure drop required for operations<br>• Narrower spread of solid residence time distribution [127]<br>• Better control of solid circulation<br>• High bed stability under any operation condition<br>• Prevent grain from cracking during the drying [46] | • Complex design<br>• Deuces solid circulation rate<br>• Plugging draft tube<br>• Reduces contact between gas and solids [46]<br>• Lower eat ans mass transfer<br>• Prevent gas percolation from spout to annulus | • Drying of grains and suspensions<br>• Granulation of particles<br>• Coal gasification<br>• Combustion<br>• Pyrolysis of hydrocarbon<br>• Pneumatic conveying [45] |
| Spouted bed equipped with porous draft tube (SBPDT) | • Advantages of SBNPDT are retained.<br>• More control of gas percolation through annulus<br>• Higher heat and mass transfe compare to SBNPDT [45] | • More coplex design<br>• Plugging drat tube [45] | • Drying of grain and chemical product [45] |

Table 5: Correlation for Minimum Spouting Velocity

| **Author** | **correlation** | **comments** |
|---|---|---|
| Mathur and Gishler 1955 [37] | $U_{ms} = \left(\frac{d}{D}\right)\left(\frac{D_i}{D}\right)^{1/3}\sqrt{\frac{2gH(\rho_p - \rho)}{\rho}}$ | Conventional spouted bed |
| Fane and Mitchell (1984) [48] | $U_{ms} = 2.0\, D^n \left(\frac{d_p}{D}\right)\left(\frac{D_i}{D}\right)^{1/3}\sqrt{\frac{2gH(\rho_p - \rho)}{\rho}}$ | Conventional spouted beds<br>For $D > 0.4m$<br>$n = 1 - exp\{-7D^2\}$ |
| Wu et al. (1987) [51] | $\frac{U_{ms}}{\sqrt{2gH_o}} = 10.6\left[\frac{d_p}{D_c}\right]^{1.05}\left[\frac{D_o}{D_c}\right]^{0.266}\left[\frac{H_o}{D_c}\right]^{-0.095}\left[\frac{\rho_s - \rho}{\rho}\right]^{0.256}$ | Conical spouted bed at elevated temperatures |
| Olazar et al. (1992) [52] | $(Re_o)_{ms} = 0.126Ar^{0.5}\left(\frac{D_b}{D_o}\right)^{1.68}\left(\tan\frac{\gamma}{2}\right)^{-0.57}$ | Conical spouted bed |
| San José et al., (2007) [53] | $(Re_o)_{ms} = 0.126Ar^{0.5}\left(\frac{D_b}{D_o}\right)^{1.68}\left[\tan\frac{\gamma}{2}\right]^{-0.57}\left(\frac{H_o - l_d}{H_o}\right)^{0.45}\left(\frac{D_i}{D_i - d_d}\right)^{0.17}$ | Conical – cylindrical with draft tubes<br>where $d_d \le \overline{D_s}$ ,<br>$d_d \le \overline{D_s} < D_i$ , $l_d = H_o - h_d$<br>and $h_d \ge 10d_p$ |
| Altzibar et al. (2009) [54] | $(Re_o)_{ms} = 0.204Ar^{0.475}\left(\frac{H_o}{D_o}\right)^{1.240}\left(\frac{L_H}{D_T}\right)^{0.168}\left(\tan\frac{\gamma}{2}\right)^{-0.135}$ | Conical spouted bed with draft tubes |

Table 6: Correlations available for prediction of maximum spoutable height

| Author | Correlation | Geometry |
|---|---|---|
| McNab-Briggwater [37] | $H_m = \left(\frac{D^2}{d_p}\right)\left(\frac{D}{D_i}\right)^{2/3}\left(\frac{568b^2}{Ar}\right)\left(\sqrt{(1+35.9Ar\times10^{-6})} - 1\right)^2$ | Conventional spouted bed |
| Malek- Lu [56] | $\frac{H_m}{D_c} = 418\left(\frac{D_c}{d_p}\right)^{0.75}\left(\frac{D_c}{d_i}\right)^{0.40}\left(\frac{\lambda^2}{\rho_s^{1.2}}\right)$ | Conventional spouted bed |
| Passos et al., 1993 [29] | $\frac{H_m}{L_1} = 0.605 + \frac{6.21\times10^{-2}}{A_{2D}} - \frac{2.9\times10^{-3}}{A_{2D^2}}$ | Two dimensional spouted bed $A_{2D} = \frac{Re_{mf}Re_T d_p}{ArL_N}$ |
| Morgan III & Littman, 1982 [128] | $\frac{H_m d_i}{D_c^2} = 0.218 + \frac{0.005}{A}; \quad A > 0.02$ | Conventional spouted bed For spherical particles $A = \frac{\rho_f}{(p_s - \rho_f)}\frac{U_{mF}U_T}{gd_i}$ |

Table 7: Correlation available for prediction of maximum pressure drop

| Author | correlation | geometry |
|---|---|---|
| Gelperin et al.(1961) [129] | $\frac{\Delta P_M}{H\rho_b g} = 1 + 0.062\left(\frac{D_H}{D_i}\right)^{2.54} \times \left(\frac{D_H}{D_i} - 1\right)\left[\tan\frac{\theta}{2}\right]^{-0.18}$ | Conical spouted beds |
| Gorshtein and Mukhlenov (1965) [130] | $\frac{-\Delta P_M}{\Delta P_s} = 1 + 6.65\left(\frac{H}{D_i}\right)^{1.2}\left(\tan\frac{\theta}{2}\right)^{0.5} Ar^{0.2}$ | Conical spouted beds |
| Olazar et al. (1993) [130] | $\frac{-\Delta P_M}{\Delta P_s} = 1 + 0.116\left(\frac{H}{D_i}\right)^{0.5}\left(\tan\frac{\theta}{2}\right)^{-0.8} Ar^{0.0125}$ | Conical spouted beds |
| Olazar et al. (1994) [55] | $\frac{-\Delta P_M}{\Delta P_s} = 1 + 0.35\left(\frac{H}{D}\right)^{0.1}\left(\frac{D_i}{D}\right)^{1.1} Ar^{0.1}$ | Conical cylindrical |
| Manurung [55] | $\frac{-\Delta P_M}{\Delta P_s} = \left[0.8 + \frac{6.8}{\tan\gamma}\left(\frac{D_i}{D}\right)\right] - 34.4\frac{d_p}{H}$ | Conical- cylindrical |

Table 8: Options for scaling up of conventional spouted bed

| **Options available for scale up** | | **Main characteristics** |
|---|---|---|
| changing the geometry of the conventional spouted bed (CSB) | increasing the size of a single unit [56] | Simple geometry or mechanical construction |
| | convert in to two dimensional spouted bed (2DSB) [33] | Require low pressure drop<br>Require high fluid flow rates |
| | Convert into conical spouted bed (CCSB). [131] | Require low pressure drop<br>Require high fluid flow rates<br>No limitation of the bed height |
| | Multiple unit (repeating the side by side several units) [56] | Complex design and construction<br>High investment and operating cost<br>High heat loss |
| Modification of spouting operation | Insertion of draft tube or draft plates [43] | No limitation of the bed height<br>Low pressure drop<br>Low fluid flow rates<br>Reduction of solid circulation rate<br>Low heat transfer rate |
| | Insertion of any mechanical device to improve or produce solid circulation such as mechanical conveyor spouted bed or vibrated spouted bed [94]. | |
| | Introduction of addition fluid in the annular region | Complex design and construction |

Table 9: Specifications of black pepper defined by some institutes.

| Institute | Ash % W/W Max | Acid insoluble ash % W/W Max | moisture % W/W Max | Volatile oil % V/W Min |
|---|---|---|---|---|
| ESA | 7 | 1.5 | 12 | 2 |
| CSA | 7 | 1 | 12 | 2 |
| Sri Lanka spice council | | | 12-14 | 2-2.4 |

Table 10: Standard quality specifications of black pepper approved by Sri Lanka Standard Institute.

| | Sp. Grade I | Grade I |
|---|---|---|
| Moldy berries % | 1 | 1 |
| Other extraneous matter %( insects live or dead, stones, sand, plant parts, mammalian fecal matter etc.) | 1 | 1 |
| Light berries % | Max. 4 | Max. 4 |
| Moisture % | 12 | 14 |
| Appearance | Dark black color with surface grooves | Dark black to brownish black color with surface grooves |

**Nomenclature for Appendix A**

Ar- Archimedes number $Ar = \frac{d^3\rho(\rho_p - \rho)g}{\mu^2}$

$b=U_m/U_{mf}$

D, $D_c$- diameter of the column (m)

d, $d_p$ - particle diameter , horizontally projected diameter (m)

$D_b$ , $D_H$- upper diameter of the stagnant bed in conical spouted bed (m)

Di - diameter of the contactor base(m)

$D_o$ - diameter of the gas inlet (m)

$D_T$ , $d_d$- diameter of the draft tube (m)

g- Acceleration of gravity ($m/s^2$)

H, $H_o$ - height of the stagnant bed (m)

$H_m$ – maximum spoutable bed height (m)

$L_1$- column width and column thickness in two dimensional spouted beds (m)

$L_H$- height of entrainment zone (m)

$L_N$- nozzle width in two dimensional spouted beds(m)

$l_d$- length of the draft tube (m)

$Re_{mf}$- Reynolds number of minimum fluidization

$(Re_o)_{ms}$- Reynolds number of minimum spouting , referred to Do

$Re_T$- Reynolds number of terminal velocity

$U_m$- $U_{ms}$ at maximum spoutable bed height (m/s)

$U_{mf}$ -velocity at minimum fluidization (m/s)

$U_{ms}$- minimum spouting velocity at the inlet orifice (m/s)

$U_T$ - Terminal settling velocity of isoplated particle in spouting fluid (m/s)

$\Delta P_M$- maximum pressure drop (Pa)

$\Delta P_s$ - Spouting pressure drop across bed (Pa)

$\lambda$ - Thermal conductivity of fluid (W/mK)

$\rho_f$ ,$\rho$- Density of fluid or gas( $kg/m^3$)

$\rho_s$ , $\rho_p$ - density of solid or particle ( $kg/m^3$)

$\gamma, \theta$- angle of the conical base of the contactor (degrees)

**APPENDIX B**

Figure 1: Precision balance; VWRECN 611-2300

Figure 2: Protable digital balance;  KERN PCB 350-3

Figure 3: Drying Oven; A lab Tech LDO-060E


(a) (b)

Figure 4: EXTECH CFM Thermo anemometer model 407113; (b)- Thermo-Hygrometer Model GMK-920HT

Figure 5: GC-MS)-7890A gas chromatograph (Agilent, American) equipped with a 5975C plus mass spectrometer (Agilent, American)

# APPENDIX C

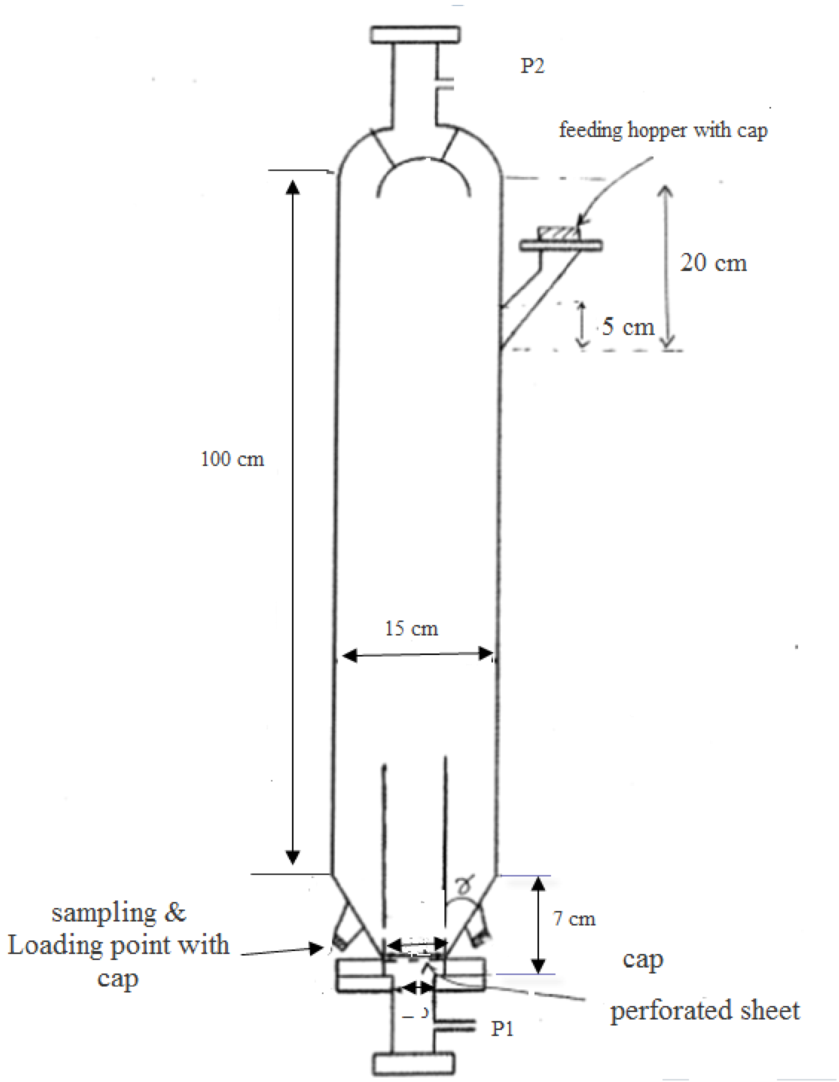


Figure 1: Spouted bed column

**Dimensions of draft tubes**

$D_T$ - diameter of tube

$L_H$ - entrainment height

$L_T$ - whole length

w - Width of draft tube faces

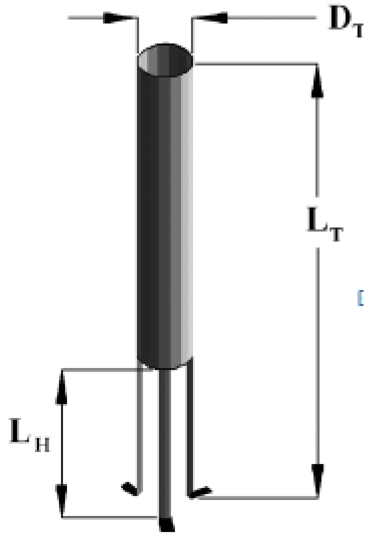


Figure 2: non porous draft tube

**Dimensions of the cyclone separator**

Appendix C Table 1: dimensions of cyclone separator

| | | |
|---|---|---|
| D | 28 | cm |
| a | 14 | cm |
| b | 7 | cm |
| De | 14 | cm |
| S | 17.5 | cm |
| h | 56 | cm |
| H | 112 | cm |
| B | 7 | cm |

:

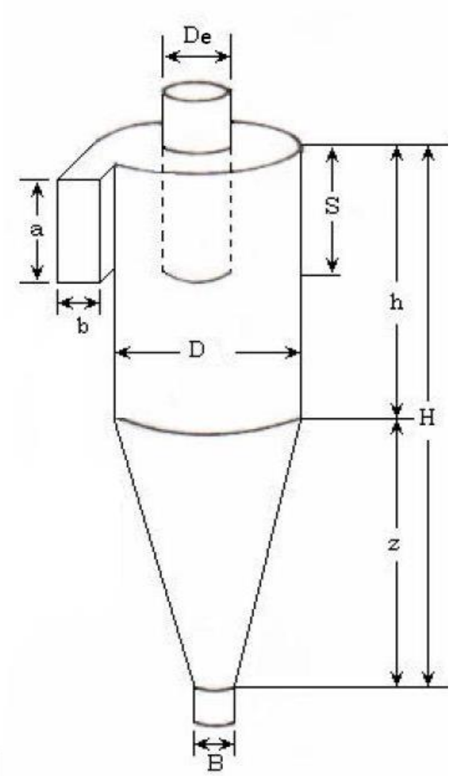


Figure 3: Reverse flow cyclone separator

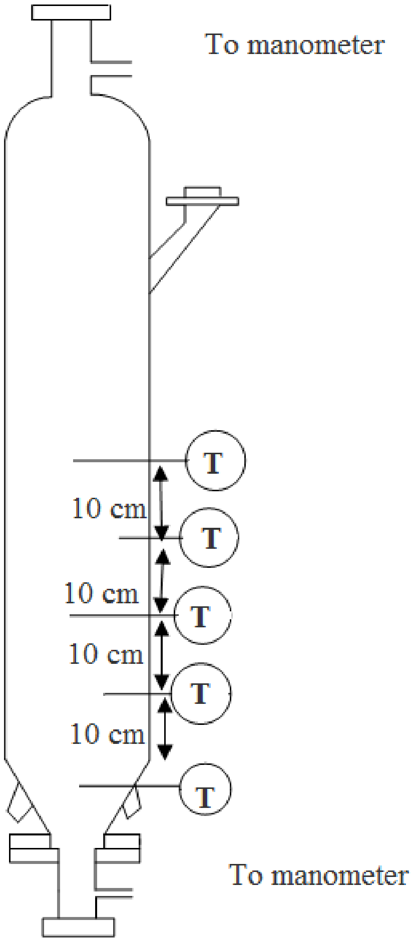


Figure 4: Arrangement of temperature sensors

# APPENDIX D

**Chromatograms  and chromatagrapgy data sheets of essential oil derived from black pepper**

## Sample No: 1

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.07.SAMPLE_1.D
Acq On : 7 Aug 2015 12:17
Operator :
Sample :
Misc :
ALS Vial : 2 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.08.07.SAMPLE_1.D\data.ms

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.531 | 211 | 238 | 259 | BV 2 | 480898 | 21075700 | 1.10% | 0.146% |
| 2 | 5.013 | 788 | 828 | 841 | BV 2 | 7025794 | 555624092 | 28.89% | 3.850% |
| 3 | 5.177 | 841 | 856 | 895 | VV 3 | 14974489 | 1923420924 | 100.00% | 13.328% |
| 4 | 5.545 | 895 | 918 | 947 | PB | 2161139 | 111208802 | 5.78% | 0.771% |
| 5 | 6.110 | 961 | 1014 | 1061 | BV 2 | 10335150 | 1761225038 | 91.57% | 12.204% |
| 6 | 6.458 | 1061 | 1073 | 1081 | VV | 3090390 | 93153745 | 4.84% | 0.645% |
| 7 | 6.712 | 1081 | 1116 | 1124 | PV | 1014920 | 53320478 | 2.77% | 0.369% |
| 8 | 6.879 | 1124 | 1144 | 1160 | VV 3 | 6218380 | 497333315 | 25.86% | 3.446% |
| 9 | 7.262 | 1160 | 1209 | 1235 | VV 6 | 5792842 | 712248559 | 37.03% | 4.935% |
| 10 | 7.463 | 1235 | 1243 | 1251 | VV 2 | 3411587 | 132897262 | 6.91% | 0.921% |
| 11 | 7.794 | 1269 | 1299 | 1306 | VV | 1179225 | 39125979 | 2.03% | 0.271% |
| 12 | 7.962 | 1306 | 1328 | 1334 | VV | 1967431 | 65403496 | 3.40% | 0.453% |
| 13 | 8.335 | 1334 | 1391 | 1403 | VV 3 | 2714041 | 169277119 | 8.80% | 1.173% |
| 14 | 8.536 | 1403 | 1425 | 1444 | VV | 5513407 | 216786759 | 11.27% | 1.502% |
| 15 | 8.704 | 1444 | 1454 | 1459 | VV | 1291134 | 36696324 | 1.91% | 0.254% |
| 16 | 8.777 | 1459 | 1466 | 1475 | VV 4 | 793572 | 39575319 | 2.06% | 0.274% |
| 17 | 8.928 | 1475 | 1492 | 1502 | VV 6 | 1545607 | 89966015 | 4.68% | 0.623% |
| 18 | 9.021 | 1502 | 1507 | 1515 | VV | 1462585 | 43332876 | 2.25% | 0.300% |
| 19 | 9.177 | 1515 | 1534 | 1538 | VV 5 | 1698074 | 87917967 | 4.57% | 0.609% |
| 20 | 9.281 | 1538 | 1551 | 1558 | VV 4 | 2836488 | 108126035 | 5.62% | 0.749% |
| 21 | 9.360 | 1558 | 1565 | 1573 | VV 2 | 2067253 | 67903550 | 3.53% | 0.471% |
| 22 | 9.675 | 1613 | 1618 | 1624 | VV 2 | 1420191 | 42455595 | 2.21% | 0.294% |
| 23 | 9.953 | 1648 | 1665 | 1675 | VV | 8356189 | 335454274 | 17.44% | 2.324% |
| 24 | 10.089 | 1675 | 1688 | 1693 | VV 2 | 2506144 | 114904121 | 5.97% | 0.796% |
| 25 | 10.152 | 1693 | 1699 | 1707 | VV 2 | 3703306 | 97833340 | 5.09% | 0.678% |
| 26 | 10.254 | 1707 | 1716 | 1723 | VV 2 | 3851557 | 109663590 | 5.70% | 0.760% |
| 27 | 10.337 | 1723 | 1730 | 1734 | VV 2 | 2243811 | 64407955 | 3.35% | 0.446% |
| 28 | 10.383 | 1734 | 1738 | 1747 | VV 3 | 2523389 | 71736369 | 3.73% | 0.497% |
| 29 | 10.469 | 1747 | 1752 | 1766 | VV 5 | 1241874 | 69600824 | 3.62% | 0.482% |
| 30 | 10.587 | 1766 | 1772 | 1779 | VV | 2681187 | 69797202 | 3.63% | 0.484% |
| 31 | 10.689 | 1779 | 1790 | 1797 | VV 5 | 1676378 | 72247997 | 3.76% | 0.501% |
| 32 | 10.772 | 1797 | 1804 | 1815 | VV | 1961371 | 69337366 | 3.60% | 0.480% |
| 33 | 10.878 | 1815 | 1822 | 1835 | VV 4 | 1326844 | 66109011 | 3.44% | 0.458% |
| 34 | 10.989 | 1835 | 1841 | 1849 | VV | 2245955 | 64605387 | 3.36% | 0.448% |
| 35 | 11.150 | 1849 | 1868 | 1886 | VV 10 | 1567030 | 125528782 | 6.53% | 0.870% |
| 36 | 11.391 | 1902 | 1909 | 1932 | VV 2 | 1505167 | 107575220 | 5.59% | 0.745% |
| 37 | 11.718 | 1932 | 1964 | 1976 | VV 8 | 1719906 | 178355385 | 9.27% | 1.236% |
| 38 | 12.042 | 1997 | 2019 | 2023 | VV | 2295448 | 121910405 | 6.34% | 0.845% |
| 39 | 12.109 | 2023 | 2030 | 2051 | VV 3 | 3064321 | 163938893 | 8.52% | 1.136% |
| 40 | 12.320 | 2051 | 2066 | 2070 | VV | 1820955 | 83711244 | 4.35% | 0.580% |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 12.410 | 2070 | 2081 | 2096 | VV | | 12032960 | 430153953 | 22.36% | 2.981% |
| 42 | 12.574 | 2096 | 2109 | 2139 | VV | | 4332183 | 241046005 | 12.53% | 1.670% |
| 43 | 12.863 | 2139 | 2158 | 2168 | VV | 2 | 2382523 | 140557553 | 7.31% | 0.974% |
| 44 | 13.008 | 2168 | 2183 | 2200 | VV | 3 | 13371476 | 821537485 | 42.71% | 5.693% |
| 45 | 13.182 | 2200 | 2212 | 2248 | VV | 4 | 3796567 | 323619675 | 16.83% | 2.242% |
| 46 | 13.648 | 2248 | 2291 | 2316 | VV | 2 | 10817649 | 1147613845 | 59.67% | 7.952% |
| 47 | 13.882 | 2316 | 2331 | 2341 | VV | 4 | 6963431 | 438870615 | 22.82% | 3.041% |
| 48 | 13.979 | 2341 | 2347 | 2356 | VV | | 557333 | 11535334 | 0.60% | 0.080% |
| 49 | 14.150 | 2356 | 2376 | 2391 | VV | | 5088834 | 156145175 | 8.12% | 1.082% |
| 50 | 14.335 | 2391 | 2407 | 2417 | VV | 8 | 795425 | 40538063 | 2.11% | 0.281% |
| 51 | 14.424 | 2417 | 2423 | 2430 | VV | | 1026088 | 22647409 | 1.18% | 0.157% |
| 52 | 14.505 | 2430 | 2436 | 2442 | VV | | 1951518 | 36848849 | 1.92% | 0.255% |
| 53 | 14.621 | 2442 | 2456 | 2460 | VV | 4 | 3265374 | 120556786 | 6.27% | 0.835% |
| 54 | 14.694 | 2460 | 2468 | 2476 | VV | | 4836245 | 132594875 | 6.89% | 0.919% |
| 55 | 14.857 | 2476 | 2496 | 2500 | VV | | 3188175 | 77070780 | 4.01% | 0.534% |
| 56 | 14.929 | 2500 | 2508 | 2520 | VV | 2 | 5077460 | 129696814 | 6.74% | 0.899% |
| 57 | 15.172 | 2539 | 2549 | 2566 | VV | 2 | 447543 | 21674350 | 1.13% | 0.150% |
| 58 | 15.331 | 2566 | 2576 | 2583 | VV | | 4747920 | 100403768 | 5.22% | 0.696% |
| 59 | 15.409 | 2583 | 2589 | 2599 | VV | | 869671 | 21704927 | 1.13% | 0.150% |
| 60 | 15.775 | 2615 | 2651 | 2665 | BV | | 8689315 | 610847443 | 31.76% | 4.233% |
| 61 | 16.019 | 2684 | 2693 | 2701 | VV | 2 | 2052667 | 38541663 | 2.00% | 0.267% |
| 62 | 16.105 | 2701 | 2707 | 2712 | VV | 3 | 718660 | 13914848 | 0.72% | 0.096% |
| 63 | 16.199 | 2712 | 2723 | 2729 | VV | | 3626466 | 90551046 | 4.71% | 0.627% |
| 64 | 16.323 | 2729 | 2744 | 2750 | VV | 4 | 3382375 | 104281522 | 5.42% | 0.723% |
| 65 | 16.392 | 2750 | 2756 | 2768 | VV | | 4985748 | 105690582 | 5.49% | 0.732% |
| 66 | 16.529 | 2768 | 2779 | 2787 | VV | | 1417881 | 30747228 | 1.60% | 0.213% |
| 67 | 16.673 | 2787 | 2803 | 2817 | VV | 2 | 1714492 | 53052837 | 2.76% | 0.368% |
| 68 | 16.806 | 2817 | 2826 | 2847 | VV | 2 | 626620 | 21545496 | 1.12% | 0.149% |
| 69 | 17.376 | 2911 | 2922 | 2933 | PV | 2 | 776492 | 16229965 | 0.84% | 0.112% |
| 70 | 17.897 | 2998 | 3011 | 3024 | VV | 4 | 595731 | 21086188 | 1.10% | 0.146% |
| 71 | 18.540 | 3099 | 3120 | 3133 | BV | | 424812 | 7355786 | 0.38% | 0.051% |
| 72 | 19.499 | 3262 | 3282 | 3288 | BV | | 410582 | 11483280 | 0.60% | 0.080% |
| 73 | 24.977 | 4166 | 4210 | 4219 | BV | 3 | 526396 | 16014516 | 0.83% | 0.111% |
| 74 | 25.669 | 4293 | 4327 | 4358 | BB | | 665768 | 20375334 | 1.06% | 0.141% |

Sum of corrected areas: 14431326310

SMART.M Tue Sep 08 13:51:16 2015

```
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Operator      :
Acquired      :  7 Aug 2015   12:17      using AcqMethod Plant Extracts.M
Instrument    :    UOSJP GCMSD
Sample Name   :
Misc Info     :
Vial Number   : 2                                      ERR
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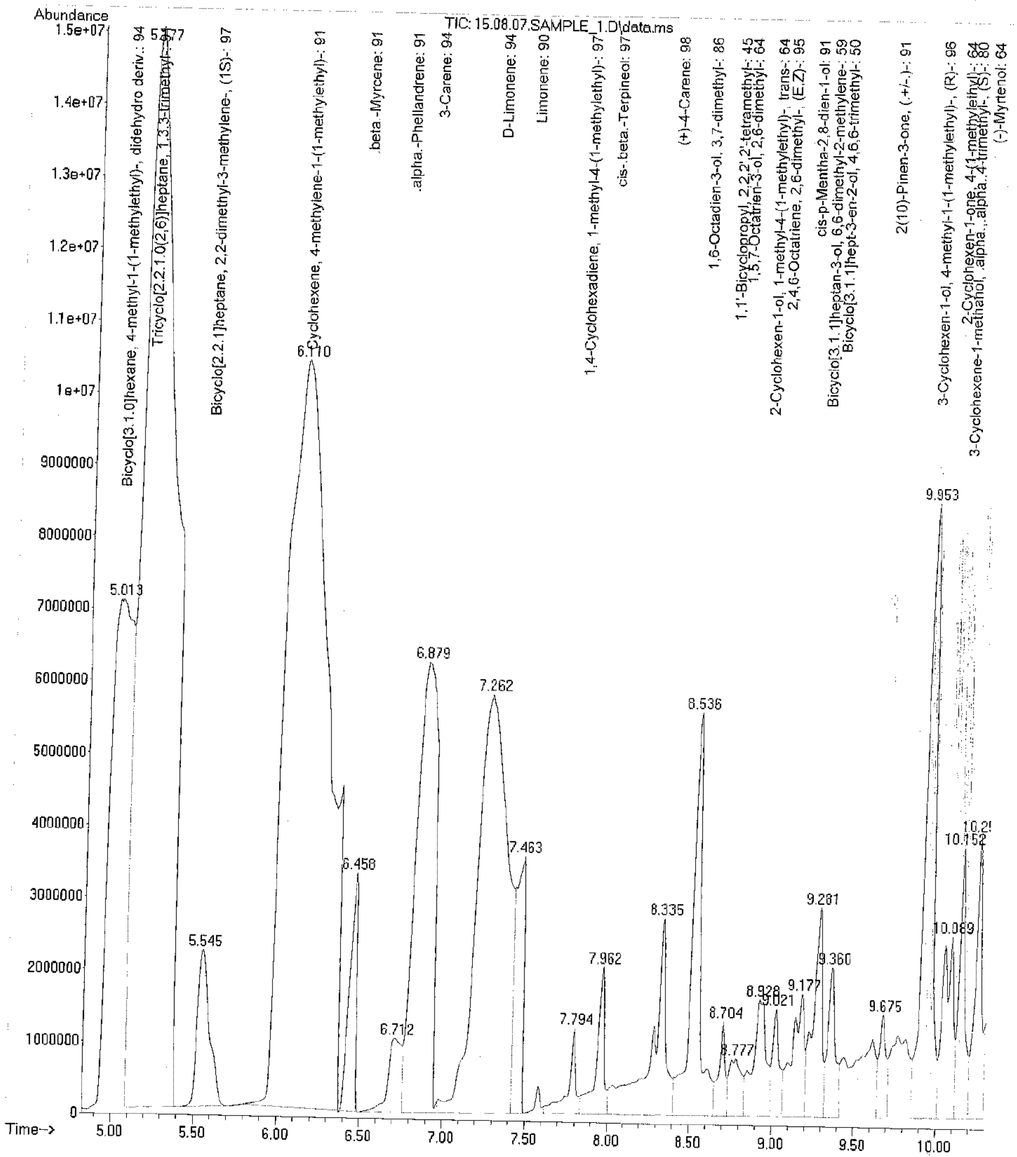

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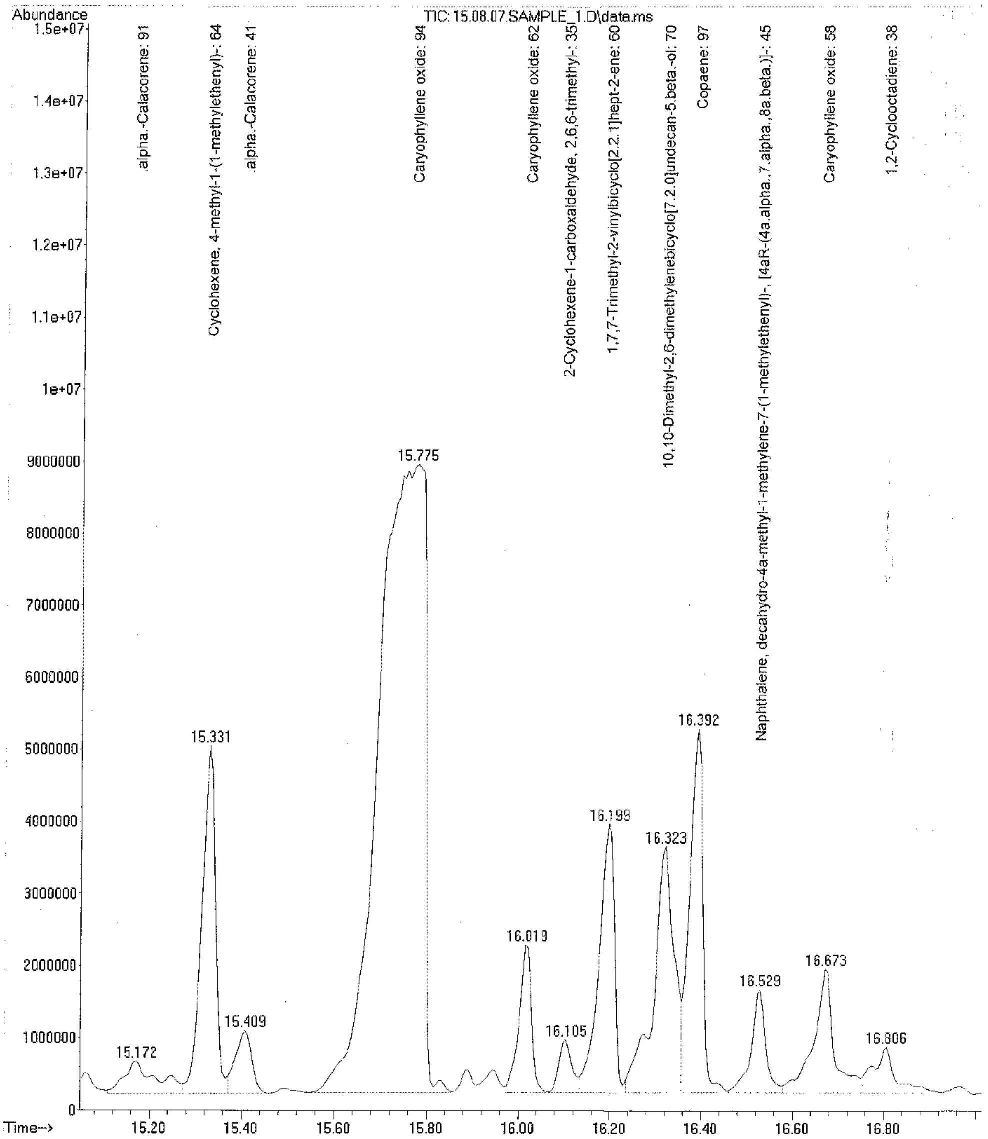
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_1.D
Operator    :
Acquired    :  7 Aug 2015   12:17      using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :                                             ERR
Vial Number:  2
```



**Sample No: 2**

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.07.SAMPLE_2.D
Acq On : 7 Aug 2015 15:20
Operator :
Sample :
Misc :
ALS Vial : 2 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.08.07.SAMPLE_2.D\data.ms

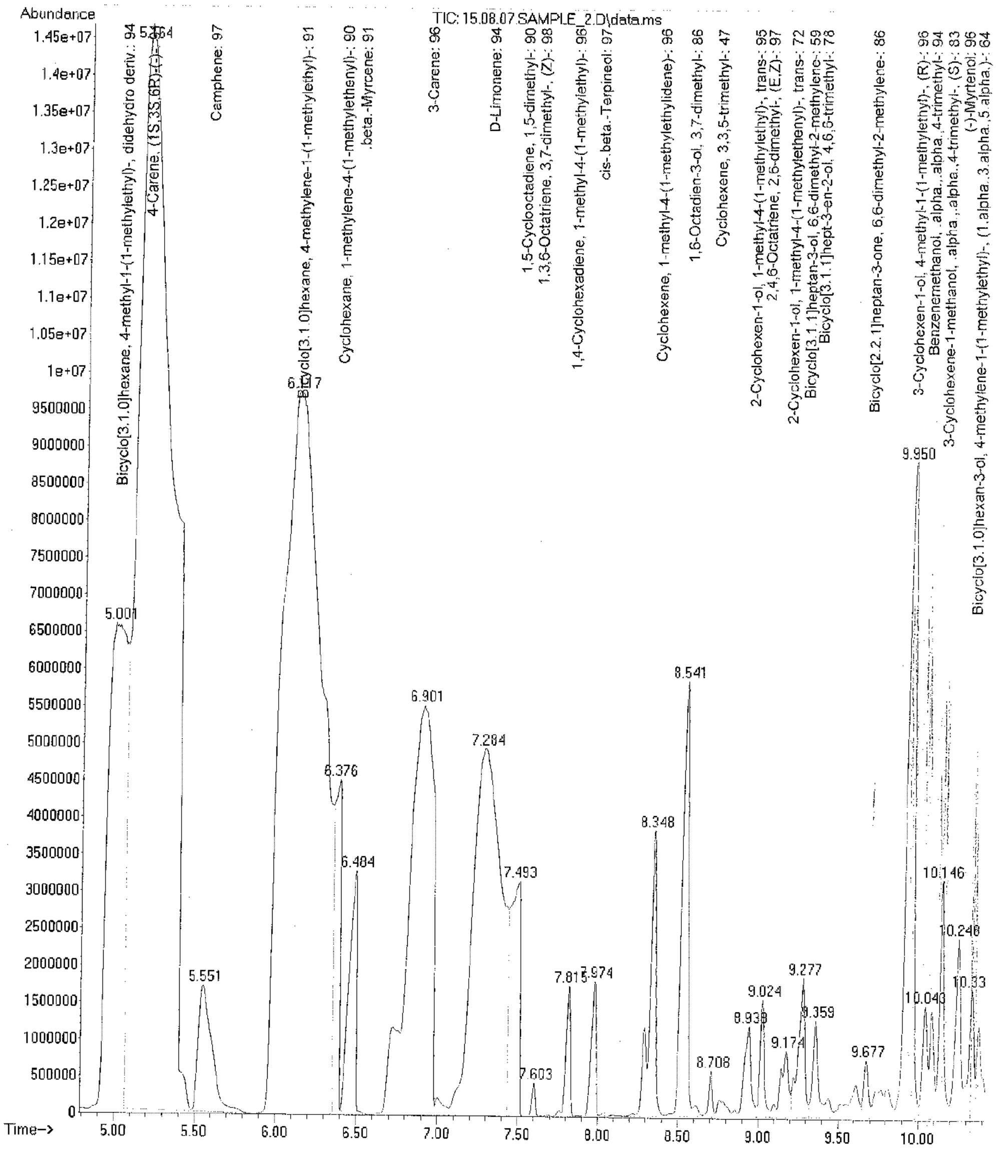
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.506 | 203 | 233 | 255 | BV 2 | 795577 | 27095255 | 1.27% | 0.224% |
| 2 | 5.001 | 785 | 826 | 836 | BV 2 | 6518875 | 496333472 | 23.29% | 4.107% |
| 3 | 5.164 | 836 | 853 | 907 | VV 2 | 14599325 | 2131072142 | 100.00% | 17.634% |
| 4 | 5.551 | 907 | 919 | 965 | VB | 1686035 | 99078228 | 4.65% | 0.820% |
| 5 | 6.117 | 969 | 1015 | 1055 | BV 3 | 9715195 | 1634628394 | 76.70% | 13.526% |
| 6 | 6.376 | 1055 | 1058 | 1065 | VV | 4410115 | 113981538 | 5.35% | 0.943% |
| 7 | 6.484 | 1065 | 1077 | 1093 | VB | 3148130 | 108268156 | 5.08% | 0.896% |
| 8 | 6.901 | 1102 | 1147 | 1177 | BV 4 | 5512570 | 571899152 | 26.84% | 4.732% |
| 9 | 7.284 | 1177 | 1212 | 1238 | VV 4 | 4951262 | 596833752 | 28.01% | 4.939% |
| 10 | 7.493 | 1238 | 1248 | 1259 | VV 4 | 3099677 | 142690063 | 6.70% | 1.181% |
| 11 | 7.603 | 1259 | 1266 | 1277 | PV | 431872 | 6036437 | 0.28% | 0.050% |
| 12 | 7.815 | 1277 | 1302 | 1318 | VV | 1692395 | 32678391 | 1.53% | 0.270% |
| 13 | 7.974 | 1318 | 1329 | 1359 | PB | 1816278 | 37710996 | 1.77% | 0.312% |
| 14 | 8.348 | 1362 | 1393 | 1405 | BV 3 | 3885131 | 106776754 | 5.01% | 0.884% |
| 15 | 8.541 | 1405 | 1425 | 1445 | VV | 5769619 | 163349071 | 7.67% | 1.352% |
| 16 | 8.708 | 1445 | 1453 | 1459 | VV | 603436 | 10004000 | 0.47% | 0.083% |
| 17 | 8.938 | 1475 | 1492 | 1501 | VV 4 | 1174616 | 37427396 | 1.76% | 0.310% |
| 18 | 9.024 | 1501 | 1507 | 1516 | VV | 1560778 | 29184916 | 1.37% | 0.241% |
| 19 | 9.174 | 1516 | 1532 | 1538 | VV 3 | 891392 | 31721739 | 1.49% | 0.262% |
| 20 | 9.277 | 1538 | 1550 | 1557 | VV 3 | 1862381 | 57488696 | 2.70% | 0.476% |
| 21 | 9.359 | 1557 | 1564 | 1583 | VV 2 | 1301210 | 38971289 | 1.83% | 0.322% |
| 22 | 9.677 | 1613 | 1618 | 1623 | VV | 764332 | 15677249 | 0.74% | 0.130% |
| 23 | 9.950 | 1648 | 1664 | 1673 | VV | 8757184 | 280002089 | 13.14% | 2.317% |
| 24 | 10.043 | 1673 | 1680 | 1691 | VV 2 | 1486192 | 58070163 | 2.72% | 0.481% |
| 25 | 10.146 | 1691 | 1697 | 1705 | VV | 3122577 | 63305029 | 2.97% | 0.524% |
| 26 | 10.248 | 1705 | 1714 | 1722 | VV 3 | 2384908 | 57606715 | 2.70% | 0.477% |
| 27 | 10.333 | 1722 | 1729 | 1745 | VV 7 | 1728167 | 65979183 | 3.10% | 0.546% |
| 28 | 10.581 | 1765 | 1771 | 1778 | VV | 1443517 | 27736410 | 1.30% | 0.230% |
| 29 | 10.686 | 1778 | 1789 | 1797 | VV 2 | 871777 | 26208849 | 1.23% | 0.217% |
| 30 | 10.768 | 1797 | 1802 | 1814 | VV | 901637 | 19400397 | 0.91% | 0.161% |
| 31 | 10.876 | 1814 | 1821 | 1834 | VV 3 | 606828 | 17277429 | 0.81% | 0.143% |
| 32 | 10.987 | 1834 | 1839 | 1847 | VV | 1168535 | 23001692 | 1.08% | 0.190% |
| 33 | 11.150 | 1847 | 1867 | 1886 | VV 7 | 743701 | 34311723 | 1.61% | 0.284% |
| 34 | 11.386 | 1886 | 1907 | 1930 | VV 4 | 689985 | 39227821 | 1.84% | 0.325% |
| 35 | 11.712 | 1943 | 1962 | 1975 | VV 10 | 638971 | 42727729 | 2.00% | 0.354% |
| 36 | 12.038 | 1995 | 2018 | 2022 | VV 2 | 1143134 | 40710097 | 1.91% | 0.337% |
| 37 | 12.098 | 2022 | 2028 | 2048 | VV 3 | 1929619 | 73831448 | 3.46% | 0.611% |
| 38 | 12.407 | 2048 | 2080 | 2094 | VV | 11676369 | 372225870 | 17.47% | 3.080% |
| 39 | 12.571 | 2094 | 2108 | 2135 | VV | 3730152 | 124882968 | 5.86% | 1.033% |
| 40 | 12.861 | 2150 | 2157 | 2167 | VV 3 | 1652038 | 64345574 | 3.02% | 0.532% |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 13.010 | 2167 | 2182 | 2195 | VV 3 | 14318982 | 732052256 | 34.35% | 6.058% |
| 42 | 13.181 | 2195 | 2211 | 2241 | VV 5 | 3884948 | 242808158 | 11.39% | 2.009% |
| 43 | 13.652 | 2241 | 2291 | 2334 | VV 4 | 12659093 | 1581254717 | 74.20% | 13.085% |
| 44 | 13.958 | 2334 | 2343 | 2351 | PV | 437642 | 7748540 | 0.36% | 0.064% |
| 45 | 14.125 | 2351 | 2371 | 2386 | VV | 5058779 | 136035062 | 6.38% | 1.126% |
| 46 | 14.256 | 2386 | 2393 | 2397 | VV | 436024 | 7795951 | 0.37% | 0.065% |
| 47 | 14.323 | 2397 | 2405 | 2414 | VV 4 | 659106 | 25499888 | 1.20% | 0.211% |
| 48 | 14.413 | 2414 | 2420 | 2426 | VV | 1152669 | 22398732 | 1.05% | 0.185% |
| 49 | 14.493 | 2426 | 2433 | 2439 | VV | 1832190 | 35314606 | 1.66% | 0.292% |
| 50 | 14.610 | 2439 | 2453 | 2458 | VV 7 | 3477558 | 126002170 | 5.91% | 1.043% |
| 51 | 14.678 | 2458 | 2465 | 2473 | VV | 5116575 | 127905497 | 6.00% | 1.058% |
| 52 | 14.842 | 2473 | 2492 | 2497 | VV | 3575259 | 78616709 | 3.69% | 0.651% |
| 53 | 14.913 | 2497 | 2505 | 2518 | VV | 6129872 | 146422109 | 6.87% | 1.212% |
| 54 | 15.310 | 2562 | 2572 | 2579 | VV | 3461727 | 61827372 | 2.90% | 0.512% |
| 55 | 15.383 | 2579 | 2584 | 2593 | VV 3 | 513942 | 11639868 | 0.55% | 0.096% |
| 56 | 15.740 | 2593 | 2645 | 2661 | VV 3 | 9693039 | 476215158 | 22.35% | 3.941% |
| 57 | 16.002 | 2681 | 2689 | 2699 | VV 2 | 1419829 | 30343394 | 1.42% | 0.251% |
| 58 | 16.095 | 2699 | 2705 | 2710 | VV | 802083 | 14030817 | 0.66% | 0.116% |
| 59 | 16.183 | 2710 | 2720 | 2726 | VV 2 | 3849246 | 82924781 | 3.89% | 0.686% |
| 60 | 16.309 | 2726 | 2741 | 2748 | VV 4 | 1921722 | 73072297 | 3.43% | 0.605% |
| 61 | 16.380 | 2748 | 2753 | 2765 | VV | 5656998 | 110066545 | 5.16% | 0.911% |
| 62 | 16.517 | 2765 | 2776 | 2785 | PV | 679456 | 14410659 | 0.68% | 0.119% |
| 63 | 16.662 | 2785 | 2801 | 2810 | PV 5 | 932616 | 20755199 | 0.97% | 0.172% |

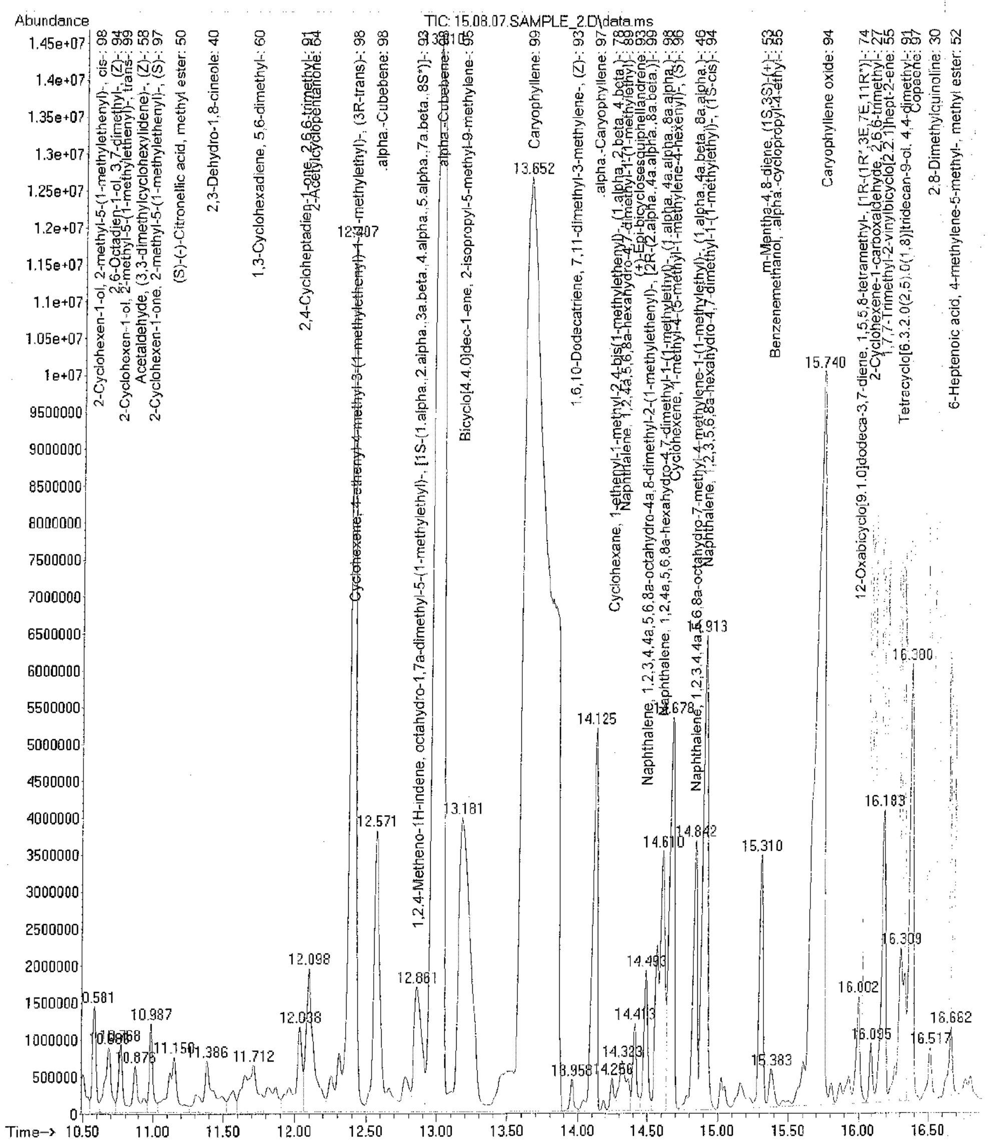
Sum of corrected areas: 12084898760

SMART.M Fri Sep 11 10:17:31 2015

File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_2.D
Operator    :
Acquired    :  7 Aug 2015  15:20      using AcqMethod Plant Extracts.M
Instrument :   UOSJP GCMSD
Sample Name:
Misc Info  :                                              ERR
Vial Number: 2



```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_2.D
Operator    :
Acquired    :  7 Aug 2015  15:20      using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :                                                  ERR
Vial Number: 2
```



# Sample No : 3

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.20.SAMPLE_3.D
Acq On : 20 Aug 2015 14:06
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.08.20.SAMPLE_3.D\data.ms

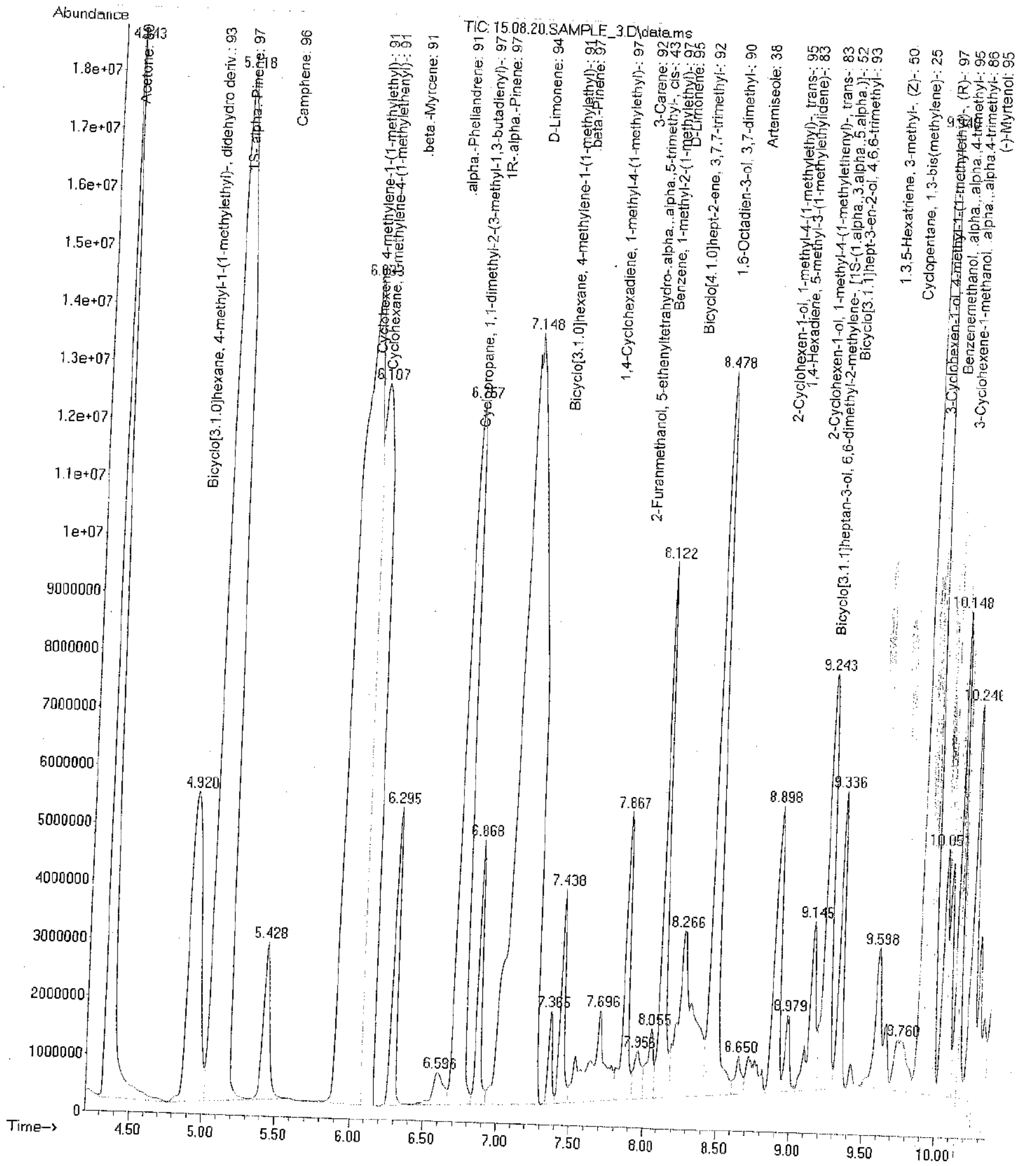
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.428 | 202 | 227 | 253 | BV | 12802398 | 481822728 | 35.09% | 2.774% |
| 2 | 4.343 | 712 | 721 | 793 | VV | 18103311 | 519883445 | 37.87% | 2.994% |
| 3 | 4.920 | 793 | 819 | 836 | PV | 5338789 | 299917308 | 21.85% | 1.727% |
| 4 | 5.118 | 836 | 852 | 884 | VV 3 | 17680147 | 1253753977 | 91.32% | 7.219% |
| 5 | 5.428 | 884 | 905 | 934 | VB | 2704874 | 86910375 | 6.33% | 0.500% |
| 6 | 6.033 | 956 | 1007 | 1015 | BV 4 | 14254918 | 1241002000 | 90.39% | 7.146% |
| 7 | 6.107 | 1015 | 1020 | 1037 | VV 3 | 12468590 | 595523106 | 43.38% | 3.429% |
| 8 | 6.295 | 1037 | 1051 | 1074 | PB | 4978035 | 109071645 | 7.94% | 0.628% |
| 9 | 6.596 | 1079 | 1103 | 1114 | BV 3 | 554155 | 27535505 | 2.01% | 0.159% |
| 10 | 6.757 | 1114 | 1130 | 1141 | VV | 12041216 | 497830095 | 36.26% | 2.867% |
| 11 | 6.868 | 1141 | 1149 | 1158 | VV | 4514382 | 83470956 | 6.08% | 0.481% |
| 12 | 7.148 | 1158 | 1196 | 1224 | VV 7 | 13239391 | 1360045167 | 99.06% | 7.831% |
| 13 | 7.365 | 1224 | 1233 | 1238 | PV | 1586241 | 27825778 | 2.03% | 0.160% |
| 14 | 7.438 | 1238 | 1245 | 1254 | VV | 3651305 | 68464535 | 4.99% | 0.394% |
| 15 | 7.696 | 1254 | 1289 | 1306 | VV 2 | 1560114 | 122456780 | 8.92% | 0.705% |
| 16 | 7.867 | 1306 | 1318 | 1326 | VV 2 | 4947316 | 118228581 | 8.61% | 0.681% |
| 17 | 7.956 | 1326 | 1333 | 1339 | VV 2 | 833217 | 30983688 | 2.26% | 0.178% |
| 18 | 8.055 | 1339 | 1350 | 1353 | VV | 1198491 | 38535605 | 2.81% | 0.222% |
| 19 | 8.122 | 1353 | 1361 | 1370 | VV | 9116371 | 191736493 | 13.97% | 1.104% |
| 20 | 8.266 | 1370 | 1385 | 1410 | VV 4 | 2855906 | 209265906 | 15.24% | 1.205% |
| 21 | 8.478 | 1410 | 1421 | 1443 | VV | 12391799 | 403403707 | 29.38% | 2.323% |
| 22 | 8.650 | 1443 | 1450 | 1457 | VV 3 | 648634 | 19771111 | 1.44% | 0.114% |
| 23 | 8.898 | 1482 | 1492 | 1500 | VV 4 | 4912409 | 139225751 | 10.14% | 0.802% |
| 24 | 8.979 | 1500 | 1506 | 1515 | VV 4 | 1228235 | 31094988 | 2.26% | 0.179% |
| 25 | 9.145 | 1515 | 1534 | 1541 | VV 3 | 2886053 | 91734417 | 6.68% | 0.528% |
| 26 | 9.243 | 1541 | 1551 | 1560 | VV 9 | 7170060 | 227942925 | 16.60% | 1.313% |
| 27 | 9.336 | 1560 | 1567 | 1575 | VV 2 | 5146296 | 107358643 | 7.82% | 0.618% |
| 28 | 9.598 | 1591 | 1611 | 1626 | BV 3 | 2414509 | 96038019 | 7.00% | 0.553% |
| 29 | 9.760 | 1626 | 1638 | 1652 | VV 6 | 870257 | 55346191 | 4.03% | 0.319% |
| 30 | 9.948 | 1652 | 1670 | 1681 | VV 4 | 16607300 | 888003182 | 64.68% | 5.113% |
| 31 | 10.051 | 1681 | 1688 | 1698 | VV | 4210823 | 156852303 | 11.42% | 0.903% |
| 32 | 10.148 | 1698 | 1704 | 1711 | VV 2 | 8286404 | 170257580 | 12.40% | 0.980% |
| 33 | 10.246 | 1711 | 1721 | 1737 | VV 2 | 6844295 | 214002213 | 15.59% | 1.232% |
| 34 | 10.400 | 1737 | 1747 | 1752 | VV 2 | 3050260 | 87855477 | 6.40% | 0.506% |
| 35 | 10.454 | 1752 | 1756 | 1771 | VV 6 | 1813101 | 73496356 | 5.35% | 0.423% |
| 6 | 10.581 | 1771 | 1777 | 1784 | VV | 5522124 | 105296380 | 7.67% | 0.606% |
| 7 | 10.682 | 1784 | 1795 | 1803 | VV 3 | 2552249 | 71805420 | 5.23% | 0.413% |
| 8 | 10.765 | 1803 | 1809 | 1821 | VV | 3086774 | 54241410 | 3.95% | 0.312% |
| 9 | 10.981 | 1821 | 1845 | 1853 | PV | 3861028 | 85868148 | 6.25% | 0.494% |
| 0 | 11.114 | 1853 | 1868 | 1882 | VV 7 | 1623965 | 57433590 | 4.18% | 0.331% |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 11.300 | 1882 | 1899 | 1907 | PV 2 | 472292 | 13268647 | 0.97% | 0.076% |
| 42 | 11.393 | 1907 | 1915 | 1928 | VV 3 | 1609849 | 64359201 | 4.69% | 0.371% |
| 43 | 11.710 | 1947 | 1969 | 1983 | VV 6 | 2201645 | 137713783 | 10.03% | 0.793% |
| 44 | 11.884 | 1983 | 1998 | 2010 | VV 4 | 3155885 | 130026056 | 9.47% | 0.749% |
| 45 | 12.040 | 2010 | 2025 | 2031 | VV 4 | 3634032 | 114887275 | 8.37% | 0.662% |
| 46 | 12.123 | 2031 | 2039 | 2060 | VV 3 | 2799164 | 143234257 | 10.43% | 0.825% |
| 47 | 12.401 | 2060 | 2086 | 2103 | VV | 13527582 | 403655582 | 29.40% | 2.324% |
| 48 | 12.569 | 2103 | 2114 | 2126 | VV 2 | 5154005 | 147980417 | 10.78% | 0.852% |
| 49 | 12.851 | 2147 | 2162 | 2172 | VV 2 | 1970448 | 73954919 | 5.39% | 0.426% |
| 50 | 12.998 | 2172 | 2187 | 2195 | VV 2 | 16661802 | 610007677 | 44.43% | 3.512% |
| 51 | 13.170 | 2195 | 2216 | 2231 | VV 6 | 5122752 | 273610241 | 19.93% | 1.575% |
| 52 | 13.289 | 2231 | 2236 | 2246 | VV 2 | 1247770 | 41402126 | 3.02% | 0.238% |
| 53 | 13.452 | 2246 | 2264 | 2278 | VV 7 | 1033607 | 69689007 | 5.08% | 0.401% |
| 54 | 13.642 | 2278 | 2296 | 2332 | VV 4 | 15097540 | 1372933235 | 100.00% | 7.905% |
| 55 | 14.089 | 2351 | 2372 | 2388 | PV | 5634273 | 138113740 | 10.06% | 0.795% |
| 56 | 14.312 | 2388 | 2410 | 2426 | VV 9 | 1158191 | 70087342 | 5.10% | 0.404% |
| 57 | 14.477 | 2426 | 2437 | 2444 | VV 7 | 2417347 | 67553007 | 4.92% | 0.389% |
| 58 | 14.569 | 2444 | 2453 | 2463 | VV 4 | 3986105 | 165470489 | 12.05% | 0.953% |
| 59 | 14.670 | 2463 | 2470 | 2484 | VV | 6245560 | 157120017 | 11.44% | 0.905% |
| 60 | 14.845 | 2484 | 2500 | 2505 | VV | 4668612 | 116463141 | 8.48% | 0.671% |
| 61 | 14.906 | 2505 | 2510 | 2523 | VV 3 | 6254565 | 145337712 | 10.59% | 0.837% |
| 62 | 15.020 | 2523 | 2529 | 2544 | VV | 565460 | 17178152 | 1.25% | 0.099% |
| 63 | 15.163 | 2544 | 2554 | 2560 | VV | 1128928 | 30515440 | 2.22% | 0.176% |
| 64 | 15.325 | 2560 | 2581 | 2592 | VV 4 | 6664394 | 223551355 | 16.28% | 1.287% |
| 65 | 15.418 | 2592 | 2597 | 2608 | VV | 1293011 | 34602829 | 2.52% | 0.199% |
| 66 | 15.734 | 2608 | 2650 | 2672 | VV | 11561102 | 907328138 | 66.09% | 5.224% |
| 67 | 15.895 | 2672 | 2678 | 2682 | VV | 561649 | 11360373 | 0.83% | 0.065% |
| 68 | 16.027 | 2692 | 2700 | 2707 | VV | 2640595 | 55992153 | 4.08% | 0.322% |
| 69 | 16.109 | 2707 | 2714 | 2719 | VV 2 | 746524 | 17726835 | 1.29% | 0.102% |
| 70 | 16.218 | 2719 | 2733 | 2739 | VV 4 | 3171524 | 123310308 | 8.98% | 0.710% |
| 71 | 16.348 | 2739 | 2754 | 2760 | VV 3 | 5832932 | 213052213 | 15.52% | 1.227% |
| 72 | 16.422 | 2760 | 2767 | 2777 | VV | 6223830 | 176667507 | 12.87% | 1.017% |
| 73 | 16.565 | 2777 | 2791 | 2799 | VV | 4199314 | 93761060 | 6.83% | 0.540% |
| 74 | 16.710 | 2799 | 2816 | 2823 | VV 3 | 4284790 | 111709326 | 8.14% | 0.643% |
| 75 | 16.816 | 2823 | 2834 | 2855 | VV 2 | 537856 | 21082820 | 1.54% | 0.121% |
| 76 | 17.392 | 2918 | 2931 | 2947 | PV 8 | 550746 | 14168315 | 1.03% | 0.082% |
| 77 | 17.908 | 3006 | 3019 | 3034 | VV 3 | 1472808 | 50380200 | 3.67% | 0.290% |
| 78 | 18.217 | 3034 | 3071 | 3088 | PV 10 | 1450926 | 66401920 | 4.84% | 0.382% |
| 79 | 18.604 | 3121 | 3137 | 3152 | VV 8 | 549900 | 29338375 | 2.14% | 0.169% |
| 80 | 19.046 | 3205 | 3212 | 3218 | PV | 553738 | 9332233 | 0.68% | 0.054% |
| 81 | 19.226 | 3235 | 3242 | 3250 | VV 2 | 445355 | 10135155 | 0.74% | 0.058% |
| 82 | 19.308 | 3250 | 3256 | 3273 | VV | 600994 | 11522830 | 0.84% | 0.066% |
| 83 | 23.078 | 3865 | 3895 | 3913 | BV 6 | 462482 | 23868178 | 1.74% | 0.137% |
| 84 | 24.535 | 4125 | 4141 | 4154 | PV 2 | 508188 | 19682657 | 1.43% | 0.113% |
| 85 | 24.736 | 4154 | 4175 | 4200 | VV 7 | 627893 | 48181678 | 3.51% | 0.277% |
| 86 | 24.993 | 4211 | 4219 | 4226 | VV 4 | 946023 | 28833933 | 2.10% | 0.166% |
| 87 | 25.064 | 4226 | 4231 | 4251 | VV | 847472 | 25342050 | 1.85% | 0.146% |
| 88 | 25.674 | 4290 | 4334 | 4349 | VV 2 | 1038715 | 33863464 | 2.47% | 0.195% |

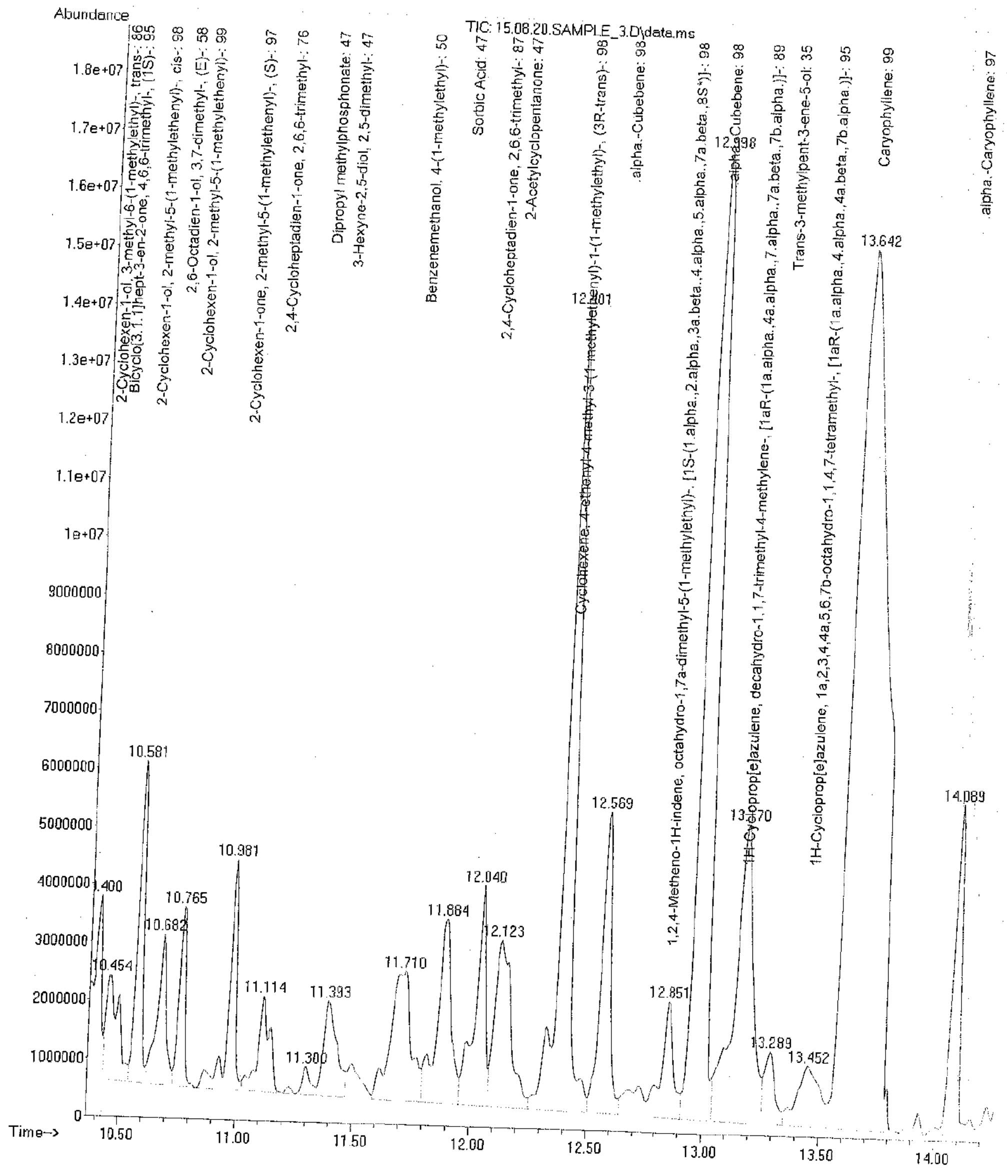
Sum of corrected areas: 17367048848

MART.M Fri Sep 11 10:24:42 2015

File :C:\msdchem\1\data\Commercial 2015.08.07\15.08.20.SAMPLE_3.D
Operator :
Acquired : 20 Aug 2015 14:06 using AcqMethod PLANT EXTRACTS.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1
ERR

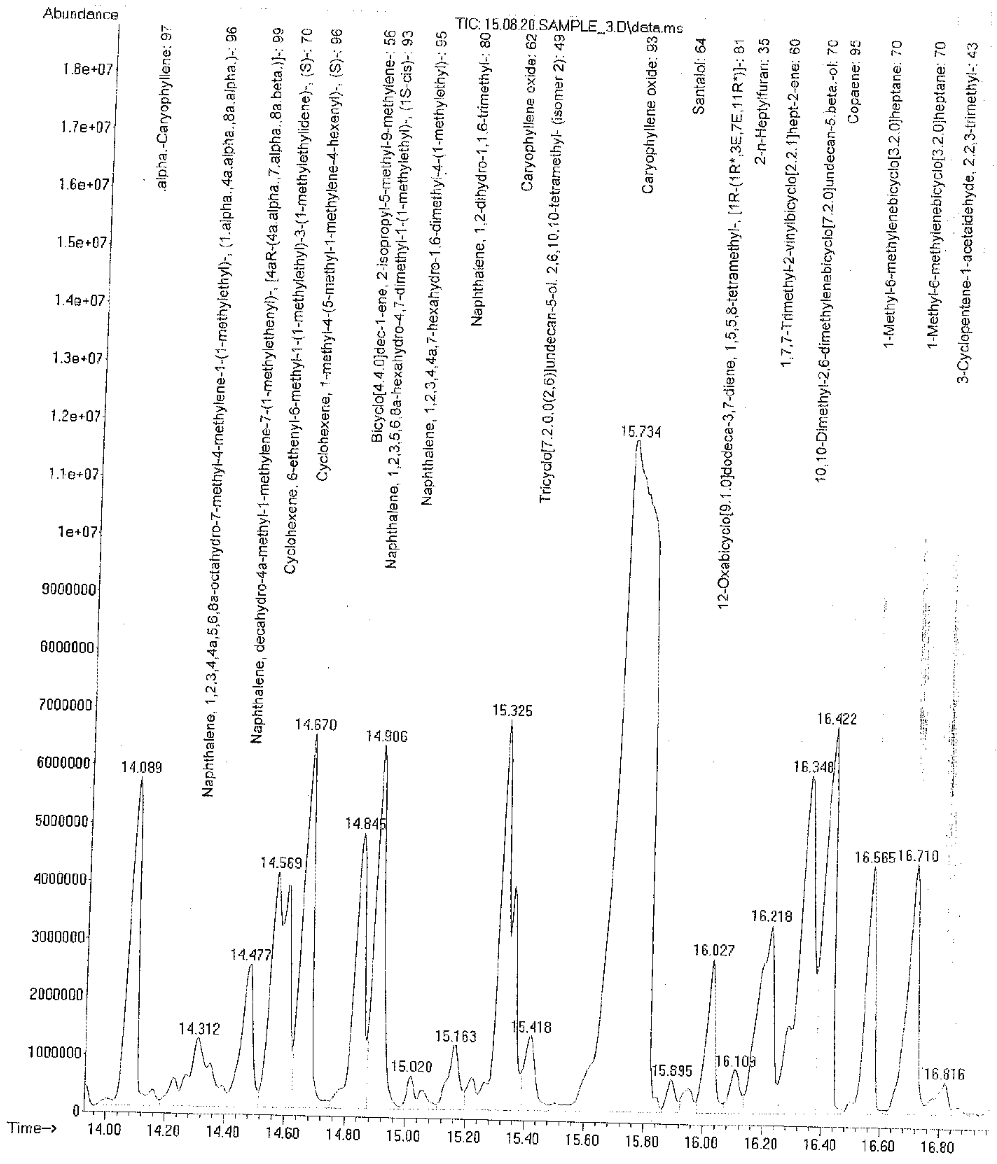


File :C:\msdchem\1\data\Commercial 2015.08.07\15.08.20.SAMPLE_3.D
Operator :
Acquired : 20 Aug 2015 14:06 using AcqMethod PLANT EXTRACTS.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1 ERR



File :C:\msdchem\1\data\Commercial 2015.08.07\15.08.20 SAMPLE_3.D
Operator :
Acquired : 20 Aug 2015 14:06 using AcqMethod PLANT EXTRACTS.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1

ERR



## Sample No: 4

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.09.03.SAMPLE_H.D
Acq On : 3 Sep 2015 12:17
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

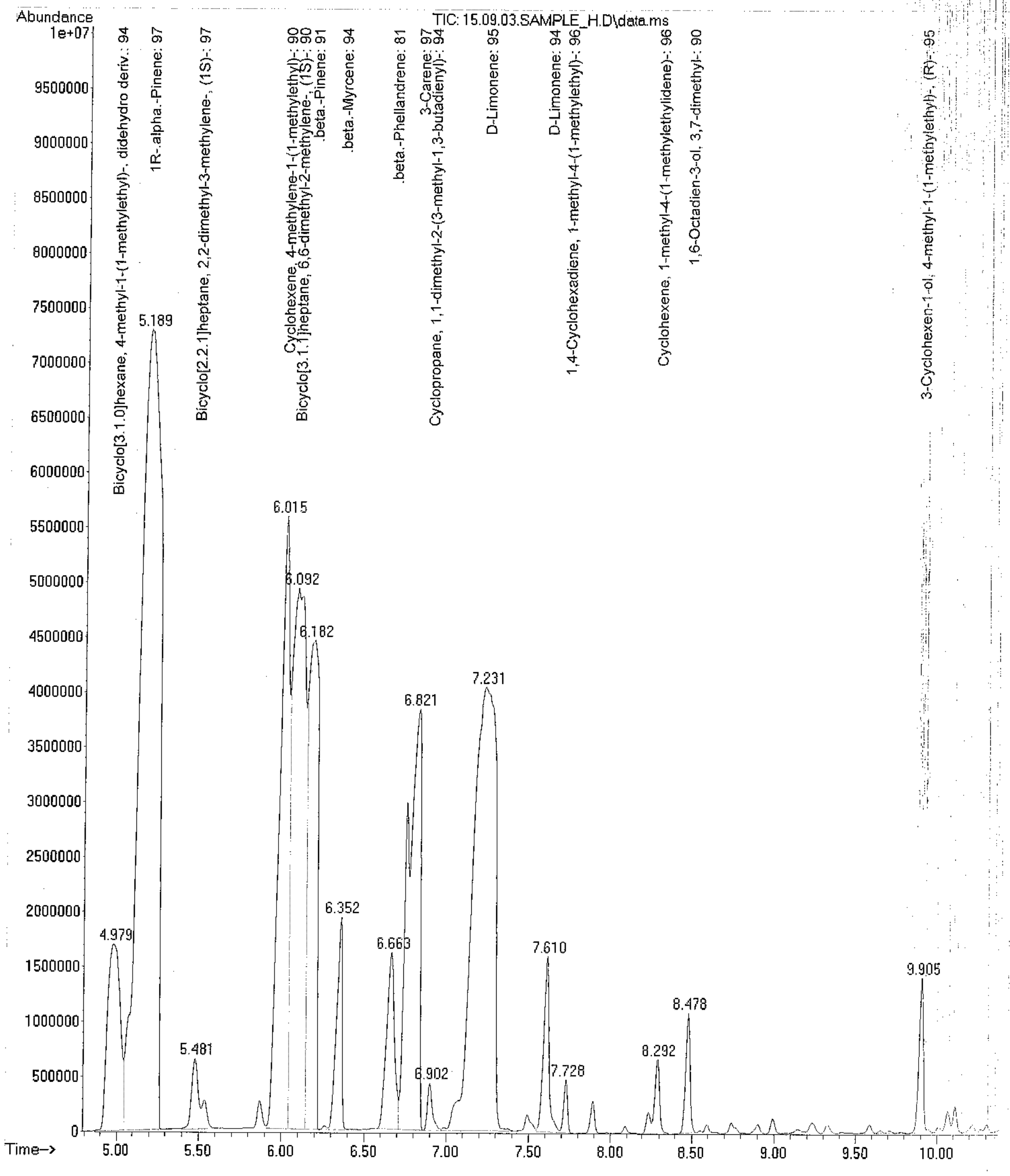
Signal : TIC: 15.09.03.SAMPLE_H.D\data.ms

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.503 | 213 | 240 | 248 | BV | 6634414 | 138336107 | 22.81% | 4.112% |
| 2 | 1.575 | 248 | 252 | 276 | VB | 9048946 | 220686582 | 36.39% | 6.560% |
| 3 | 2.813 | 447 | 462 | 473 | BB | 1094950 | 25914118 | 4.27% | 0.770% |
| 4 | 4.979 | 797 | 829 | 840 | BV | 1685321 | 88311134 | 14.56% | 2.625% |
| 5 | 5.189 | 840 | 864 | 881 | VB 3 | 7277523 | 606461253 | 100.00% | 18.026% |
| 6 | 5.481 | 900 | 914 | 941 | BB | 633523 | 22617632 | 3.73% | 0.672% |
| 7 | 6.015 | 986 | 1004 | 1009 | VV | 5506356 | 211079539 | 34.81% | 6.274% |
| 8 | 6.092 | 1009 | 1017 | 1026 | VV | 4873573 | 281036047 | 46.34% | 8.353% |
| 9 | 6.182 | 1026 | 1032 | 1042 | VV 3 | 4434092 | 179290653 | 29.56% | 5.329% |
| 10 | 6.352 | 1042 | 1061 | 1071 | PB | 1837987 | 43816848 | 7.23% | 1.302% |
| 11 | 6.663 | 1098 | 1114 | 1122 | BV 2 | 1585352 | 52959817 | 8.73% | 1.574% |
| 12 | 6.821 | 1122 | 1141 | 1148 | VV 2 | 3761298 | 197963666 | 32.64% | 5.884% |
| 13 | 6.902 | 1148 | 1154 | 1166 | PV | 422878 | 9067153 | 1.50% | 0.270% |
| 14 | 7.231 | 1166 | 1210 | 1244 | VB 6 | 4020995 | 376119691 | 62.02% | 11.180% |
| 15 | 7.610 | 1263 | 1274 | 1287 | VV | 1519915 | 37205632 | 6.13% | 1.106% |
| 16 | 7.728 | 1287 | 1294 | 1311 | VV | 458686 | 7756058 | 1.28% | 0.231% |
| 17 | 8.292 | 1372 | 1390 | 1406 | BV | 644683 | 15921342 | 2.63% | 0.473% |
| 18 | 8.478 | 1406 | 1421 | 1431 | PV | 1007953 | 18932479 | 3.12% | 0.563% |
| 19 | 9.905 | 1597 | 1663 | 1675 | BV | 1423351 | 28222722 | 4.65% | 0.839% |
| 20 | 12.383 | 2067 | 2083 | 2089 | BV | 1819995 | 31638217 | 5.22% | 0.940% |
| 21 | 12.976 | 2168 | 2183 | 2204 | VV | 4631681 | 117901120 | 19.44% | 3.504% |
| 22 | 13.152 | 2204 | 2213 | 2242 | VB 4 | 794942 | 26429930 | 4.36% | 0.786% |
| 23 | 13.656 | 2278 | 2298 | 2328 | BB 9 | 6341412 | 468257675 | 77.21% | 13.918% |
| 24 | 14.057 | 2348 | 2366 | 2375 | BV | 1579805 | 28756334 | 4.74% | 0.855% |
| 25 | 14.583 | 2442 | 2455 | 2460 | VV 5 | 564346 | 18038170 | 2.97% | 0.536% |
| 26 | 14.642 | 2460 | 2465 | 2477 | VV | 1236786 | 22771880 | 3.75% | 0.677% |
| 27 | 14.805 | 2477 | 2493 | 2498 | VV | 574939 | 10455659 | 1.72% | 0.311% |
| 28 | 14.873 | 2498 | 2505 | 2519 | VV 2 | 1436171 | 25052992 | 4.13% | 0.745% |
| 29 | 15.686 | 2610 | 2642 | 2665 | BB | 1418399 | 37373557 | 6.16% | 1.111% |
| 30 | 16.357 | 2737 | 2756 | 2770 | BV | 678752 | 15977249 | 2.63% | 0.475% |

Sum of corrected areas: 3364351256

MART.M Fri Sep 11 11:49:02 2015

File        :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_H.D
Operator    :
Acquired    :  3 Sep 2015  12:17     using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 1



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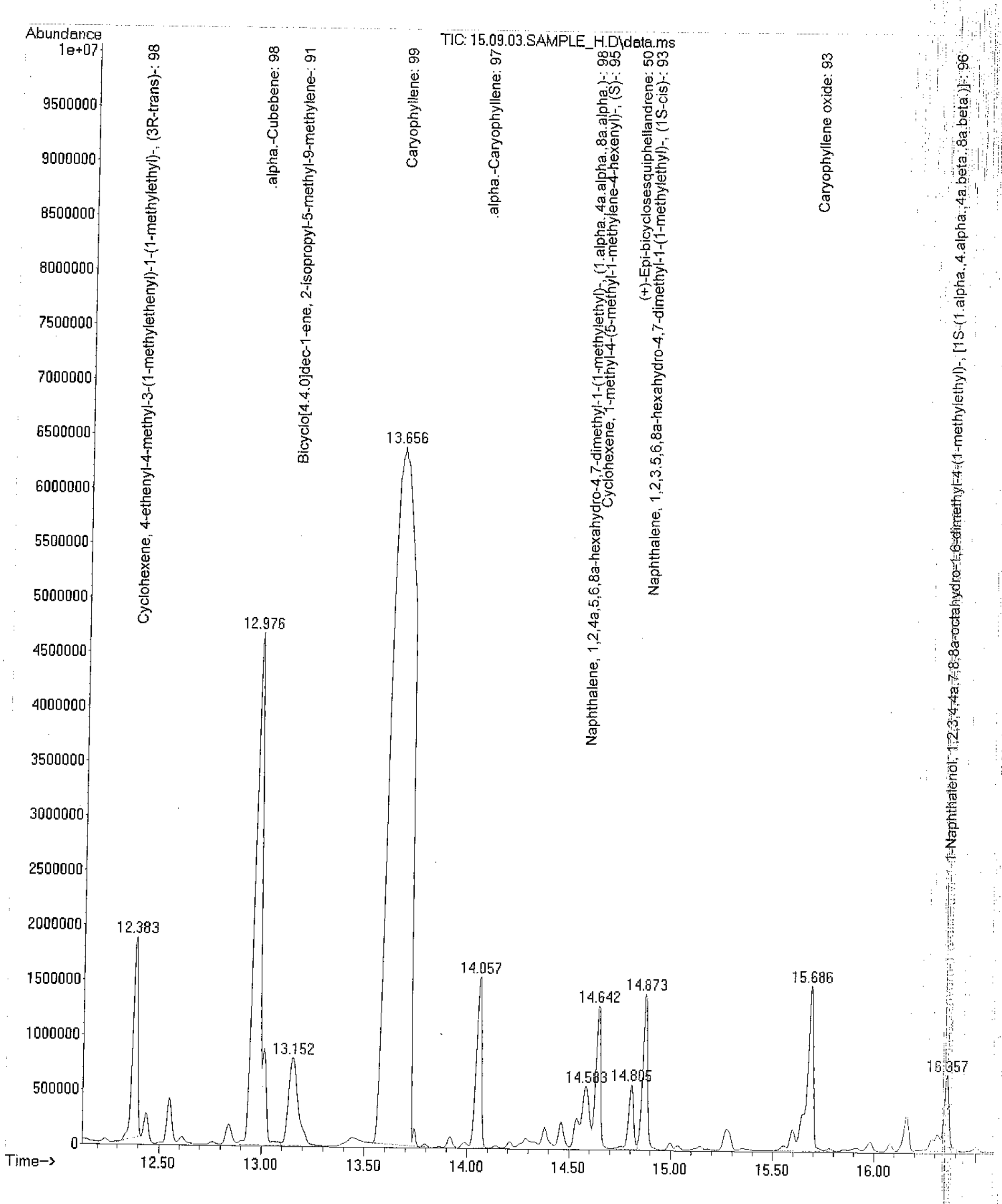
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_H.D
Operator    :
Acquired    :  3 Sep 2015  12:17      using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 1
```



## Sample No: 5

Area Percent Report

```
Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.10.SAMPLE_4.D
Acq On    : 10 Aug 2015  14:40
Operator  :
Sample    :
Misc      :
ALS Vial  : 1   Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method    : C:\MSDCHEM\1\METHODS\SMART.M
Title     : autoint1.e

Signal    : TIC: 15.08.10.SAMPLE_4.D\data.ms
```

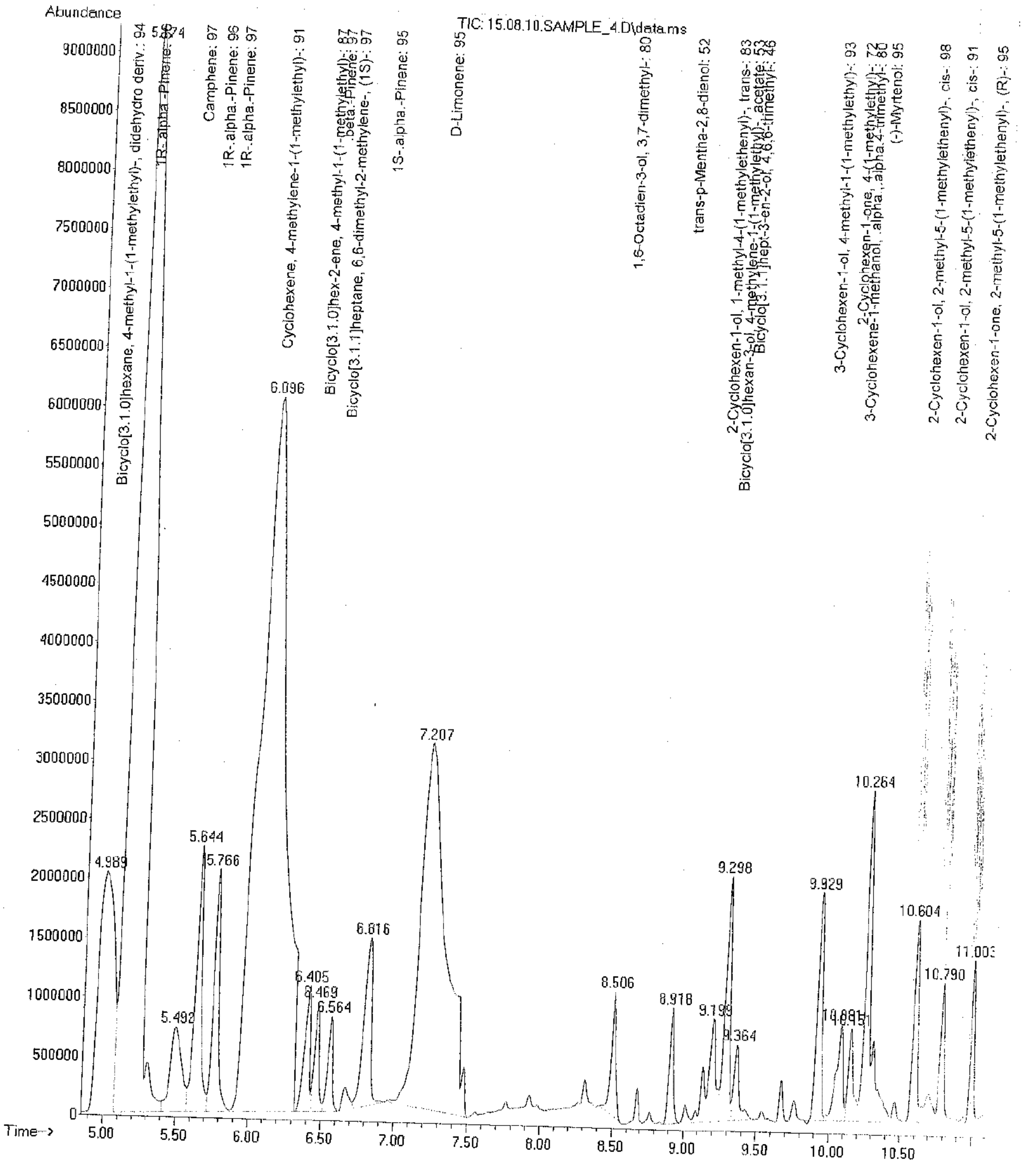
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.513 | 209 | 238 | 258 | BB 2 | 678095 | 20095849 | 2.71% | 0.382% |
| 2 | 4.989 | 801 | 826 | 841 | BV 2 | 2014936 | 145371804 | 19.63% | 2.764% |
| 3 | 5.174 | 841 | 858 | 897 | VV 3 | 9187644 | 735526417 | 99.32% | 13.985% |
| 4 | 5.492 | 897 | 912 | 926 | VV 5 | 715585 | 38370541 | 5.18% | 0.730% |
| 5 | 5.644 | 926 | 937 | 950 | VV | 2220531 | 66892446 | 9.03% | 1.272% |
| 6 | 5.766 | 950 | 958 | 977 | VV | 2022670 | 56161354 | 7.58% | 1.068% |
| 7 | 6.096 | 977 | 1014 | 1055 | VV 2 | 6026358 | 740553527 | 100.00% | 14.080% |
| 8 | 6.405 | 1055 | 1066 | 1071 | VV | 977368 | 26979224 | 3.64% | 0.513% |
| 9 | 6.469 | 1071 | 1077 | 1084 | VV | 916435 | 21438596 | 2.89% | 0.408% |
| 10 | 6.564 | 1084 | 1093 | 1103 | VV | 775952 | 18544251 | 2.50% | 0.353% |
| 11 | 6.816 | 1120 | 1136 | 1156 | VB 2 | 1410508 | 49559144 | 6.69% | 0.942% |
| 12 | 7.207 | 1162 | 1202 | 1254 | BV 5 | 3080385 | 365379310 | 49.34% | 6.947% |
| 13 | 8.506 | 1408 | 1422 | 1435 | BV 2 | 1016989 | 24103587 | 3.25% | 0.458% |
| 14 | 8.918 | 1482 | 1492 | 1502 | BV | 955438 | 20798684 | 2.81% | 0.395% |
| 15 | 9.199 | 1516 | 1540 | 1548 | VV 3 | 864136 | 35050147 | 4.73% | 0.666% |
| .6 | 9.298 | 1548 | 1556 | 1563 | VV | 1944380 | 50561750 | 6.83% | 0.961% |
| .7 | 9.364 | 1563 | 1568 | 1589 | VB | 638228 | 15642751 | 2.11% | 0.297% |
| .8 | 9.929 | 1646 | 1663 | 1670 | BV 3 | 1921667 | 45457153 | 6.14% | 0.864% |
| .9 | 10.081 | 1670 | 1689 | 1695 | VV 7 | 818843 | 26793340 | 3.62% | 0.509% |
| 0 | 10.151 | 1695 | 1701 | 1710 | VV 2 | 770926 | 18768077 | 2.53% | 0.357% |
| 1 | 10.264 | 1710 | 1720 | 1749 | VV 2 | 2772515 | 85288114 | 11.52% | 1.622% |
| 2 | 10.604 | 1765 | 1777 | 1787 | PV | 1703671 | 38526298 | 5.20% | 0.732% |
| 3 | 10.790 | 1802 | 1809 | 1838 | VB | 1151560 | 24247642 | 3.27% | 0.461% |
| 4 | 11.003 | 1838 | 1845 | 1882 | BB | 1328558 | 31209304 | 4.21% | 0.593% |
| 5 | 12.405 | 2005 | 2083 | 2100 | BV | 4238218 | 151849281 | 20.50% | 2.887% |
| 6 | 12.575 | 2100 | 2111 | 2152 | VV 2 | 1371742 | 76527156 | 10.33% | 1.455% |
| 7 | 12.864 | 2152 | 2160 | 2171 | VV 2 | 692736 | 26866522 | 3.63% | 0.511% |
| 8 | 13.023 | 2171 | 2187 | 2207 | VV 4 | 7211960 | 454989816 | 61.44% | 8.651% |
| 9 | 13.188 | 2207 | 2215 | 2252 | VV 3 | 1413705 | 92565705 | 12.50% | 1.760% |
| 0 | 13.663 | 2252 | 2296 | 2341 | VV 3 | 5131415 | 512369078 | 69.19% | 9.742% |
| 1 | 14.158 | 2361 | 2380 | 2386 | BV | 1984511 | 56201987 | 7.59% | 1.069% |
| 2 | 14.356 | 2386 | 2413 | 2434 | VV | 440036 | 24638471 | 3.33% | 0.468% |
| 3 | 14.528 | 2434 | 2442 | 2448 | VV | 1322396 | 28388382 | 3.83% | 0.540% |
| 4 | 14.632 | 2448 | 2460 | 2465 | VV 5 | 1661869 | 54135306 | 7.31% | 1.029% |
| 5 | 14.734 | 2465 | 2477 | 2495 | VV 6 | 2501233 | 180931011 | 24.43% | 3.440% |
| 6 | 14.980 | 2495 | 2519 | 2530 | VV 4 | 1245612 | 63486840 | 8.57% | 1.207% |
|  | 15.386 | 2575 | 2588 | 2619 | BB 2 | 2304511 | 72557539 | 9.80% | 1.380% |
|  | 15.784 | 2619 | 2655 | 2680 | BV 7 | 3260286 | 274268705 | 37.04% | 5.215% |
|  | 16.081 | 2680 | 2705 | 2711 | VV 3 | 596975 | 15769527 | 2.13% | 0.300% |
|  | 16.256 | 2711 | 2735 | 2741 | VV | 885431 | 29224551 | 3.95% | 0.556% |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 16.380 | 2741 | 2756 | 2761 | VV | 4 | 1060173 | 29692825 | 4.01% | 0.565% |
| 42 | 16.448 | 2761 | 2768 | 2778 | VV | | 1432674 | 33450465 | 4.52% | 0.636% |
| 43 | 16.584 | 2778 | 2791 | 2797 | PV | | 715767 | 14386193 | 1.94% | 0.274% |
| 44 | 16.731 | 2797 | 2815 | 2827 | PV | 6 | 750949 | 21251529 | 2.87% | 0.404% |
| 45 | 17.939 | 3012 | 3020 | 3033 | VV | 3 | 452383 | 12794486 | 1.73% | 0.243% |
| 46 | 33.629 | 5619 | 5678 | 5704 | BV | 7 | 436330 | 56121092 | 7.58% | 1.067% |
| 47 | 44.419 | 7363 | 7506 | 7563 | BV | 8 | 665763 | 275794650 | 37.24% | 5.244% |

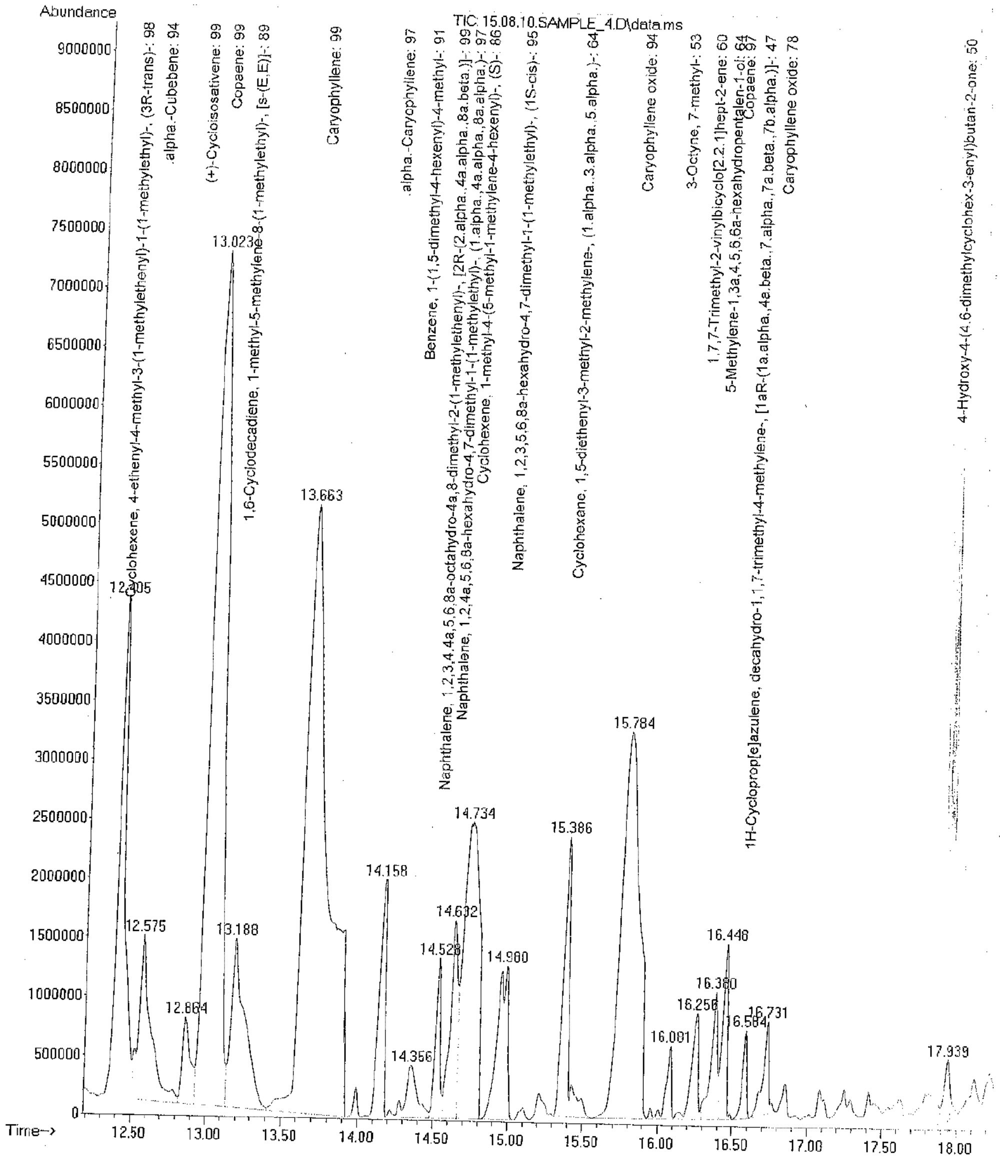
Sum of corrected areas: 5259580425

SMART.M Fri Sep 11 10:35:02 2015

```
File            :C:\msdchem\1\data\Commercial 2015.08.07\15.08.10.SAMPLE_4.D
Operator        :
Acquired        : 10 Aug 2015  14:40      using AcqMethod PLANT EXTRACTS.M
Instrument :      UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 1
```



File : C:\msdchem\1\data\Commercial 2015.08.07\15.08.10.SAMPLE_4.D
Operator :
Acquired : 10 Aug 2015 14:40 using AcqMethod PLANT EXTRACTS.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1



**Sample No: 6**

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.09.03.SAMPLE_17.D
Acq On : 3 Sep 2015 10:32
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

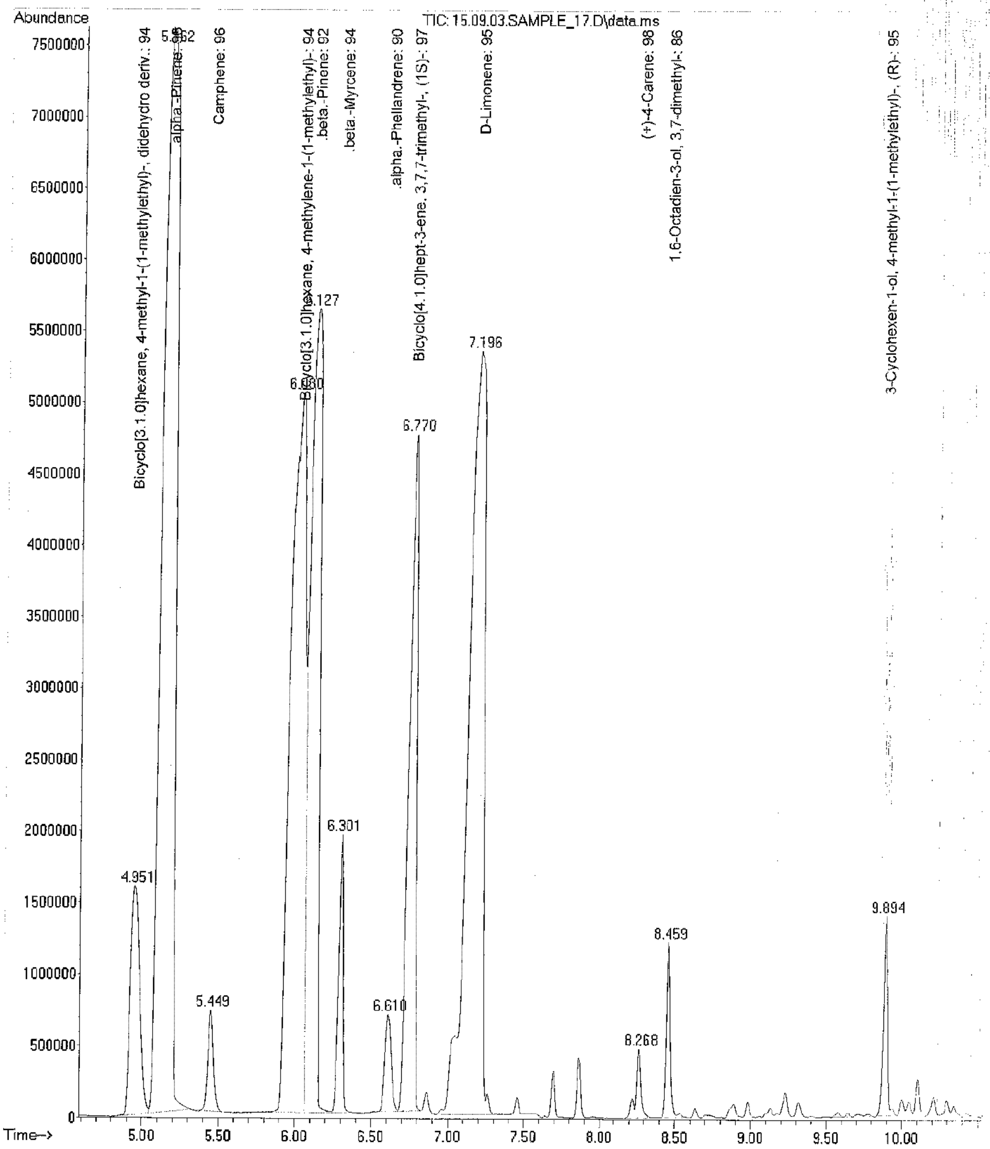
Signal : TIC: 15.09.03.SAMPLE_17.D\data.ms

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.951 | 800 | 824 | 839 | BV 2 | 1583932 | 71108643 | 15.45% | 2.723% |
| 2 | 5.162 | 839 | 860 | 886 | VB 3 | 7550933 | 460249717 | 100.00% | 17.622% |
| 3 | 5.449 | 886 | 908 | 933 | BB | 693608 | 18027353 | 3.92% | 0.690% |
| 4 | 6.030 | 970 | 1007 | 1013 | BV 2 | 5025703 | 331003471 | 71.92% | 12.674% |
| 5 | 6.127 | 1013 | 1023 | 1043 | VV 2 | 5609027 | 251562310 | 54.66% | 9.632% |
| 6 | 6.301 | 1043 | 1053 | 1079 | VB | 1911508 | 37660231 | 8.18% | 1.442% |
| 7 | 6.610 | 1092 | 1105 | 1116 | BV | 670882 | 19248409 | 4.18% | 0.737% |
| 8 | 6.770 | 1116 | 1132 | 1142 | VV | 4631057 | 160022917 | 34.77% | 6.127% |
| 9 | 7.196 | 1160 | 1204 | 1234 | BB 5 | 5289960 | 370115444 | 80.42% | 14.171% |
| 10 | 8.268 | 1368 | 1386 | 1404 | BV | 472826 | 11869161 | 2.58% | 0.454% |
| 11 | 8.459 | 1404 | 1418 | 1442 | VB | 1200866 | 23324956 | 5.07% | 0.893% |
| 12 | 9.894 | 1599 | 1661 | 1674 | BV | 1341652 | 27498163 | 5.97% | 1.053% |
| 13 | 12.380 | 2062 | 2082 | 2099 | BV | 1769008 | 33416890 | 7.26% | 1.279% |
| 14 | 12.551 | 2099 | 2111 | 2134 | PB | 437616 | 8742089 | 1.90% | 0.335% |
| 15 | 12.973 | 2172 | 2183 | 2192 | BV | 4761566 | 103109479 | 22.40% | 3.948% |
| 16 | 13.150 | 2192 | 2213 | 2239 | PB 5 | 873317 | 27310408 | 5.93% | 1.046% |
| 17 | 13.649 | 2274 | 2297 | 2328 | BB 7 | 6600321 | 448314029 | 97.41% | 17.165% |
| 18 | 14.052 | 2356 | 2366 | 2375 | BV | 1611253 | 27656632 | 6.01% | 1.059% |
| 19 | 14.580 | 2441 | 2455 | 2459 | VV 3 | 564722 | 17379718 | 3.78% | 0.665% |
| 20 | 14.640 | 2459 | 2465 | 2476 | VV | 1434020 | 24691325 | 5.36% | 0.945% |
| 21 | 14.804 | 2476 | 2493 | 2498 | VV | 588439 | 10361346 | 2.25% | 0.397% |
| 22 | 14.871 | 2498 | 2504 | 2520 | VV 2 | 1386647 | 24618690 | 5.35% | 0.943% |
| 23 | 15.285 | 2520 | 2574 | 2581 | PV 8 | 427389 | 11655781 | 2.53% | 0.446% |
| 24 | 15.695 | 2600 | 2644 | 2665 | BV | 2620080 | 71534876 | 15.54% | 2.739% |
| 25 | 16.163 | 2703 | 2723 | 2729 | BV 3 | 455806 | 9512234 | 2.07% | 0.364% |
| 26 | 16.357 | 2751 | 2756 | 2769 | VV | 667613 | 11742589 | 2.55% | 0.450% |

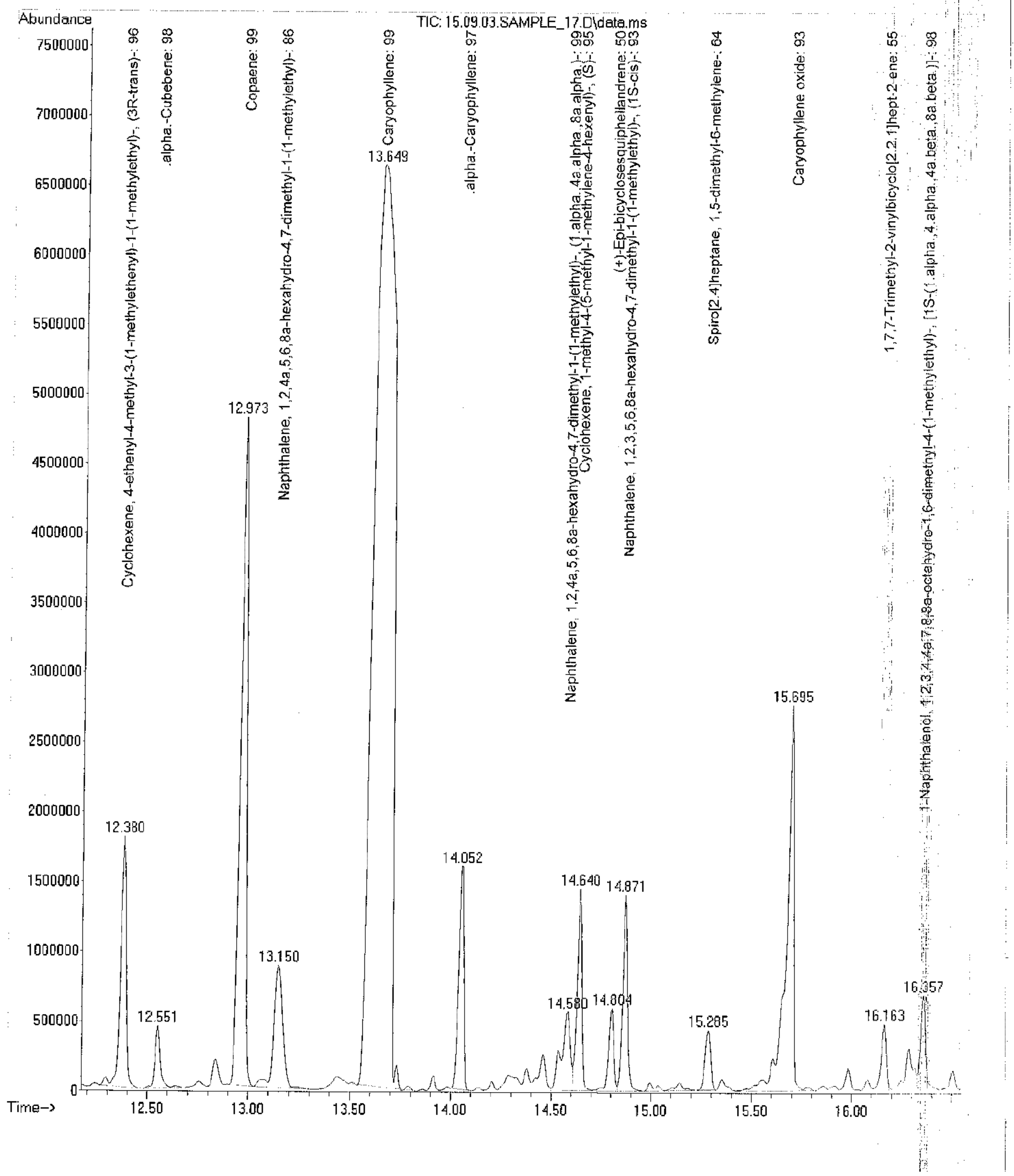
Sum of corrected areas: 2611736861

SMART.M Fri Sep 11 11:25:47 2015

```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_17.D
Operator    :
Acquired    :  3 Sep 2015  10:32     using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 1
```



```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_17.D
Operator    :
Acquired    :  3 Sep 2015  10:32     using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 1
```



**Sample No: 7**

Area Percent Report

```
Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.09.03.SAMPLE_D.D
Acq On    :  3 Sep 2015  14:02
Operator  :
Sample    :
Misc      :
ALS Vial  : 1   Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method    : C:\MSDCHEM\1\METHODS\SMART.M
Title     : autoint1.e

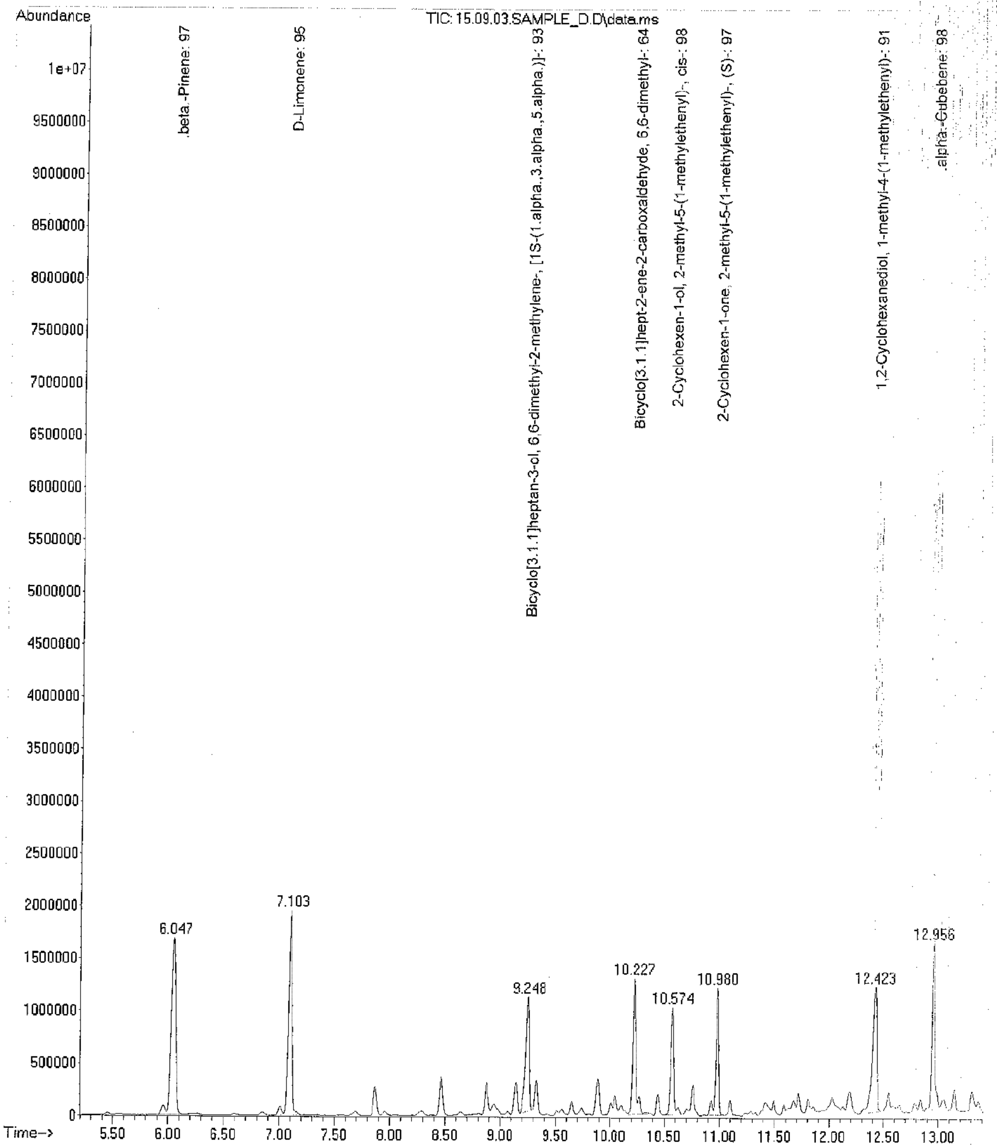
Signal     : TIC: 15.09.03.SAMPLE_D.D\data.ms
```

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.495 | 208 | 238 | 287 | BB | 9434131 | 394697267 | 100.00% | 33.879% |
| 2 | 6.047 | 985 | 1010 | 1025 | BB | 1683190 | 46933579 | 11.89% | 4.029% |
| 3 | 7.103 | 1158 | 1188 | 1207 | BB | 1951406 | 45223835 | 11.46% | 3.882% |
| 4 | 9.248 | 1540 | 1552 | 1559 | PV | 1088004 | 24079577 | 6.10% | 2.067% |
| 5 | 10.227 | 1708 | 1718 | 1743 | VB 2 | 1270965 | 26956239 | 6.83% | 2.314% |
| 6 | 10.574 | 1766 | 1776 | 1792 | BV 2 | 1019359 | 20708112 | 5.25% | 1.778% |
| 7 | 10.980 | 1828 | 1845 | 1857 | BV | 1172376 | 22483727 | 5.70% | 1.930% |
| 8 | 12.423 | 2064 | 2090 | 2100 | BV 2 | 1178449 | 34468998 | 8.73% | 2.959% |
| 9 | 12.956 | 2166 | 2180 | 2191 | PV | 1547748 | 28482261 | 7.22% | 2.445% |
| 10 | 14.540 | 2440 | 2448 | 2458 | VV 4 | 462250 | 12861758 | 3.26% | 1.104% |
| 11 | 14.636 | 2458 | 2464 | 2486 | VV | 1576565 | 26518458 | 6.72% | 2.276% |
| 12 | 14.807 | 2486 | 2494 | 2499 | PV | 435759 | 6861575 | 1.74% | 0.589% |
| 13 | 15.299 | 2567 | 2577 | 2584 | BV | 1771420 | 30486740 | 7.72% | 2.617% |
| 14 | 15.745 | 2630 | 2652 | 2667 | BV | 5998024 | 254187394 | 64.40% | 21.819% |
| 15 | 16.001 | 2680 | 2696 | 2711 | VV | 834918 | 18273041 | 4.63% | 1.568% |
| 16 | 16.298 | 2731 | 2746 | 2752 | VV 3 | 500394 | 13764811 | 3.49% | 1.182% |
| 17 | 16.365 | 2752 | 2757 | 2776 | VV 2 | 631824 | 15959541 | 4.04% | 1.370% |
| 18 | 16.517 | 2776 | 2783 | 2799 | VV 2 | 737793 | 16950660 | 4.29% | 1.455% |
| 19 | 16.690 | 2799 | 2812 | 2822 | VV 3 | 2013085 | 46382226 | 11.75% | 3.981% |
| 20 | 16.843 | 2822 | 2838 | 2852 | VV 3 | 691547 | 28602298 | 7.25% | 2.455% |
| 21 | 18.241 | 3061 | 3075 | 3082 | VV | 1865446 | 50122617 | 12.70% | 4.302% |

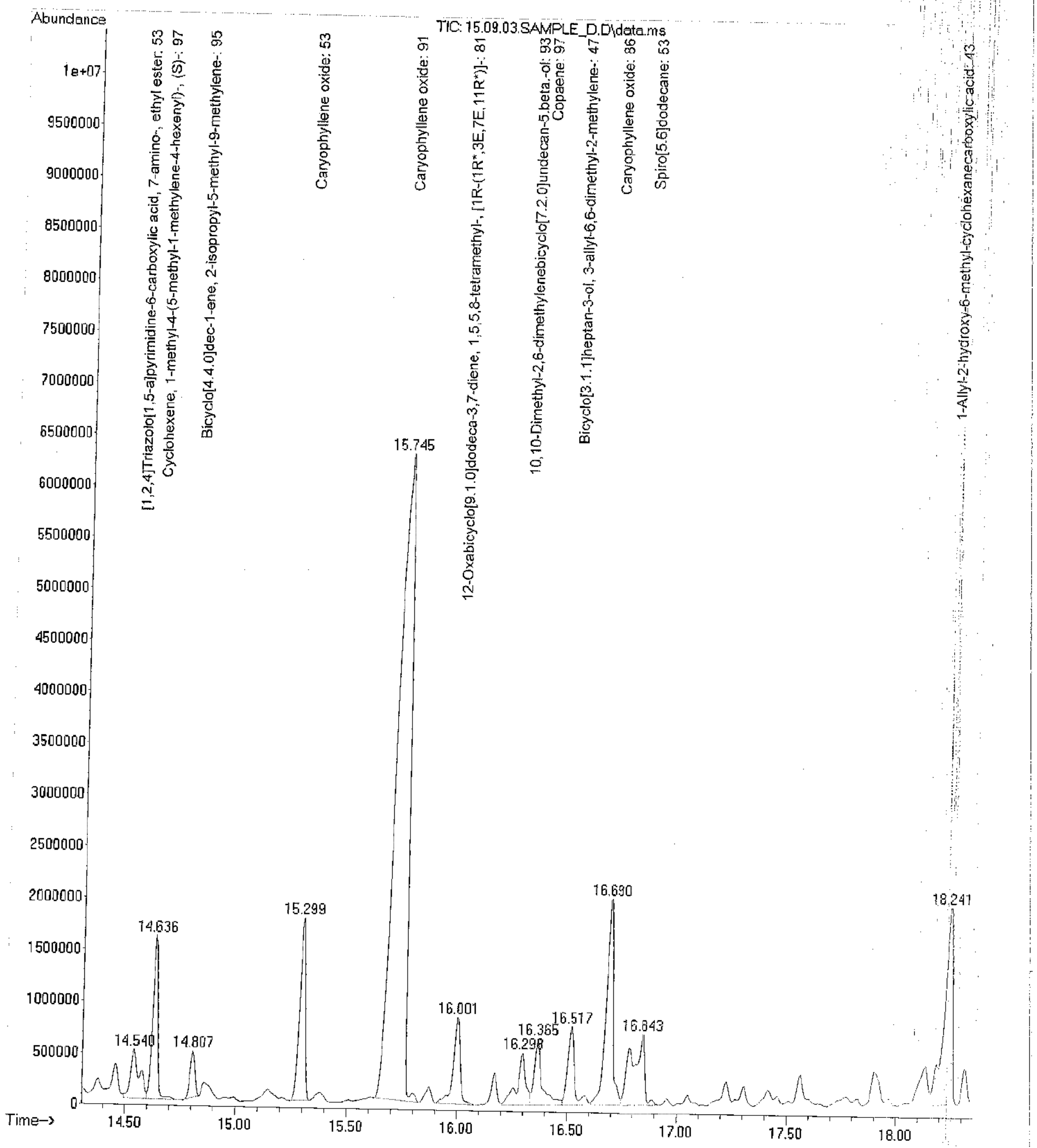
Sum of corrected areas: 1165004715

SMART.M Fri Sep 11 11:37:44 2015

```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_D.D
Operator    :
Acquired    :  3 Sep 2015  14:02      using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 1
```



File :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_D.D
Operator :
Acquired : 3 Sep 2015 14:02 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1



## Sample No : 8

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.09.03.SAMPLE_G.D
Acq On : 3 Sep 2015 11:09
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

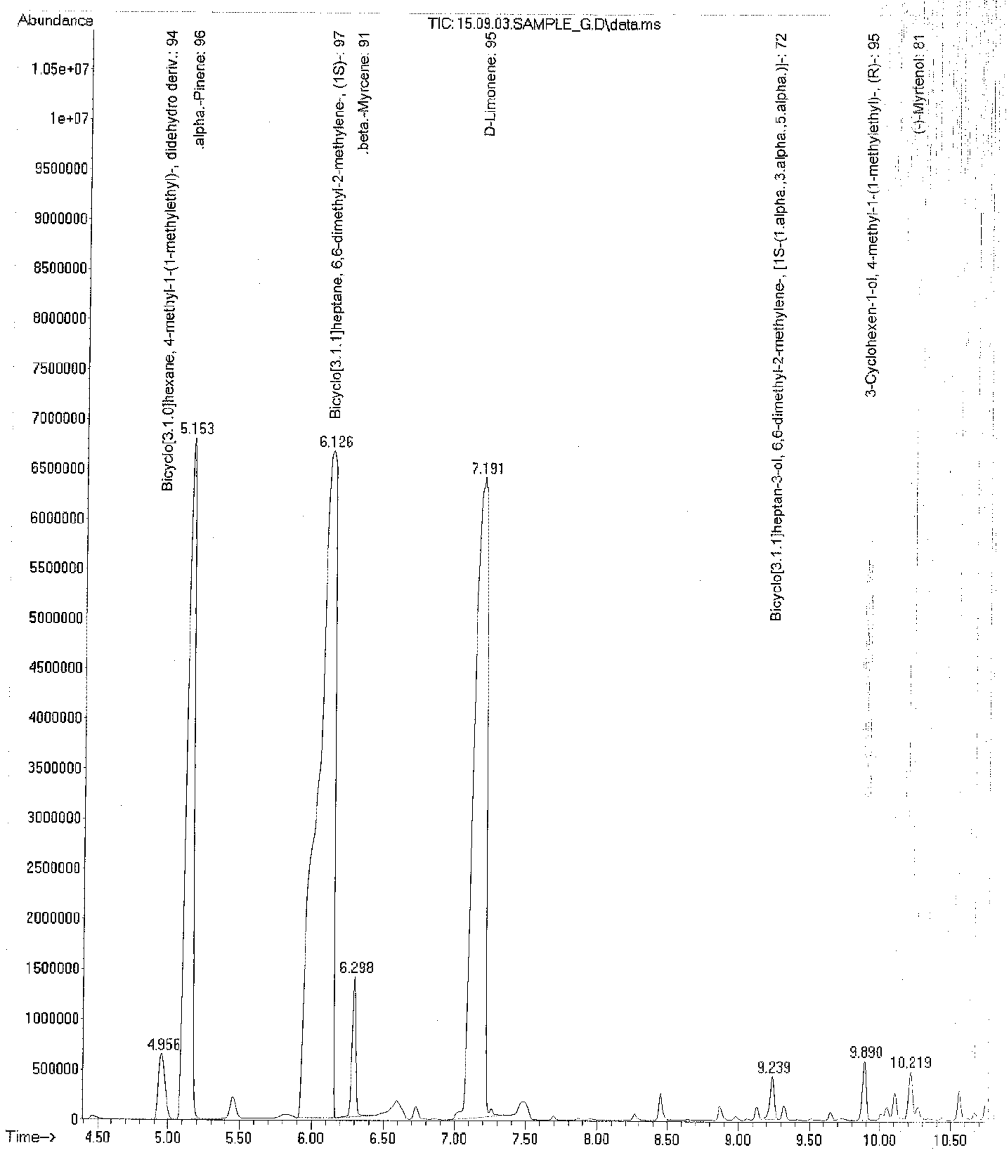
Signal : TIC: 15.09.03.SAMPLE_G.D\data.ms

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.510 | 230 | 241 | 264 | BB | 7397099 | 287066405 | 53.57% | 10.758% |
| 2 | 4.956 | 805 | 825 | 841 | BV | 647277 | 21393900 | 3.99% | 0.802% |
| 3 | 5.153 | 841 | 858 | 874 | PB | 6664334 | 233249213 | 43.52% | 8.741% |
| 4 | 6.126 | 984 | 1023 | 1032 | BV 3 | 6654467 | 535914218 | 100.00% | 20.084% |
| 5 | 6.298 | 1032 | 1052 | 1071 | PB | 1357798 | 24754224 | 4.62% | 0.928% |
| 6 | 7.191 | 1160 | 1203 | 1229 | BB 5 | 6375939 | 393376164 | 73.40% | 14.742% |
| 7 | 9.239 | 1542 | 1550 | 1558 | BV | 423280 | 8422658 | 1.57% | 0.316% |
| 8 | 9.890 | 1649 | 1661 | 1674 | BV | 594138 | 11204200 | 2.09% | 0.420% |
| 9 | 10.219 | 1710 | 1716 | 1740 | BB 3 | 470516 | 11067354 | 2.07% | 0.415% |
| 10 | 12.382 | 2065 | 2083 | 2097 | BV | 1738171 | 34930245 | 6.52% | 1.309% |
| 11 | 12.557 | 2097 | 2112 | 2138 | PB 3 | 510593 | 15060167 | 2.81% | 0.564% |
| 12 | 12.981 | 2171 | 2184 | 2204 | VV | 5346563 | 138003876 | 25.75% | 5.172% |
| 13 | 13.152 | 2204 | 2213 | 2239 | VB 6 | 1272384 | 36554374 | 6.82% | 1.370% |
| 14 | 13.652 | 2277 | 2298 | 2328 | BB 4 | 6608584 | 443417114 | 82.74% | 16.618% |
| 15 | 14.055 | 2356 | 2366 | 2376 | BV | 1815854 | 31919400 | 5.96% | 1.196% |
| 16 | 14.466 | 2430 | 2436 | 2442 | VV | 720830 | 12865725 | 2.40% | 0.482% |
| 17 | 14.584 | 2442 | 2456 | 2461 | VV 4 | 1062386 | 34769990 | 6.49% | 1.303% |
| 18 | 14.675 | 2461 | 2471 | 2479 | VV | 4399037 | 120057872 | 22.40% | 4.499% |
| 19 | 14.827 | 2479 | 2497 | 2501 | VV | 1200491 | 23854753 | 4.45% | 0.894% |
| 20 | 14.887 | 2501 | 2507 | 2520 | VV 2 | 1752836 | 32696170 | 6.10% | 1.225% |
| 21 | 15.297 | 2565 | 2577 | 2583 | BV | 822467 | 14063396 | 2.62% | 0.527% |
| 22 | 15.713 | 2613 | 2647 | 2665 | BV | 3623725 | 118194677 | 22.05% | 4.430% |
| 23 | 16.173 | 2715 | 2725 | 2732 | VV 2 | 961181 | 19667654 | 3.67% | 0.737% |
| 24 | 16.299 | 2732 | 2746 | 2753 | VV 5 | 529385 | 17747704 | 3.31% | 0.665% |
| 25 | 16.371 | 2753 | 2758 | 2770 | VV | 1685986 | 30397559 | 5.67% | 1.139% |
| 26 | 16.514 | 2770 | 2783 | 2796 | VV | 446387 | 8506690 | 1.59% | 0.319% |
| 27 | 16.659 | 2796 | 2807 | 2820 | VV 4 | 437083 | 9189728 | 1.71% | 0.344% |

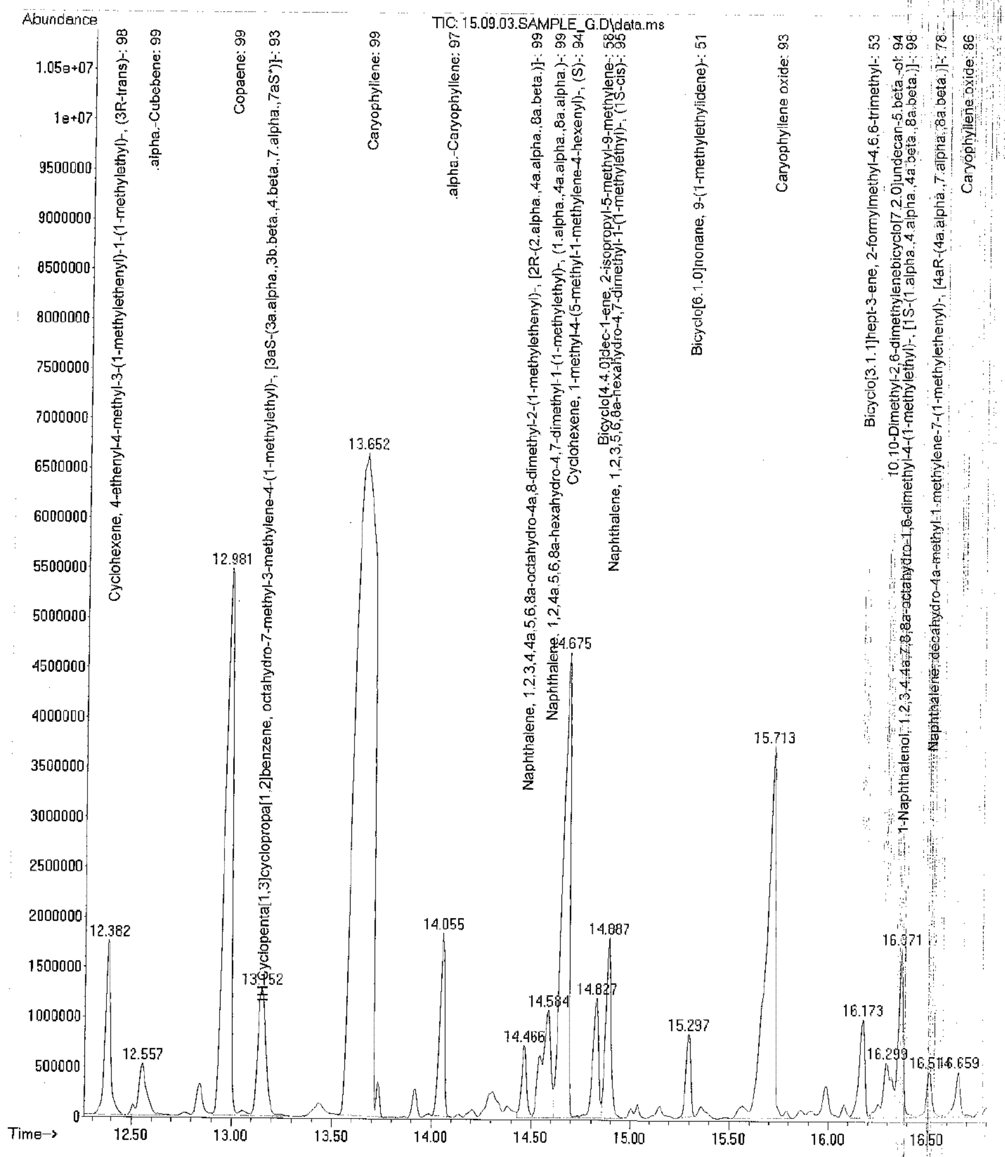
Sum of corrected areas: 2668345430

MART.M Fri Sep 11 11:44:47 2015

File :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_G.D
Operator :
Acquired : 3 Sep 2015 11:09 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1



```
File       :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_G.D
Operator   :
Acquired   :   3 Sep 2015   11:09      using AcqMethod Plant Extracts.M
Instrument :    UOSJP GCMSD
Sample Name:
Misc Info  :
Vial Number: 1
```



## Sample No: 9

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.09.01.SAMPLE_9.D
Acq On : 1 Sep 2015 14:53
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.09.01.SAMPLE_9.D\data.ms

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.487 | 211 | 237 | 254 | BV 2 | 12898895 | 461289755 | 25.71% | 3.330% |
| 2 | 1.649 | 254 | 265 | 287 | VV | 6353032 | 191407677 | 10.67% | 1.382% |
| 3 | 4.962 | 799 | 826 | 841 | BV | 2918640 | 153061078 | 8.53% | 1.105% |
| 4 | 5.167 | 841 | 861 | 871 | VV 4 | 15449994 | 946084732 | 52.74% | 6.830% |
| 5 | 5.259 | 871 | 876 | 894 | VV | 2108282 | 67147612 | 3.74% | 0.485% |
| 6 | 5.464 | 894 | 911 | 949 | VB 3 | 1426814 | 65239634 | 3.64% | 0.471% |
| 7 | 6.088 | 964 | 1016 | 1045 | BV 2 | 13389017 | 1793918449 | 100.00% | 12.951% |
| 8 | 6.336 | 1045 | 1059 | 1080 | VB | 4774164 | 106221163 | 5.92% | 0.767% |
| 9 | 6.616 | 1085 | 1106 | 1117 | BV 3 | 573439 | 22707884 | 1.27% | 0.164% |
| 10 | 6.753 | 1117 | 1129 | 1159 | VV | 4937959 | 164395716 | 9.16% | 1.187% |
| 11 | 7.161 | 1159 | 1198 | 1232 | VV 5 | 13964923 | 1648095362 | 91.87% | 11.899% |
| 12 | 7.887 | 1232 | 1321 | 1329 | PV | 1913224 | 74434985 | 4.15% | 0.537% |
| 13 | 7.961 | 1329 | 1334 | 1348 | VV | 507571 | 13868777 | 0.77% | 0.100% |
| 14 | 8.305 | 1369 | 1392 | 1405 | BV 7 | 824272 | 39865868 | 2.22% | 0.288% |
| 15 | 8.480 | 1405 | 1422 | 1444 | VV 4 | 6113902 | 177574876 | 9.90% | 1.282% |
| 16 | 8.656 | 1444 | 1452 | 1460 | PV | 3869746 | 71440071 | 3.98% | 0.516% |
| 17 | 8.749 | 1460 | 1467 | 1484 | VV 3 | 1175679 | 35243363 | 1.96% | 0.254% |
| 18 | 8.899 | 1484 | 1493 | 1503 | VV 3 | 6517779 | 169576026 | 9.45% | 1.224% |
| 19 | 8.995 | 1503 | 1509 | 1517 | VV 2 | 966291 | 25098396 | 1.40% | 0.181% |
| 20 | 9.117 | 1517 | 1530 | 1534 | VV 2 | 3744143 | 87303408 | 4.87% | 0.630% |
| 21 | 9.184 | 1534 | 1541 | 1548 | VV 2 | 5268919 | 166481130 | 9.28% | 1.202% |
| 22 | 9.284 | 1548 | 1558 | 1564 | VV | 8972343 | 293584962 | 16.37% | 2.120% |
| 23 | 9.349 | 1564 | 1569 | 1579 | VV 2 | 3511487 | 74883558 | 4.17% | 0.541% |
| 24 | 9.535 | 1591 | 1600 | 1614 | VV 3 | 1037702 | 35553068 | 1.98% | 0.257% |
| 25 | 9.660 | 1614 | 1622 | 1629 | VV | 1998504 | 39723584 | 2.21% | 0.287% |
| 26 | 9.754 | 1629 | 1637 | 1653 | VV 2 | 987524 | 27023454 | 1.51% | 0.195% |
| 27 | 9.927 | 1653 | 1667 | 1678 | PV | 7969418 | 229439234 | 12.79% | 1.656% |
| 28 | 10.068 | 1678 | 1691 | 1697 | VV 4 | 2707555 | 94695814 | 5.28% | 0.684% |
| 29 | 10.149 | 1697 | 1704 | 1713 | VV 2 | 4459399 | 107651374 | 6.00% | 0.777% |
| 30 | 10.259 | 1713 | 1723 | 1738 | VV 2 | 8311442 | 244346429 | 13.62% | 1.764% |
| 31 | 10.459 | 1751 | 1757 | 1767 | VV 2 | 808942 | 16419767 | 0.92% | 0.119% |
| 32 | 10.596 | 1767 | 1780 | 1790 | VV 2 | 5093487 | 124518567 | 6.94% | 0.899% |
| 33 | 10.691 | 1790 | 1796 | 1805 | VV 3 | 569840 | 22706419 | 1.27% | 0.164% |
| 34 | 10.780 | 1805 | 1811 | 1823 | VV | 3396492 | 68778544 | 3.83% | 0.497% |
| 35 | 10.997 | 1823 | 1848 | 1856 | PV | 4927677 | 103805875 | 5.79% | 0.749% |
| 36 | 11.150 | 1856 | 1874 | 1887 | VV 3 | 1182745 | 33441070 | 1.86% | 0.241% |
| 37 | 11.424 | 1908 | 1920 | 1940 | VV 6 | 794132 | 56342689 | 3.14% | 0.407% |
| 38 | 11.681 | 1940 | 1964 | 1980 | VV 8 | 1187409 | 74535383 | 4.15% | 0.538% |
| 39 | 11.819 | 1980 | 1987 | 2011 | VV 6 | 1061759 | 55991907 | 3.12% | 0.404% |
| 40 | 12.037 | 2011 | 2024 | 2033 | VV 6 | 712844 | 33527809 | 1.87% | 0.242% |

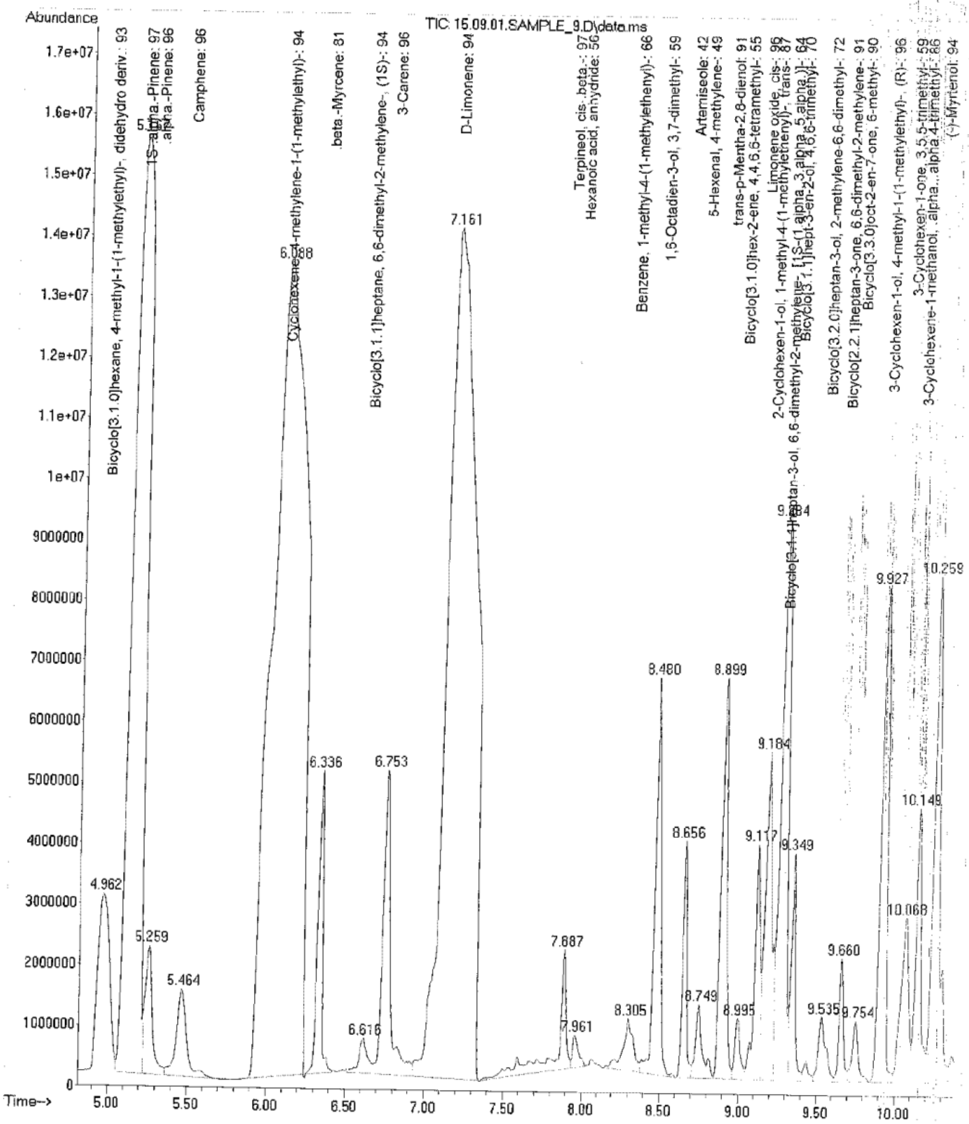
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 12.197 | 2045 | 2051 | 2067 | VV 5 | 611175 | 24803419 | 1.38% | 0.179% |
| 42 | 12.400 | 2067 | 2086 | 2100 | VV | 11828553 | 306220440 | 17.07% | 2.211% |
| 43 | 12.564 | 2100 | 2114 | 2126 | VV 4 | 3717739 | 122874534 | 6.85% | 0.887% |
| 44 | 12.684 | 2126 | 2134 | 2146 | VV | 668345 | 24592368 | 1.37% | 0.178% |
| 45 | 12.853 | 2146 | 2162 | 2172 | VV | 2604950 | 78696451 | 4.39% | 0.568% |
| 46 | 13.007 | 2172 | 2189 | 2206 | VV 2 | 14117402 | 708149763 | 39.48% | 5.113% |
| 47 | 13.171 | 2206 | 2216 | 2242 | VB 4 | 5394838 | 190628226 | 10.63% | 1.376% |
| 48 | 13.450 | 2252 | 2264 | 2280 | BV 6 | 678236 | 33830328 | 1.89% | 0.244% |
| 49 | 13.649 | 2280 | 2297 | 2331 | VV 7 | 12318525 | 1083009903 | 60.37% | 7.819% |
| 50 | 13.935 | 2331 | 2346 | 2354 | PV | 724922 | 17495674 | 0.98% | 0.126% |
| 51 | 14.083 | 2354 | 2371 | 2379 | VV | 4831409 | 117561516 | 6.55% | 0.849% |
| 52 | 14.224 | 2379 | 2395 | 2399 | VV 4 | 479196 | 14854175 | 0.83% | 0.107% |
| 53 | 14.317 | 2399 | 2411 | 2427 | VV 6 | 1518311 | 71835198 | 4.00% | 0.519% |
| 54 | 14.487 | 2427 | 2439 | 2445 | VV | 3916132 | 85664530 | 4.78% | 0.618% |
| 55 | 14.600 | 2445 | 2458 | 2464 | VV 5 | 4781443 | 183899179 | 10.25% | 1.328% |
| 56 | 14.721 | 2464 | 2479 | 2491 | VV | 8169460 | 416159135 | 23.20% | 3.005% |
| 57 | 14.879 | 2491 | 2506 | 2510 | VV | 3947948 | 100503448 | 5.60% | 0.726% |
| 58 | 14.921 | 2510 | 2513 | 2526 | VV 2 | 2953665 | 66923624 | 3.73% | 0.483% |
| 59 | 15.180 | 2545 | 2557 | 2571 | VV 4 | 1018149 | 53965466 | 3.01% | 0.390% |
| 60 | 15.346 | 2571 | 2585 | 2592 | VV | 6369230 | 194354580 | 10.83% | 1.403% |
| 61 | 15.415 | 2592 | 2596 | 2602 | VV 5 | 859172 | 22799331 | 1.27% | 0.165% |
| 62 | 15.487 | 2602 | 2609 | 2620 | VV | 1064467 | 36585545 | 2.04% | 0.264% |
| 63 | 15.773 | 2620 | 2657 | 2689 | VV 10 | 9192859 | 966135537 | 53.86% | 6.975% |
| 64 | 16.065 | 2689 | 2707 | 2713 | VV 2 | 1975071 | 49595134 | 2.76% | 0.358% |
| 65 | 16.218 | 2713 | 2733 | 2739 | VV 8 | 1404082 | 44496383 | 2.48% | 0.321% |
| 66 | 16.353 | 2739 | 2755 | 2761 | VV 4 | 2083274 | 72156334 | 4.02% | 0.521% |
| 67 | 16.433 | 2761 | 2769 | 2779 | VV | 3524376 | 98989412 | 5.52% | 0.715% |
| 68 | 16.563 | 2779 | 2791 | 2798 | VV | 1491173 | 28856621 | 1.61% | 0.208% |
| 69 | 16.710 | 2798 | 2816 | 2827 | VV 3 | 1573959 | 55192047 | 3.08% | 0.398% |
| 70 | 16.839 | 2827 | 2838 | 2855 | VV 2 | 1018487 | 30432351 | 1.70% | 0.220% |
| 71 | 17.073 | 2855 | 2877 | 2889 | PV 5 | 689872 | 22933735 | 1.28% | 0.166% |
| 72 | 17.238 | 2889 | 2905 | 2925 | VV 5 | 727165 | 32105496 | 1.79% | 0.232% |
| 73 | 17.406 | 2925 | 2934 | 2950 | VV 5 | 1024751 | 32263963 | 1.80% | 0.233% |
| 74 | 17.788 | 2979 | 2998 | 3014 | VV 9 | 844215 | 48687424 | 2.71% | 0.352% |
| 75 | 17.923 | 3014 | 3021 | 3035 | VV 3 | 1443263 | 42770111 | 2.38% | 0.309% |
| 76 | 18.129 | 3035 | 3056 | 3062 | VV 3 | 614293 | 32292294 | 1.80% | 0.233% |
| 77 | 18.465 | 3088 | 3113 | 3123 | VV 3 | 481584 | 29248673 | 1.63% | 0.211% |
| 78 | 18.558 | 3123 | 3129 | 3143 | VV 3 | 722505 | 28870026 | 1.61% | 0.208% |
| 79 | 19.159 | 3219 | 3231 | 3236 | PV 2 | 568215 | 11504345 | 0.64% | 0.083% |
| 80 | 22.242 | 3748 | 3753 | 3768 | VV | 557348 | 11661871 | 0.65% | 0.084% |
| 81 | 22.460 | 3782 | 3790 | 3807 | PV 3 | 706383 | 18528259 | 1.03% | 0.134% |
| 82 | 22.783 | 3827 | 3845 | 3854 | PV 2 | 394792 | 13158526 | 0.73% | 0.095% |
| 83 | 24.686 | 4155 | 4167 | 4173 | PV 9 | 385215 | 8360600 | 0.47% | 0.060% |

Sum of corrected areas: 13851071441

SMART.M Fri Sep 11 10:49:03 2015

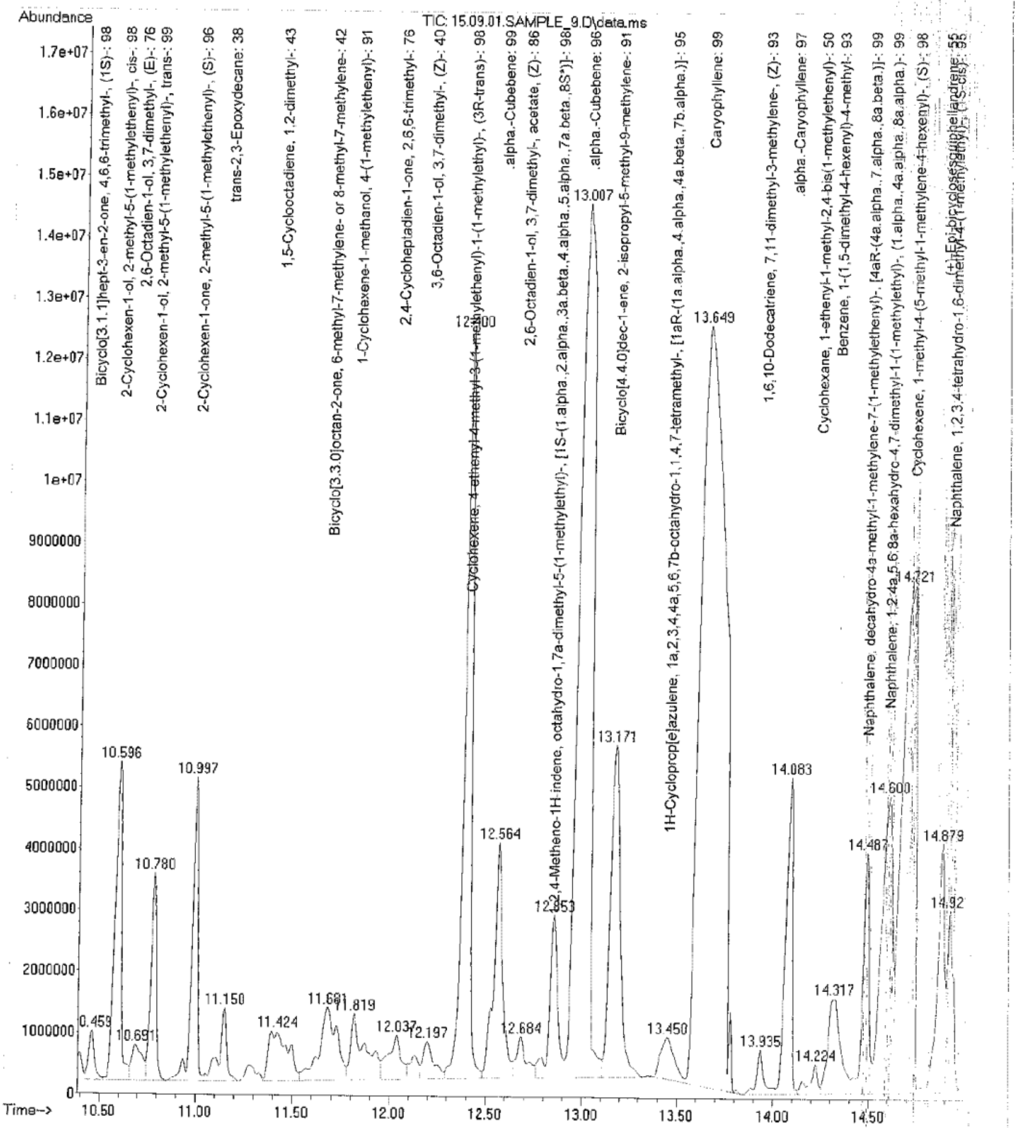
File :C:\msdchem\1\data\Commercial 2015.08.07\15.09.01.SAMPLE_9.D
Operator :
Acquired : 1 Sep 2015 14:53 using AcqMethod PLANT EXTRACTS.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1

ERR

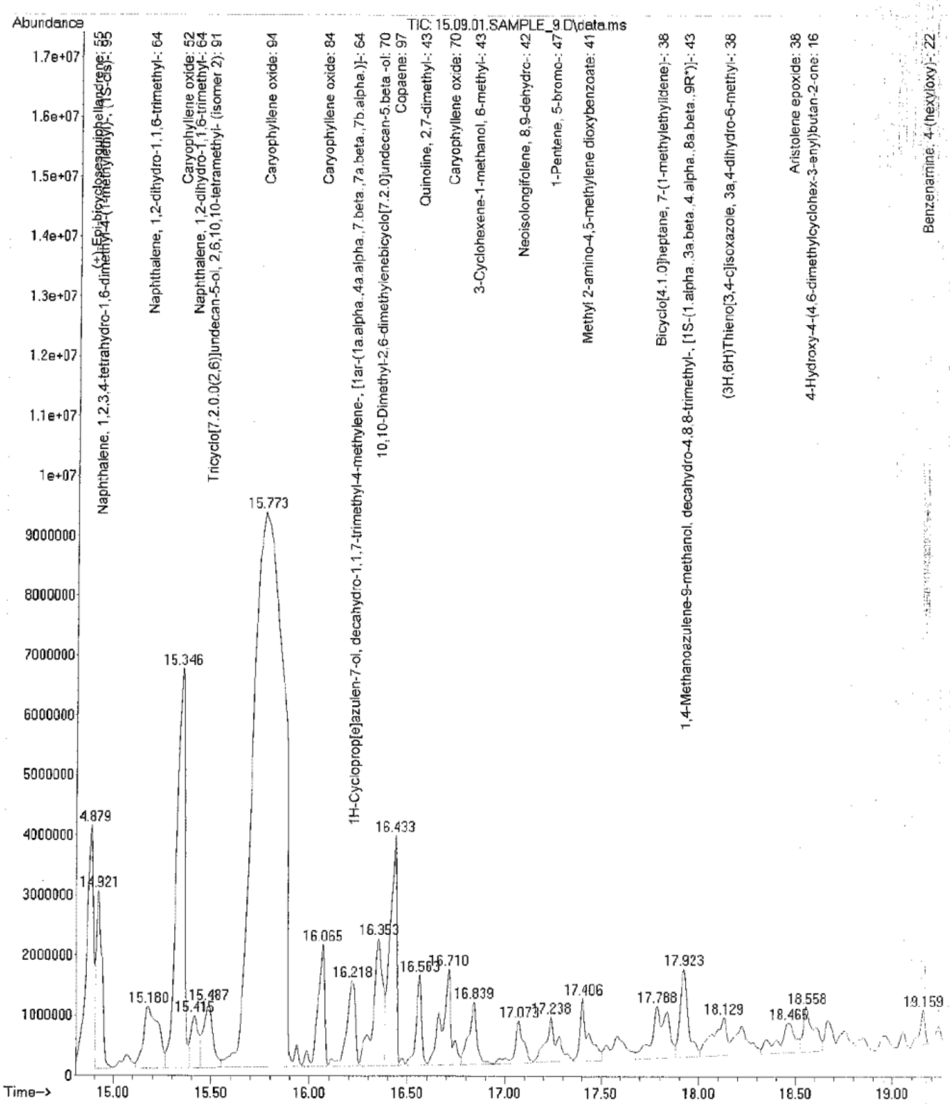


File :C:\msdchem\1\data\Commercial 2015.08.07\15.09.01.SAMPLE_9.D
Operator :
Acquired : 1 Sep 2015 14:53 using AcqMethod PLANT EXTRACTS.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1

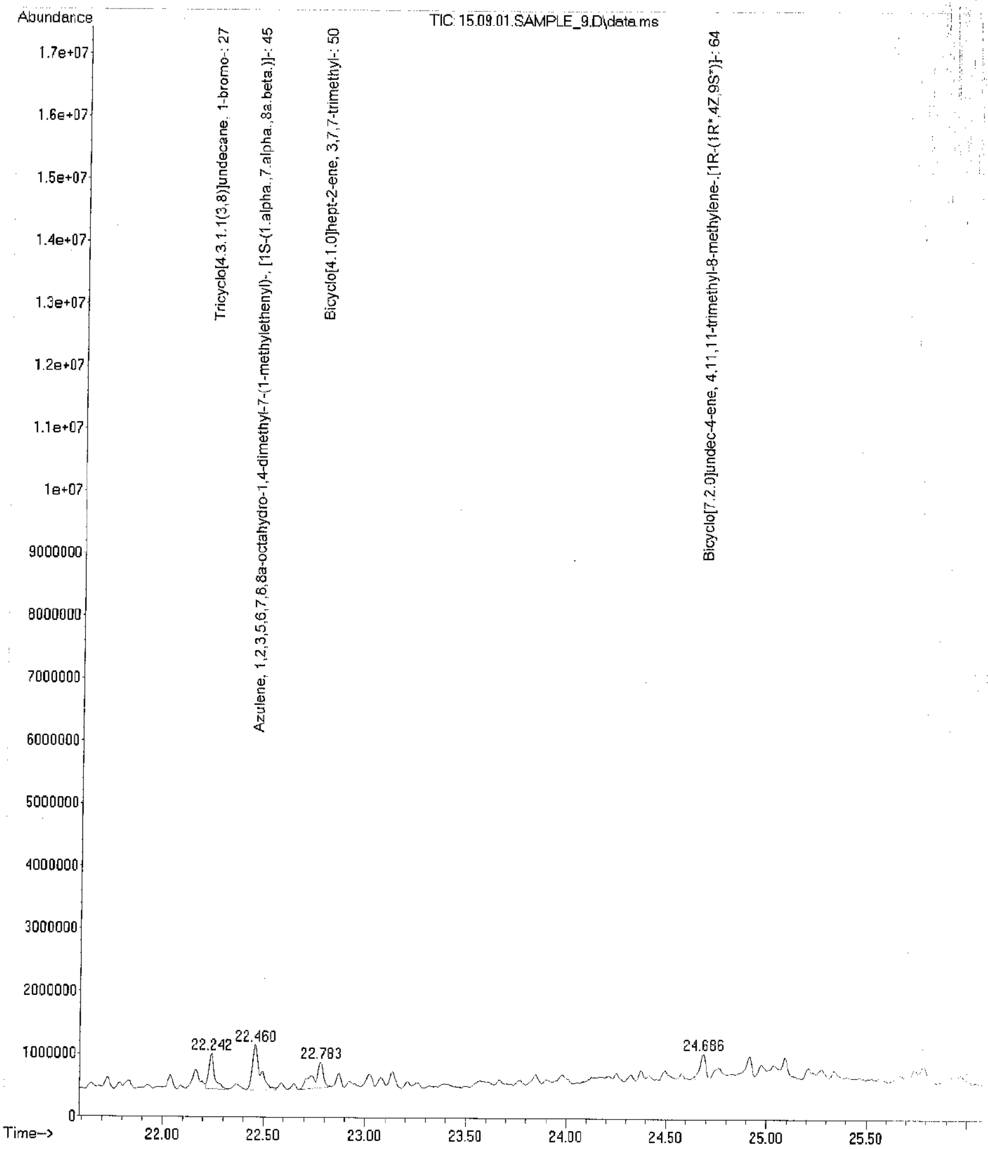
ERR



```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.09.01.SAMPLE_9.D
Operator    :
Acquired    :  1 Sep 2015  14:53      using AcqMethod PLANT EXTRACTS.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :                                             ERR
Vial Number: 1
```



```
File         :C:\msdchem\1\data\Commercial 2015.08.07\15.09.01.SAMPLE_9.D
Operator     :
Acquired     :  1 Sep 2015  14:53      using AcqMethod PLANT EXTRACTS.M
Instrument   :   UOSJP GCMSD
Sample Name:
Misc Info    :                                              ERR
Vial Number: 1
```



**Sample No :10**

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.07.SAMPLE_11.D
Acq On : 7 Aug 2015 14:00
Operator :
Sample :
Misc :
ALS Vial : 2 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.08.07.SAMPLE_11.D\data.ms

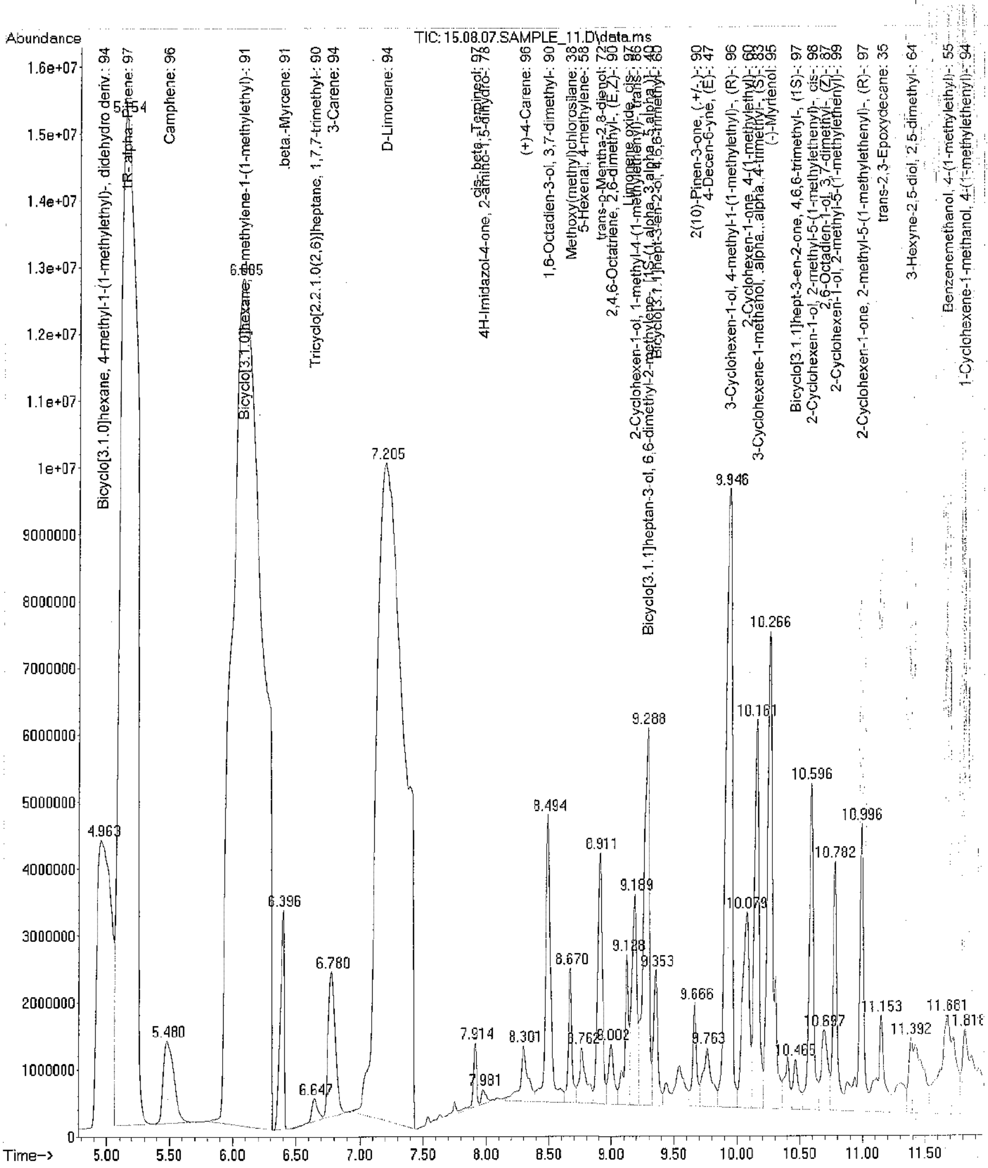
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.473 | 197 | 223 | 276 | BB | 14068658 | 619608971 | 30.26% | 4.251% |
| 2 | 4.963 | 748 | 814 | 831 | BV | 4259564 | 328230238 | 16.03% | 2.252% |
| 3 | 5.154 | 831 | 846 | 885 | VV 2 | 15072032 | 1370211275 | 66.92% | 9.401% |
| 4 | 5.480 | 885 | 902 | 939 | PB | 1227859 | 72466229 | 3.54% | 0.497% |
| 5 | 6.085 | 955 | 1004 | 1046 | BV 2 | 12665159 | 2047609708 | 100.00% | 14.048% |
| 6 | 6.396 | 1046 | 1057 | 1062 | PV | 3127290 | 73785889 | 3.60% | 0.506% |
| 7 | 6.647 | 1062 | 1099 | 1110 | PV | 332895 | 10405096 | 0.51% | 0.071% |
| 8 | 6.780 | 1110 | 1122 | 1142 | VB | 2152667 | 82051494 | 4.01% | 0.563% |
| 9 | 7.205 | 1151 | 1194 | 1236 | BV 7 | 9812089 | 1429012522 | 69.79% | 9.804% |
| 10 | 7.914 | 1292 | 1314 | 1320 | VV | 940484 | 17980422 | 0.88% | 0.123% |
| 11 | 7.981 | 1320 | 1325 | 1335 | VB | 196751 | 4900187 | 0.24% | 0.034% |
| 12 | 8.301 | 1354 | 1380 | 1394 | BV 6 | 806039 | 35316797 | 1.72% | 0.242% |
| 13 | 8.494 | 1394 | 1412 | 1434 | VV 2 | 4198271 | 122150350 | 5.97% | 0.838% |
| 14 | 8.670 | 1434 | 1442 | 1450 | VV | 1988968 | 41193723 | 2.01% | 0.283% |
| 15 | 8.762 | 1450 | 1458 | 1473 | VV 2 | 806523 | 31825833 | 1.55% | 0.218% |
| 16 | 8.911 | 1473 | 1483 | 1492 | VV 4 | 3716558 | 106447088 | 5.20% | 0.730% |
| 17 | 9.002 | 1492 | 1498 | 1506 | VV 3 | 878831 | 24660282 | 1.20% | 0.169% |
| 18 | 9.128 | 1506 | 1520 | 1523 | VV 2 | 2189885 | 55298925 | 2.70% | 0.379% |
| 19 | 9.189 | 1523 | 1530 | 1536 | VV 2 | 3120073 | 88576293 | 4.33% | 0.608% |
| 20 | 9.288 | 1536 | 1547 | 1553 | VV 2 | 5406382 | 174589745 | 8.53% | 1.198% |
| 21 | 9.353 | 1553 | 1558 | 1567 | VV 2 | 1996176 | 47629452 | 2.33% | 0.327% |
| 22 | 9.666 | 1603 | 1611 | 1617 | VV | 1497012 | 35801930 | 1.75% | 0.246% |
| 23 | 9.763 | 1617 | 1627 | 1641 | VV 5 | 877995 | 41681910 | 2.04% | 0.286% |
| 24 | 9.946 | 1641 | 1658 | 1667 | VV 3 | 9130199 | 332462576 | 16.24% | 2.281% |
| 25 | 10.079 | 1667 | 1681 | 1687 | VV 3 | 2900140 | 109517334 | 5.35% | 0.751% |
| 26 | 10.161 | 1687 | 1695 | 1702 | VV 2 | 5811500 | 150211509 | 7.34% | 1.031% |
| 27 | 10.266 | 1702 | 1712 | 1728 | VV 2 | 7140490 | 220459445 | 10.77% | 1.513% |
| 28 | 10.465 | 1741 | 1746 | 1755 | VV | 746095 | 22285725 | 1.09% | 0.153% |
| 29 | 10.596 | 1755 | 1768 | 1778 | VV | 4856398 | 124682302 | 6.09% | 0.855% |
| 30 | 10.697 | 1778 | 1785 | 1792 | VV 3 | 1189206 | 42687575 | 2.08% | 0.293% |
| 31 | 10.782 | 1792 | 1800 | 1812 | VV | 3670113 | 88637555 | 4.33% | 0.608% |
| 32 | 10.996 | 1812 | 1836 | 1846 | VV | 4176015 | 113811545 | 5.56% | 0.781% |
| 33 | 11.153 | 1846 | 1863 | 1876 | VV 2 | 1413461 | 57924735 | 2.83% | 0.397% |
| 34 | 11.392 | 1897 | 1903 | 1927 | VV 5 | 1052706 | 82055857 | 4.01% | 0.563% |
| 35 | 11.681 | 1927 | 1952 | 1969 | VV 8 | 1480650 | 121455509 | 5.93% | 0.833% |
| 36 | 11.818 | 1969 | 1975 | 2001 | VV 7 | 1251419 | 88956592 | 4.34% | 0.610% |
| 37 | 12.413 | 2055 | 2076 | 2090 | VV | 13128263 | 517533601 | 25.28% | 3.551% |
| 38 | 12.573 | 2090 | 2103 | 2144 | VV 2 | 4399303 | 279482658 | 13.65% | 1.917% |
| 39 | 12.861 | 2144 | 2152 | 2163 | VV 2 | 2706002 | 120374589 | 5.88% | 0.826% |
| 40 | 13.011 | 2163 | 2177 | 2196 | VV 3 | 12962561 | 862119076 | 42.10% | 5.915% |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 13.189 | 2196 | 2208 | 2242 | VV 7 | 3793224 | 257136991 | 12.56% | 1.764% |
| 42 | 13.658 | 2242 | 2287 | 2312 | VV 5 | 10213041 | 1100296147 | 53.74% | 7.549% |
| 43 | 13.856 | 2312 | 2320 | 2331 | VV 4 | 6568588 | 284400634 | 13.89% | 1.951% |
| 44 | 13.976 | 2331 | 2341 | 2348 | VV | 1019671 | 18166081 | 0.89% | 0.125% |
| 45 | 14.141 | 2348 | 2369 | 2376 | VV | 4864596 | 148043850 | 7.23% | 1.016% |
| 46 | 14.345 | 2384 | 2403 | 2425 | VV 7 | 1382092 | 84300516 | 4.12% | 0.578% |
| 47 | 14.518 | 2425 | 2433 | 2438 | VV | 3554178 | 78607942 | 3.84% | 0.539% |
| 48 | 14.626 | 2438 | 2451 | 2457 | VV 6 | 4528591 | 173905036 | 8.49% | 1.193% |
| 49 | 14.747 | 2457 | 2471 | 2483 | VV 4 | 5513636 | 360530715 | 17.61% | 2.473% |
| 50 | 14.973 | 2483 | 2510 | 2520 | VV 8 | 3310657 | 154367164 | 7.54% | 1.059% |
| 51 | 15.202 | 2537 | 2548 | 2565 | VV 2 | 559189 | 26833730 | 1.31% | 0.184% |
| 52 | 15.366 | 2565 | 2576 | 2590 | VV 2 | 3761196 | 115396551 | 5.64% | 0.792% |
| 53 | 15.476 | 2590 | 2595 | 2605 | VV 2 | 598054 | 20445548 | 1.00% | 0.140% |
| 54 | 15.789 | 2605 | 2648 | 2670 | VV 7 | 6872527 | 629451668 | 30.74% | 4.318% |
| 55 | 16.065 | 2670 | 2695 | 2701 | VV 2 | 1264856 | 40998465 | 2.00% | 0.281% |
| 56 | 16.227 | 2711 | 2722 | 2731 | VV 6 | 1658450 | 58582054 | 2.86% | 0.402% |
| 57 | 16.456 | 2731 | 2761 | 2769 | VV 2 | 3451534 | 173706116 | 8.48% | 1.192% |
| 58 | 16.573 | 2769 | 2781 | 2788 | VV | 900311 | 17636814 | 0.86% | 0.121% |
| 59 | 16.709 | 2788 | 2804 | 2815 | PV 2 | 700984 | 29235502 | 1.43% | 0.201% |
| 60 | 16.838 | 2815 | 2826 | 2844 | VV 2 | 655287 | 18918833 | 0.92% | 0.130% |
| 61 | 17.074 | 2844 | 2866 | 2878 | PV 7 | 538077 | 21304319 | 1.04% | 0.146% |
| 62 | 17.284 | 2878 | 2901 | 2914 | VV 9 | 529505 | 33705520 | 1.65% | 0.231% |
| 63 | 17.409 | 2914 | 2922 | 2938 | VV 3 | 1290857 | 39220985 | 1.92% | 0.269% |
| 64 | 17.814 | 2972 | 2991 | 3002 | VV 6 | 692402 | 46479428 | 2.27% | 0.319% |
| 65 | 17.925 | 3002 | 3010 | 3023 | VV 3 | 1445220 | 47420483 | 2.32% | 0.325% |
| 66 | 18.099 | 3023 | 3039 | 3050 | VV 3 | 718906 | 45079555 | 2.20% | 0.309% |
| 67 | 18.222 | 3050 | 3060 | 3077 | VV 6 | 693271 | 38226643 | 1.87% | 0.262% |
| 68 | 18.466 | 3077 | 3101 | 3109 | VV 6 | 552120 | 43985993 | 2.15% | 0.302% |
| 69 | 18.560 | 3109 | 3117 | 3131 | VV | 1676060 | 53781292 | 2.63% | 0.369% |
| 70 | 18.673 | 3131 | 3137 | 3143 | VV 6 | 654127 | 22426855 | 1.10% | 0.154% |
| 71 | 19.157 | 3207 | 3219 | 3224 | VV 4 | 778972 | 25460881 | 1.24% | 0.175% |
| 72 | 19.232 | 3224 | 3231 | 3239 | VV 5 | 672593 | 23539244 | 1.15% | 0.161% |
| 73 | 19.314 | 3239 | 3245 | 3263 | VV | 775528 | 27575992 | 1.35% | 0.189% |
| 74 | 19.839 | 3322 | 3334 | 3359 | VV 4 | 525123 | 24302244 | 1.19% | 0.167% |
| 75 | 20.671 | 3447 | 3475 | 3491 | VV 2 | 458175 | 17934736 | 0.88% | 0.123% |
| 76 | 20.965 | 3491 | 3525 | 3540 | VV | 657004 | 17203704 | 0.84% | 0.118% |
| 77 | 22.245 | 3736 | 3742 | 3754 | VV | 614894 | 12945953 | 0.63% | 0.089% |
| 78 | 22.463 | 3770 | 3778 | 3796 | PV 3 | 876148 | 21589538 | 1.05% | 0.148% |
| 79 | 22.785 | 3816 | 3833 | 3842 | BV | 521808 | 16822281 | 0.82% | 0.115% |
| 80 | 24.688 | 4134 | 4155 | 4161 | VV 5 | 475073 | 9679764 | 0.47% | 0.066% |

Sum of corrected areas: 14575738308

SMART.M Fri Sep 11 11:02:02 2015

File :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_11.D
Operator :
Acquired : 7 Aug 2015 14:00 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info : ERR
Vial Number: 2



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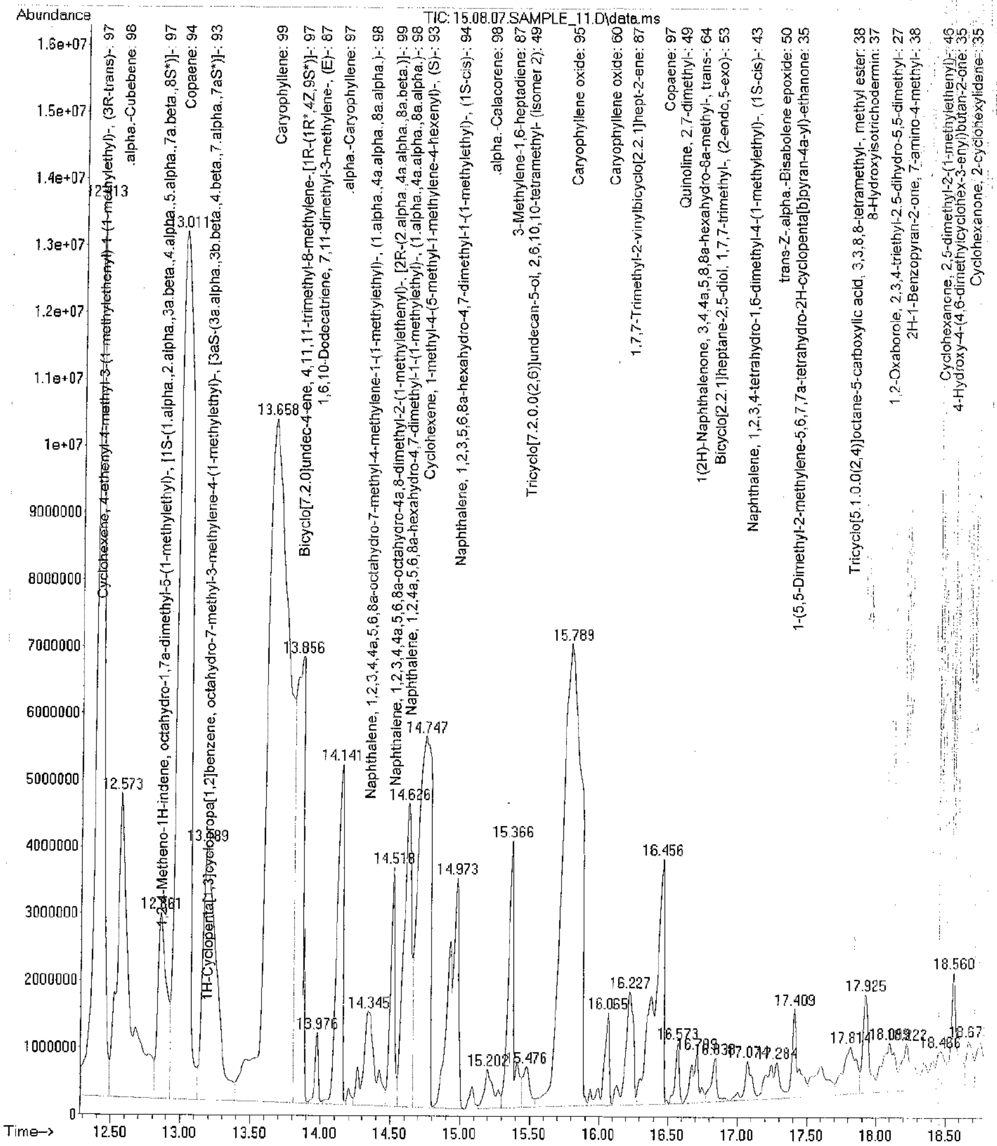
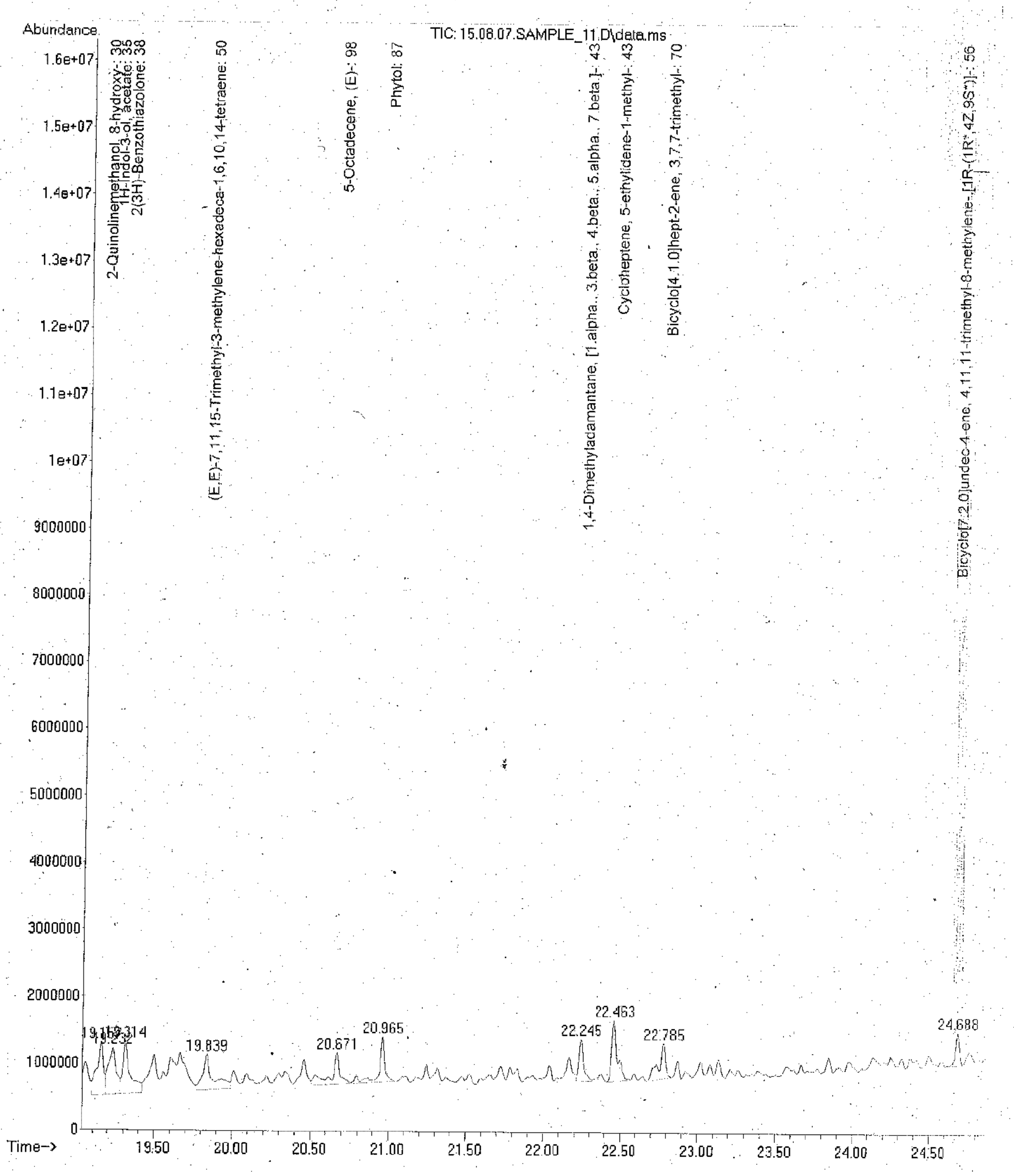
File          :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_11.D
Operator      :
Acquired      :   7 Aug 2015   14:00       using AcqMethod Plant Extracts.M
Instrument :     UOSJP GCMSD
Sample Name:
Misc Info    :                                                         ERR
Vial Number:  2
```



File :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_11.D
Operator :
Acquired : 7 Aug 2015 14:00 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 2

ERR



## Sample No : 11

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.09.01.SAMPLE_12.D
Acq On : 1 Sep 2015 12:25
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.09.01.SAMPLE_12.D\data.ms

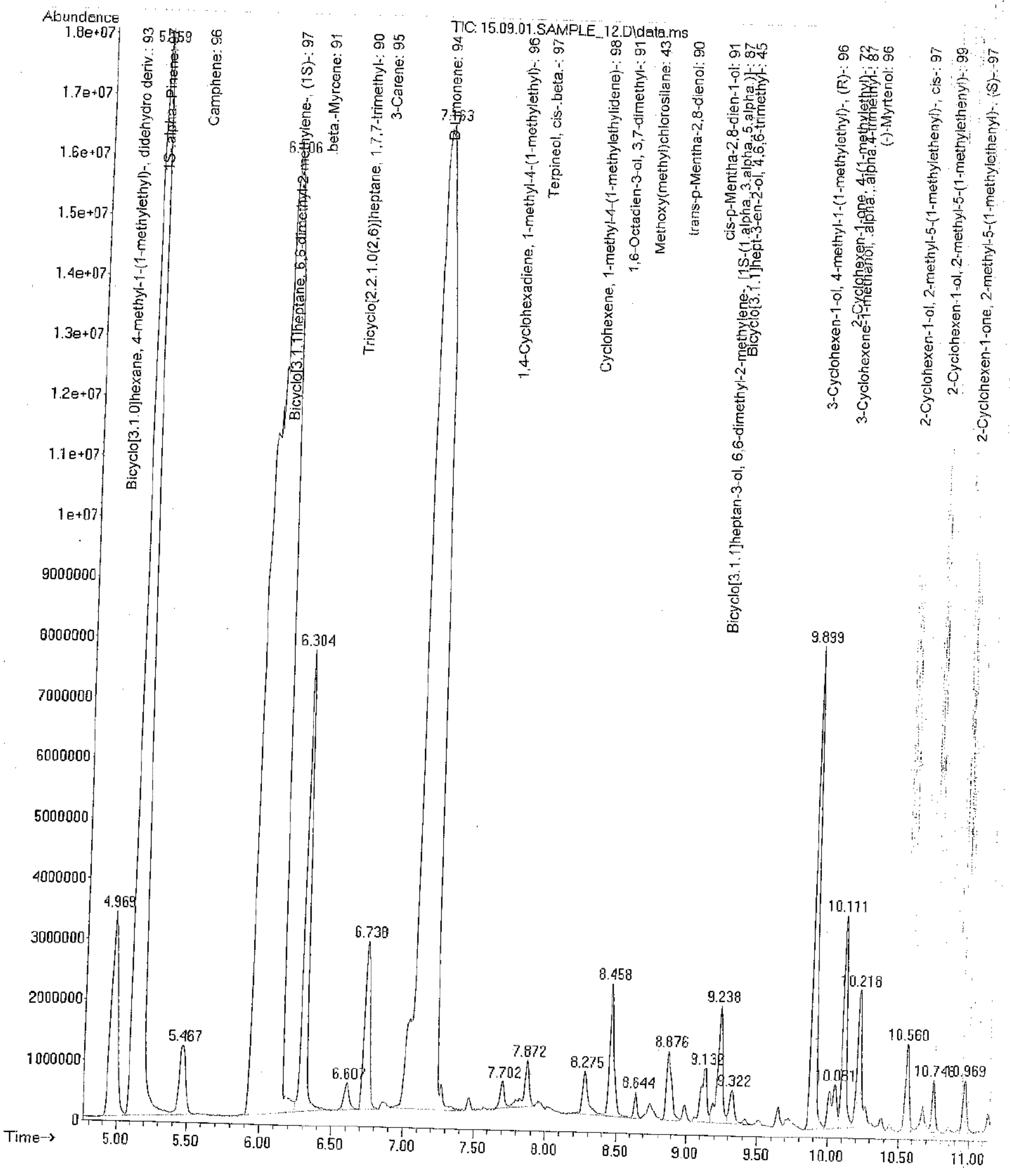
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.969 | 804 | 827 | 842 | BV | 3189108 | 110520493 | 6.87% | 1.297% |
| 2 | 5.159 | 842 | 859 | 898 | VV | 17719307 | 770527340 | 47.89% | 9.044% |
| 3 | 5.467 | 898 | 911 | 937 | VB 2 | 1149635 | 36861518 | 2.29% | 0.433% |
| 4 | 6.106 | 967 | 1019 | 1043 | BV 3 | 15694184 | 1608984986 | 100.00% | 18.886% |
| 5 | 6.304 | 1043 | 1053 | 1080 | VB | 7471052 | 161374793 | 10.03% | 1.894% |
| 6 | 6.607 | 1080 | 1104 | 1116 | BV | 440619 | 11462684 | 0.71% | 0.135% |
| 7 | 6.738 | 1116 | 1127 | 1142 | PV | 2733883 | 68430375 | 4.25% | 0.803% |
| 8 | 7.163 | 1160 | 1198 | 1245 | BB 5 | 16135362 | 1338518883 | 83.19% | 15.712% |
| 9 | 7.702 | 1269 | 1290 | 1299 | BV | 445754 | 8379934 | 0.52% | 0.098% |
| 10 | 7.872 | 1299 | 1319 | 1329 | VV 2 | 762685 | 19215715 | 1.19% | 0.226% |
| 11 | 8.275 | 1367 | 1387 | 1410 | BV 2 | 699330 | 19492428 | 1.21% | 0.229% |
| 12 | 8.458 | 1410 | 1418 | 1443 | VV 2 | 2120904 | 49850064 | 3.10% | 0.585% |
| 13 | 8.644 | 1443 | 1449 | 1456 | PV | 429479 | 7493200 | 0.47% | 0.088% |
| 14 | 8.876 | 1482 | 1489 | 1502 | VV 4 | 1102175 | 29310940 | 1.82% | 0.344% |
| 15 | 9.132 | 1516 | 1532 | 1538 | VV 9 | 880037 | 26937410 | 1.67% | 0.316% |
| 16 | 9.238 | 1538 | 1550 | 1558 | VV 3 | 1904315 | 47834124 | 2.97% | 0.561% |
| 17 | 9.322 | 1558 | 1564 | 1588 | VB 3 | 540495 | 14141478 | 0.88% | 0.166% |
| 18 | 9.899 | 1650 | 1662 | 1675 | PV | 7467529 | 152568415 | 9.48% | 1.791% |
| 19 | 10.051 | 1675 | 1688 | 1693 | VV 5 | 723107 | 26333254 | 1.64% | 0.309% |
| 20 | 10.111 | 1693 | 1698 | 1707 | VV | 3503087 | 65431078 | 4.07% | 0.768% |
| 21 | 10.218 | 1707 | 1716 | 1736 | VV 3 | 2255479 | 53733740 | 3.34% | 0.631% |
| 22 | 10.560 | 1764 | 1774 | 1783 | BV | 1440180 | 25703433 | 1.60% | 0.302% |
| 23 | 10.748 | 1801 | 1806 | 1817 | VV | 853008 | 15442464 | 0.96% | 0.181% |
| 24 | 10.969 | 1832 | 1843 | 1857 | VV | 853423 | 15983001 | 0.99% | 0.188% |
| 25 | 12.383 | 2054 | 2083 | 2097 | BV | 8061151 | 153767760 | 9.56% | 1.805% |
| 26 | 12.555 | 2097 | 2112 | 2123 | PV 2 | 2079865 | 50437206 | 3.13% | 0.592% |
| 27 | 12.842 | 2145 | 2161 | 2170 | BV 3 | 1218901 | 26463381 | 1.64% | 0.311% |
| 28 | 12.981 | 2170 | 2184 | 2204 | VV | 14856606 | 438223618 | 27.24% | 5.144% |
| 29 | 13.154 | 2204 | 2213 | 2246 | VB 2 | 4328059 | 133680097 | 8.31% | 1.569% |
| 30 | 13.443 | 2246 | 2262 | 2278 | BV 7 | 436529 | 23363547 | 1.45% | 0.274% |
| 31 | 13.638 | 2278 | 2295 | 2337 | VV 4 | 15709173 | 1119595931 | 69.58% | 13.142% |
| 32 | 13.919 | 2337 | 2343 | 2349 | PV | 948513 | 14091452 | 0.88% | 0.165% |
| 33 | 14.057 | 2349 | 2366 | 2375 | VV | 6142399 | 120727292 | 7.50% | 1.417% |
| 34 | 14.306 | 2396 | 2409 | 2418 | VV 5 | 1275129 | 53556081 | 3.33% | 0.629% |
| 35 | 14.384 | 2418 | 2422 | 2430 | VV 4 | 617340 | 17010685 | 1.06% | 0.200% |
| 36 | 14.466 | 2430 | 2436 | 2442 | VV | 2962592 | 54262504 | 3.37% | 0.637% |
| 37 | 14.584 | 2442 | 2456 | 2461 | VV 5 | 4000841 | 148733313 | 9.24% | 1.746% |
| 38 | 14.674 | 2461 | 2471 | 2478 | VV | 11049173 | 341783095 | 21.24% | 4.012% |
| 39 | 14.823 | 2478 | 2496 | 2501 | VV | 3469327 | 70135988 | 4.36% | 0.823% |
| 40 | 14.891 | 2501 | 2508 | 2522 | VV 2 | 7369950 | 153877080 | 9.56% | 1.806% |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 15.042 | 2522 | 2533 | 2541 | PV | 3 | 555119 | 16015572 | 1.00% | 0.188% |
| 42 | 15.151 | 2541 | 2552 | 2566 | VV | | 809249 | 22044661 | 1.37% | 0.259% |
| 43 | 15.296 | 2566 | 2576 | 2583 | VV | | 2583780 | 49308626 | 3.06% | 0.579% |
| 44 | 15.389 | 2583 | 2592 | 2602 | VV | | 571745 | 19197274 | 1.19% | 0.225% |
| 45 | 15.709 | 2602 | 2646 | 2665 | VV | | 9667535 | 354747191 | 22.05% | 4.164% |
| 46 | 15.914 | 2665 | 2681 | 2686 | PV | 6 | 418606 | 16269289 | 1.01% | 0.191% |
| 47 | 15.988 | 2686 | 2693 | 2704 | VV | 3 | 1185963 | 28186230 | 1.75% | 0.331% |
| 48 | 16.083 | 2704 | 2710 | 2714 | VV | 2 | 619159 | 10822109 | 0.67% | 0.127% |
| 49 | 16.171 | 2714 | 2725 | 2732 | VV | | 4037820 | 89294408 | 5.55% | 1.048% |
| 50 | 16.377 | 2732 | 2759 | 2770 | VV | 2 | 7898649 | 251203800 | 15.61% | 2.949% |
| 51 | 16.514 | 2770 | 2783 | 2791 | PV | 2 | 1403889 | 27341040 | 1.70% | 0.321% |
| 52 | 16.658 | 2791 | 2807 | 2820 | VV | 5 | 1330636 | 30670532 | 1.91% | 0.360% |

Sum of corrected areas: 8519341511

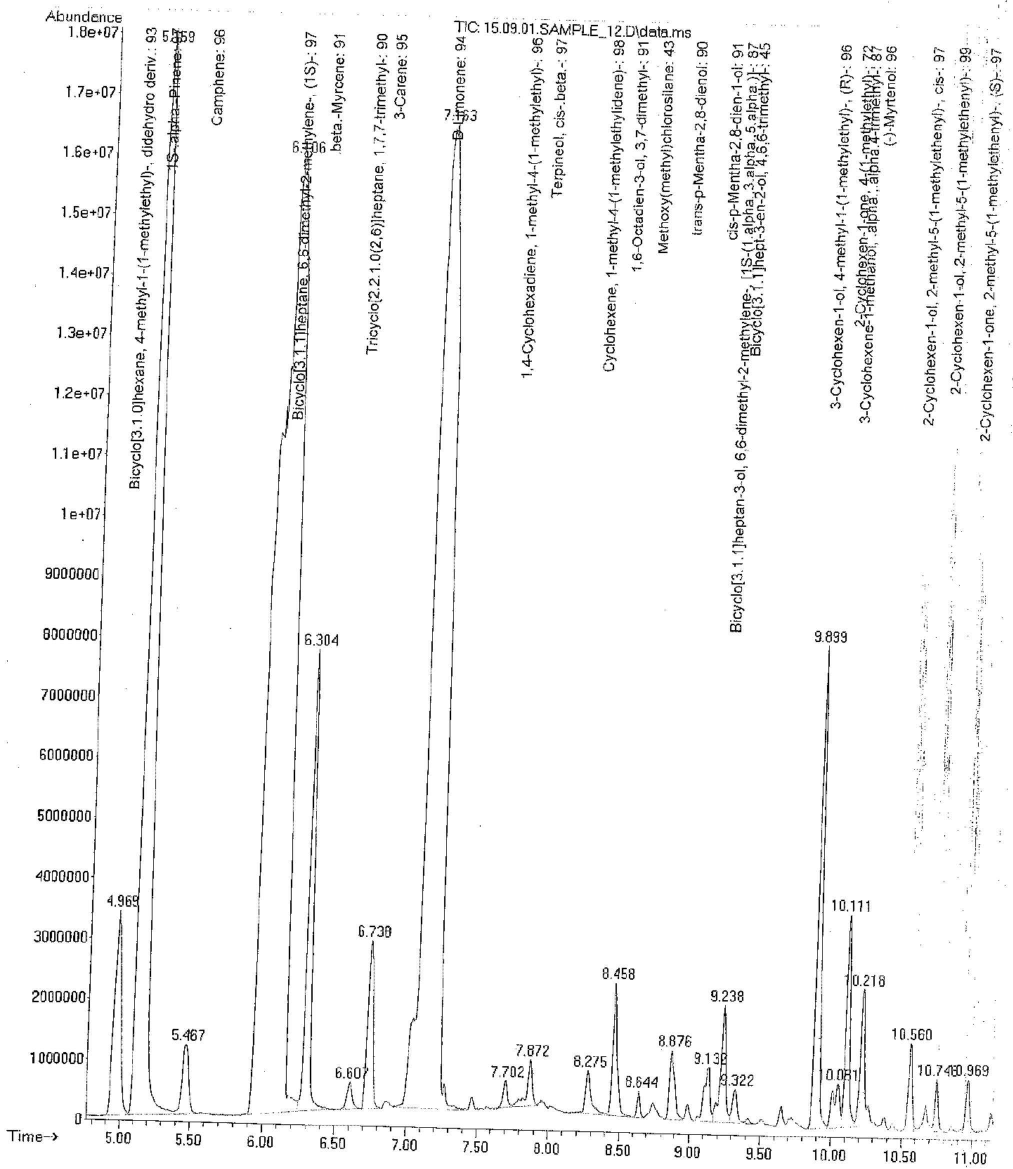
SMART.M Fri Sep 11 11:05:45 2015

File :C:\msdchem\1\data\Commercial 2015.08.07\15.09.01.SAMPLE_12.D
Operator :
Acquired : 1 Sep 2015 12:25 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1 ERR



File :C:\msdchem\1\data\Commercial 2015.08.07\15.09.01.SAMPLE_12.D
Operator :
Acquired : 1 Sep 2015 12:25 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1

ERR



## Sample No :12

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.25.SAMPLE_13.D
Acq On : 25 Aug 2015 12:19
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.08.25.SAMPLE_13.D\data.ms

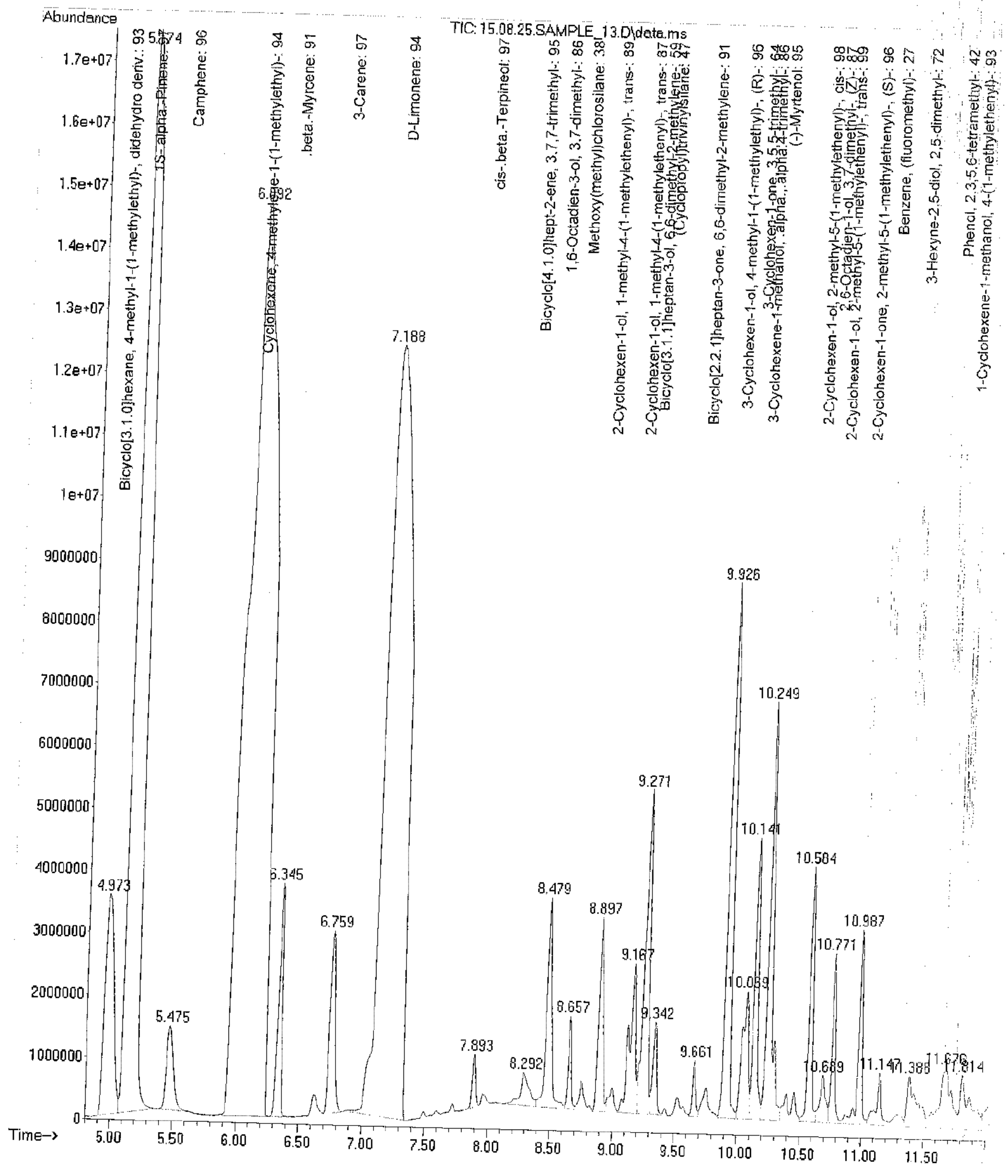
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.502 | 205 | 240 | 282 | BB | 15175834 | 418899076 | 22.08% | 3.494% |
| 2 | 4.973 | 806 | 828 | 844 | BV | 3517200 | 176342533 | 9.30% | 1.471% |
| 3 | 5.174 | 844 | 862 | 896 | VB 2 | 17362090 | 1061464272 | 55.96% | 8.855% |
| 4 | 5.475 | 898 | 913 | 940 | BB | 1324678 | 47775226 | 2.52% | 0.399% |
| 5 | 6.092 | 970 | 1017 | 1047 | BV 3 | 14659560 | 1896871904 | 100.00% | 15.823% |
| 6 | 6.345 | 1047 | 1060 | 1083 | VB | 3739011 | 73546037 | 3.88% | 0.614% |
| 7 | 6.759 | 1120 | 1130 | 1146 | VB | 2907359 | 80236750 | 4.23% | 0.669% |
| 8 | 7.188 | 1156 | 1203 | 1232 | BV 5 | 12359090 | 1427062314 | 75.23% | 11.904% |
| 9 | 7.893 | 1304 | 1322 | 1329 | BV | 825632 | 14173519 | 0.75% | 0.118% |
| 10 | 8.292 | 1356 | 1390 | 1407 | BV 7 | 496566 | 25742301 | 1.36% | 0.215% |
| 11 | 8.479 | 1407 | 1422 | 1445 | VV 5 | 3254249 | 91078848 | 4.80% | 0.760% |
| 12 | 8.657 | 1445 | 1452 | 1460 | VV | 1455591 | 26009330 | 1.37% | 0.217% |
| 13 | 8.897 | 1484 | 1492 | 1502 | PV 4 | 3065444 | 70726541 | 3.73% | 0.590% |
| 14 | 9.167 | 1517 | 1538 | 1544 | VV 4 | 2391031 | 84952209 | 4.48% | 0.709% |
| 15 | 9.271 | 1544 | 1556 | 1562 | VV | 5065934 | 133528928 | 7.04% | 1.114% |
| 16 | 9.342 | 1562 | 1568 | 1577 | VV | 1473259 | 29835816 | 1.57% | 0.249% |
| 17 | 9.661 | 1615 | 1622 | 1628 | VV | 868031 | 16481233 | 0.87% | 0.137% |
| 18 | 9.926 | 1652 | 1667 | 1678 | VV 2 | 8329097 | 223581313 | 11.79% | 1.865% |
| 19 | 10.069 | 1678 | 1691 | 1696 | VV 3 | 2021176 | 71000751 | 3.74% | 0.592% |
| 20 | 10.141 | 1696 | 1703 | 1712 | VV | 4481412 | 96705266 | 5.10% | 0.807% |
| 21 | 10.249 | 1712 | 1721 | 1738 | VV 2 | 6711802 | 163551310 | 8.62% | 1.364% |
| 22 | 10.584 | 1765 | 1778 | 1786 | VV | 4051647 | 83423250 | 4.40% | 0.696% |
| 23 | 10.689 | 1786 | 1796 | 1803 | VV | 744063 | 23974600 | 1.26% | 0.200% |
| 24 | 10.771 | 1803 | 1810 | 1821 | VV | 2744797 | 52548856 | 2.77% | 0.438% |
| 25 | 10.987 | 1821 | 1846 | 1857 | VV | 3099485 | 65314948 | 3.44% | 0.545% |
| 26 | 11.147 | 1857 | 1874 | 1887 | VV 2 | 821479 | 25191961 | 1.33% | 0.210% |
| 27 | 11.388 | 1908 | 1914 | 1939 | VV 5 | 791981 | 43224807 | 2.28% | 0.361% |
| 28 | 11.676 | 1939 | 1963 | 1980 | VV 9 | 956481 | 65346653 | 3.44% | 0.545% |
| 29 | 11.814 | 1980 | 1986 | 2012 | VV 6 | 841242 | 46871575 | 2.47% | 0.391% |
| 30 | 12.401 | 2065 | 2086 | 2100 | VV | 12741174 | 340696570 | 17.96% | 2.842% |
| 31 | 12.567 | 2100 | 2114 | 2127 | VV 3 | 4304895 | 146543880 | 7.73% | 1.222% |
| 32 | 12.681 | 2127 | 2133 | 2155 | VV 2 | 794238 | 46704918 | 2.46% | 0.390% |
| 33 | 12.855 | 2155 | 2163 | 2173 | VV | 2494187 | 77774716 | 4.10% | 0.649% |
| 34 | 13.008 | 2173 | 2189 | 2204 | VV 3 | 15194111 | 736725236 | 38.84% | 6.146% |
| 35 | 13.174 | 2204 | 2217 | 2246 | VV 2 | 5180082 | 230823490 | 12.17% | 1.926% |
| 36 | 13.458 | 2246 | 2265 | 2281 | VV 6 | 852335 | 60083290 | 3.17% | 0.501% |
| 37 | 13.647 | 2281 | 2297 | 2334 | VV 5 | 13167853 | 1224667854 | 64.56% | 10.216% |
| 38 | 13.941 | 2334 | 2347 | 2353 | PV | 668288 | 12087041 | 0.64% | 0.101% |
| 39 | 14.095 | 2353 | 2373 | 2380 | VV | 4700683 | 113352161 | 5.98% | 0.946% |
| 40 | 14.322 | 2400 | 2411 | 2429 | VV 8 | 1286617 | 59034205 | 3.11% | 0.492% |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 14.492 | 2429 | 2440 | 2446 | VV | | 3358927 | 70620244 | 3.72% | 0.589% |
| 42 | 14.601 | 2446 | 2458 | 2465 | VV | 5 | 3904252 | 159728777 | 8.42% | 1.332% |
| 43 | 14.724 | 2465 | 2479 | 2487 | VV | | 7355404 | 347480191 | 18.32% | 2.899% |
| 44 | 14.931 | 2487 | 2514 | 2527 | VV | 7 | 3970773 | 159771678 | 8.42% | 1.333% |
| 45 | 15.179 | 2546 | 2556 | 2570 | VV | | 989547 | 30813322 | 1.62% | 0.257% |
| 46 | 15.337 | 2570 | 2583 | 2591 | VV | | 4343180 | 105438005 | 5.56% | 0.880% |
| 47 | 15.429 | 2591 | 2599 | 2616 | VV | 5 | 969908 | 33540325 | 1.77% | 0.280% |
| 48 | 15.761 | 2616 | 2655 | 2674 | VV | 10 | 8686491 | 702012627 | 37.01% | 5.856% |
| 49 | 16.034 | 2684 | 2701 | 2708 | VV | 3 | 1925472 | 50904683 | 2.68% | 0.425% |
| 50 | 16.208 | 2708 | 2731 | 2738 | VV | 9 | 1986657 | 79931143 | 4.21% | 0.667% |
| 51 | 16.342 | 2738 | 2753 | 2760 | VV | 4 | 2336189 | 94516809 | 4.98% | 0.788% |
| 52 | 16.424 | 2760 | 2767 | 2777 | VV | | 4698257 | 122444013 | 6.46% | 1.021% |
| 53 | 16.557 | 2777 | 2790 | 2797 | VV | | 1874465 | 38513576 | 2.03% | 0.321% |
| 54 | 16.700 | 2797 | 2814 | 2825 | VV | 5 | 1832301 | 56060114 | 2.96% | 0.468% |
| 55 | 16.827 | 2825 | 2836 | 2854 | VV | 4 | 747146 | 23826343 | 1.26% | 0.199% |
| 56 | 17.065 | 2854 | 2876 | 2889 | PV | 7 | 565928 | 19885949 | 1.05% | 0.166% |
| 57 | 17.271 | 2889 | 2911 | 2924 | VV | 8 | 456206 | 24856836 | 1.31% | 0.207% |
| 58 | 17.396 | 2924 | 2932 | 2949 | PV | 4 | 1111579 | 26307888 | 1.39% | 0.219% |
| 59 | 17.806 | 2985 | 3001 | 3013 | BV | 10 | 537451 | 25877536 | 1.36% | 0.216% |
| 60 | 17.915 | 3013 | 3020 | 3033 | VV | 4 | 1193534 | 32989192 | 1.74% | 0.275% |
| 61 | 18.094 | 3033 | 3050 | 3060 | PV | 8 | 493038 | 24371054 | 1.28% | 0.203% |
| 62 | 18.214 | 3060 | 3071 | 3088 | VV | 9 | 451054 | 16872680 | 0.89% | 0.141% |
| 63 | 18.554 | 3119 | 3128 | 3142 | VV | | 948717 | 22386874 | 1.18% | 0.187% |
| 64 | 19.153 | 3218 | 3230 | 3235 | PV | 4 | 449400 | 10456777 | 0.55% | 0.087% |
| 65 | 19.227 | 3235 | 3242 | 3251 | VV | 3 | 427892 | 9709602 | 0.51% | 0.081% |
| 66 | 22.463 | 3770 | 3790 | 3807 | BV | 2 | 589658 | 14436467 | 0.76% | 0.120% |

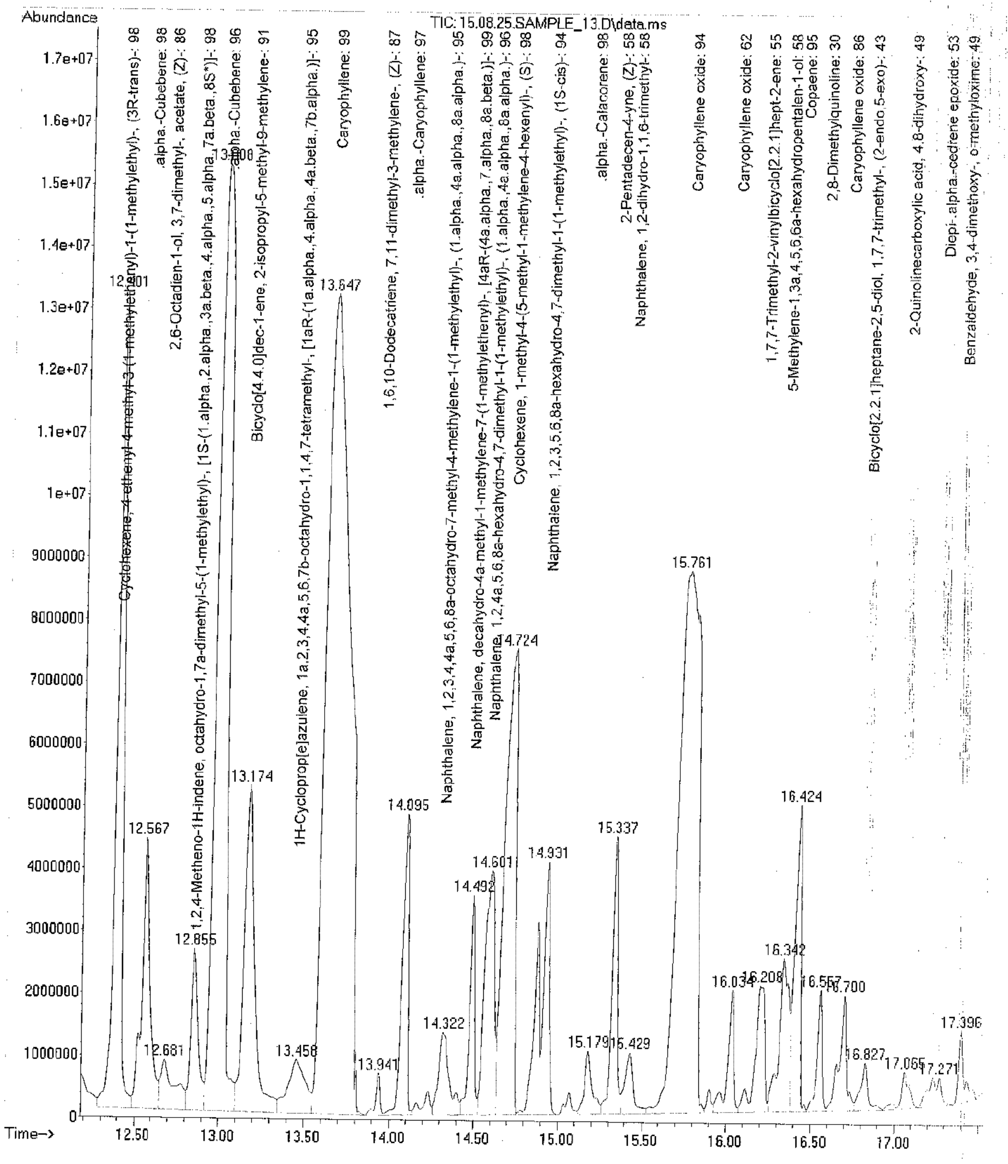
Sum of corrected areas: 11987708191

SMART.M Fri Sep 11 11:07:44 2015

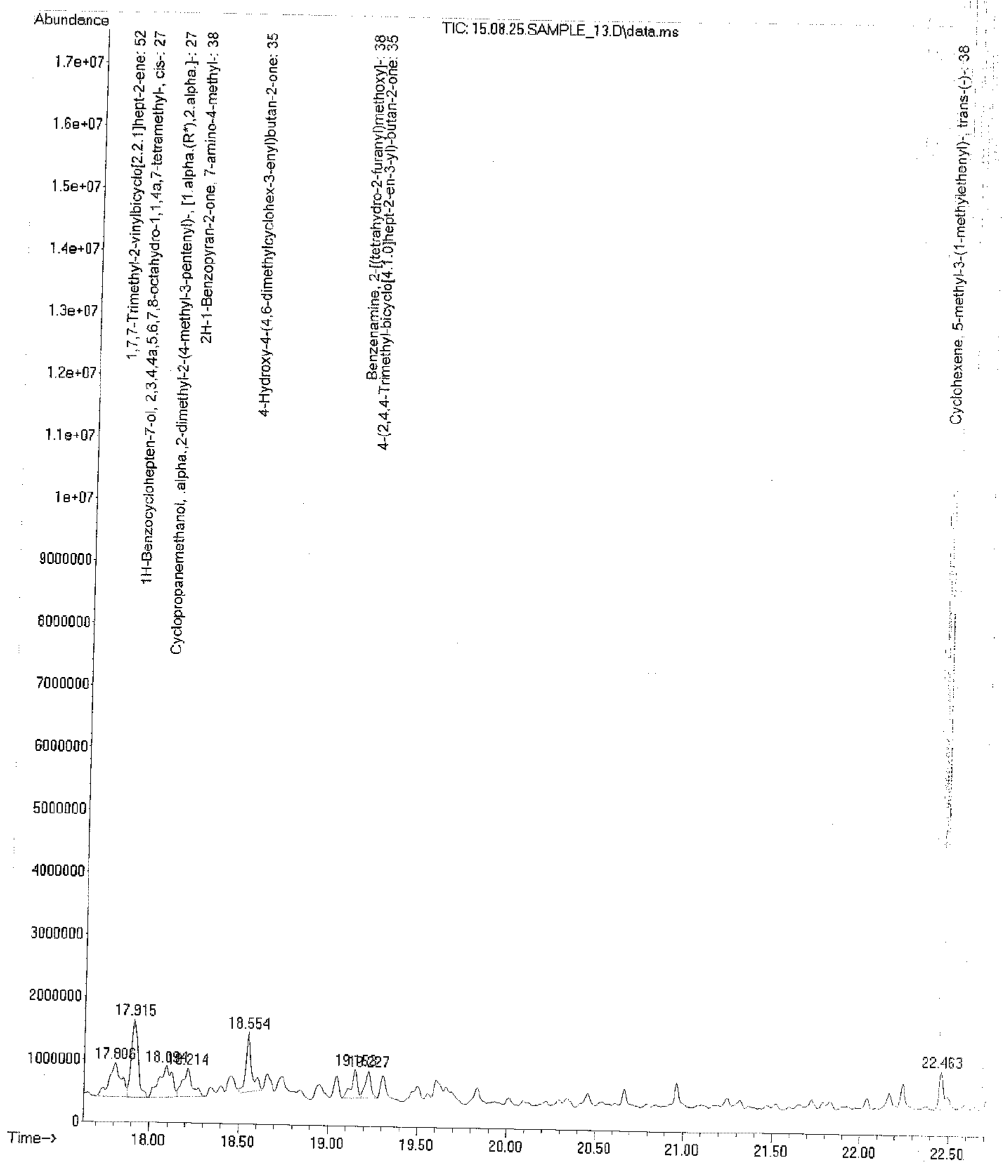
```
File         : C:\msdchem\1\data\Commercial 2015.08.07\15.08.25.SAMPLE_13.D
Operator     :
Acquired     : 25 Aug 2015  12:19     using AcqMethod Plant Extracts.M
Instrument   :    UOSJP GCMSD
Sample Name  :
Misc Info    :
Vial Number  : 1
```



```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.25.SAMPLE_13.D
Operator    :
Acquired    : 25 Aug 2015  12:19     using AcqMethod Plant Extracts.M
Instrument  :    UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 1
```



```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.25.SAMPLE_13.D
Operator    :
Acquired    : 25 Aug 2015   12:19      using AcqMethod Plant Extracts.M
Instrument  :
   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 1
```



## Sample No : 13

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.09.03.SAMPLE_C.D
Acq On : 3 Sep 2015 13:27
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

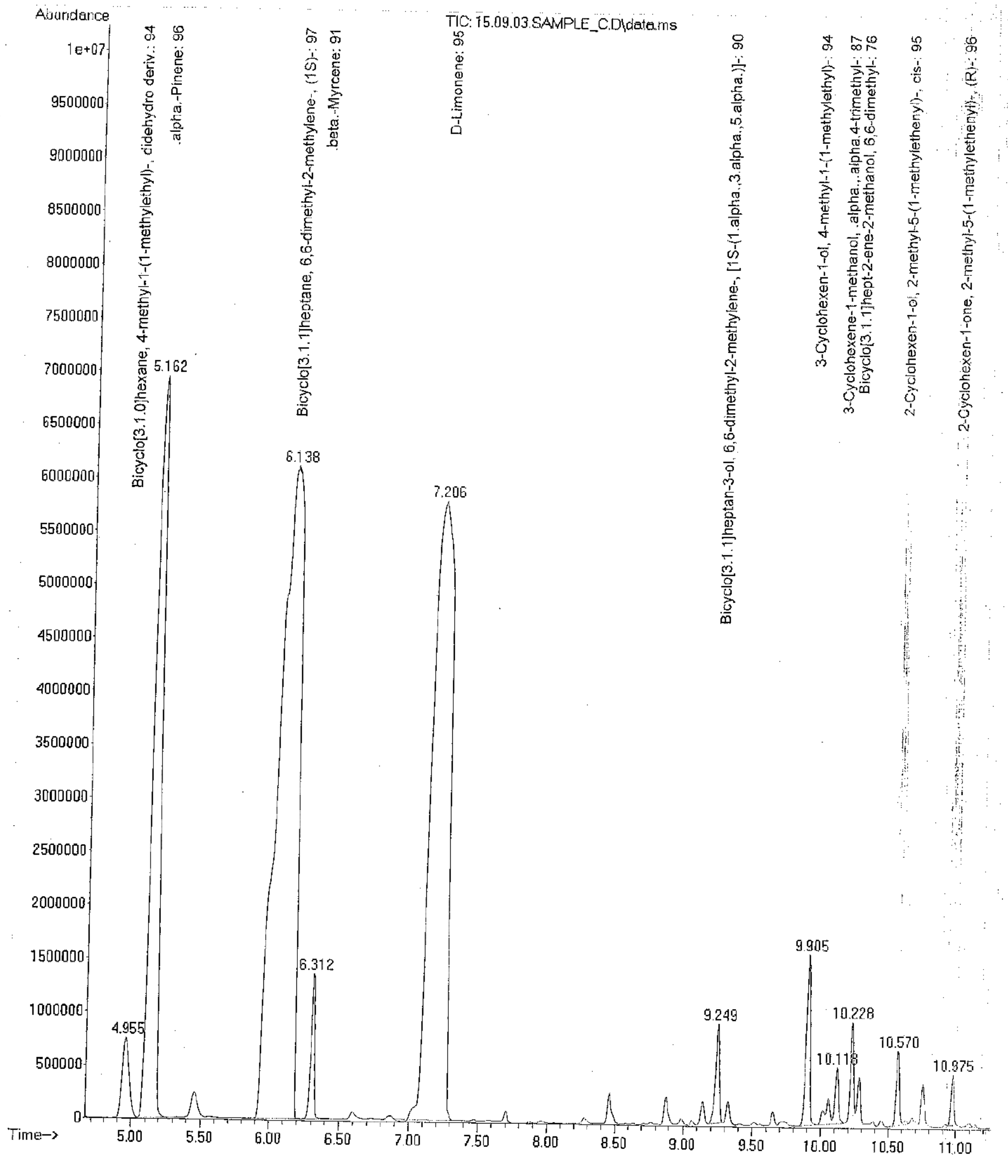
Signal : TIC: 15.09.03.SAMPLE_C.D\data.ms

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.485 | 228 | 237 | 263 | BB | 7754719 | 261734853 | 42.24% | 8.142% |
| 2 | 4.955 | 805 | 825 | 840 | BV | 742984 | 28384873 | 4.58% | 0.883% |
| 3 | 5.162 | 840 | 860 | 885 | VB | 6834177 | 282378970 | 45.58% | 8.784% |
| 4 | 6.138 | 980 | 1025 | 1042 | BV 2 | 6104801 | 619591719 | 100.00% | 19.273% |
| 5 | 6.312 | 1042 | 1054 | 1080 | PB | 1366499 | 24684309 | 3.98% | 0.768% |
| 6 | 7.206 | 1153 | 1206 | 1242 | BB 5 | 5789283 | 520309669 | 83.98% | 16.185% |
| 7 | 9.249 | 1540 | 1552 | 1559 | PV | 904647 | 18506172 | 2.99% | 0.576% |
| 8 | 9.905 | 1650 | 1663 | 1676 | BV | 1589151 | 31689679 | 5.11% | 0.986% |
| 9 | 10.118 | 1676 | 1699 | 1709 | VV 3 | 519214 | 16550776 | 2.67% | 0.515% |
| 10 | 10.228 | 1709 | 1718 | 1723 | PV | 874913 | 13743234 | 2.22% | 0.428% |
| 11 | 10.570 | 1763 | 1776 | 1789 | BV | 700285 | 12462694 | 2.01% | 0.388% |
| 12 | 10.975 | 1837 | 1844 | 1876 | BB | 463399 | 8261427 | 1.33% | 0.257% |
| 13 | 12.387 | 2065 | 2084 | 2099 | BV | 2590457 | 52864079 | 8.53% | 1.644% |
| 14 | 12.558 | 2099 | 2113 | 2142 | VB 3 | 647360 | 20290059 | 3.27% | 0.631% |
| 15 | 12.990 | 2171 | 2186 | 2205 | VV | 5441657 | 157141234 | 25.36% | 4.888% |
| 16 | 13.156 | 2205 | 2214 | 2242 | VB 5 | 1252154 | 36815837 | 5.94% | 1.145% |
| 17 | 13.661 | 2276 | 2299 | 2326 | BB 8 | 6073763 | 423124801 | 68.29% | 13.162% |
| 18 | 14.060 | 2349 | 2367 | 2386 | PV | 1880558 | 35130581 | 5.67% | 1.093% |
| 19 | 14.471 | 2430 | 2437 | 2443 | BV | 787442 | 13191188 | 2.13% | 0.410% |
| 20 | 14.586 | 2443 | 2456 | 2461 | PV 5 | 1119379 | 38524463 | 6.22% | 1.198% |
| 21 | 14.683 | 2461 | 2472 | 2480 | VV | 4084526 | 125665909 | 20.28% | 3.909% |
| 22 | 14.835 | 2480 | 2498 | 2503 | PV | 993173 | 19445307 | 3.14% | 0.605% |
| 23 | 14.894 | 2503 | 2508 | 2521 | VV 3 | 1508988 | 31213960 | 5.04% | 0.971% |
| 24 | 15.311 | 2570 | 2579 | 2585 | BV | 1741707 | 30664887 | 4.95% | 0.954% |
| 25 | 15.752 | 2616 | 2654 | 2667 | BV | 4678883 | 235501421 | 38.01% | 7.326% |
| 26 | 16.004 | 2684 | 2696 | 2706 | BV 2 | 565076 | 10672897 | 1.72% | 0.332% |
| 27 | 16.182 | 2706 | 2726 | 2733 | PV 4 | 714346 | 17017176 | 2.75% | 0.529% |
| 28 | 16.314 | 2733 | 2749 | 2755 | VV 4 | 1030094 | 31767750 | 5.13% | 0.988% |
| 29 | 16.386 | 2755 | 2761 | 2773 | VV | 2000893 | 38592850 | 6.23% | 1.200% |
| 30 | 16.530 | 2773 | 2785 | 2793 | PV | 859875 | 15289661 | 2.47% | 0.476% |
| 31 | 16.677 | 2793 | 2810 | 2822 | VV 4 | 901500 | 19934360 | 3.22% | 0.620% |
| 32 | 18.217 | 3035 | 3071 | 3087 | BB 4 | 783220 | 23602907 | 3.81% | 0.734% |

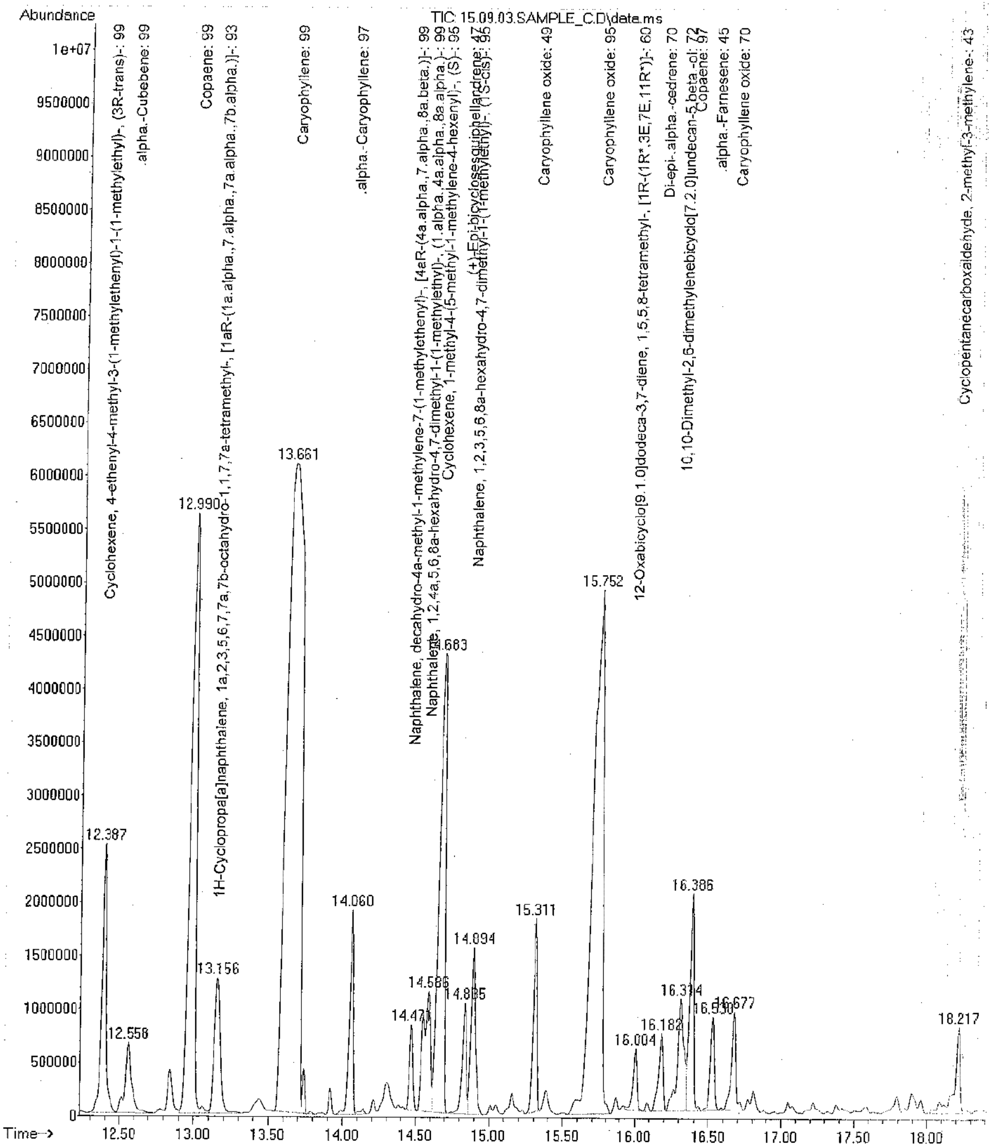
Sum of corrected areas: 3214749703

MART.M Fri Sep 11 11:34:52 2015

File :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_C.D
Operator :
Acquired : 3 Sep 2015 13:27 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1



File :C:\msdchem\1\data\Commercial 2015.08.07\15.09.03.SAMPLE_C.D
Operator :
Acquired : 3 Sep 2015 13:27 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1



**Sample No : 14**

Area Percent Report

```
Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.07.SAMPLE_14.D
Acq On    :  7 Aug 2015  14:42
Operator  :
Sample    :
Misc      :
ALS Vial  : 2   Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method    : C:\MSDCHEM\1\METHODS\SMART.M
Title     : autoint1.e

Signal    : TIC: 15.08.07.SAMPLE_14.D\data.ms
```

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.504 | 208 | 237 | 267 | BV | 14393010 | 616662446 | 29.17% | 4.519% |
| 2 | 1.731 | 267 | 275 | 303 | VB | 2448102 | 64279668 | 3.04% | 0.471% |
| 3 | 4.986 | 801 | 827 | 842 | BV | 4527115 | 334495822 | 15.82% | 2.451% |
| 4 | 5.179 | 842 | 859 | 884 | VV 4 | 15004135 | 1422264089 | 67.27% | 10.422% |
| 5 | 5.366 | 884 | 891 | 904 | VV | 1378105 | 52811859 | 2.50% | 0.387% |
| 6 | 5.501 | 904 | 914 | 942 | VV 5 | 1028942 | 69650297 | 3.29% | 0.510% |
| 7 | 6.103 | 942 | 1016 | 1061 | VV 2 | 12542075 | 2114205066 | 100.00% | 15.492% |
| 8 | 6.433 | 1061 | 1072 | 1090 | VB | 3335643 | 88506176 | 4.19% | 0.649% |
| 9 | 6.800 | 1123 | 1134 | 1164 | VB | 1400463 | 59505487 | 2.81% | 0.436% |
| 10 | 7.225 | 1164 | 1206 | 1241 | BV 5 | 9593873 | 1347254372 | 63.72% | 9.872% |
| 11 | 7.456 | 1241 | 1245 | 1253 | VV | 5013635 | 142994760 | 6.76% | 1.048% |
| 12 | 7.778 | 1271 | 1300 | 1306 | VV | 483242 | 18060055 | 0.85% | 0.132% |
| 13 | 7.934 | 1306 | 1326 | 1332 | VV | 852372 | 28404394 | 1.34% | 0.208% |
| 14 | 8.317 | 1345 | 1391 | 1406 | VV | 1702681 | 100769826 | 4.77% | 0.738% |
| 15 | 8.502 | 1406 | 1422 | 1444 | VV | 3637232 | 123086463 | 5.82% | 0.902% |
| 16 | 8.677 | 1444 | 1452 | 1459 | VV | 912714 | 27869100 | 1.32% | 0.204% |
| 17 | 8.772 | 1459 | 1468 | 1482 | VV 4 | 673862 | 36265238 | 1.72% | 0.266% |
| 18 | 8.910 | 1482 | 1491 | 1503 | VV | 2288213 | 74884318 | 3.54% | 0.549% |
| 19 | 9.013 | 1503 | 1509 | 1516 | VV | 830631 | 24080225 | 1.14% | 0.176% |
| 20 | 9.172 | 1516 | 1536 | 1542 | VV 6 | 1974541 | 84815377 | 4.01% | 0.621% |
| 21 | 9.278 | 1542 | 1554 | 1561 | VV | 3908931 | 116177454 | 5.50% | 0.851% |
| 22 | 9.350 | 1561 | 1566 | 1589 | VV | 1376671 | 49532570 | 2.34% | 0.363% |
| 23 | 9.669 | 1612 | 1620 | 1626 | VV | 960699 | 24505597 | 1.16% | 0.180% |
| 24 | 9.936 | 1650 | 1665 | 1676 | VV | 7864105 | 236729818 | 11.20% | 1.735% |
| 25 | 10.075 | 1676 | 1689 | 1693 | VV 5 | 1683394 | 58699231 | 2.78% | 0.430% |
| 26 | 10.145 | 1693 | 1701 | 1709 | VV | 4339019 | 103948448 | 4.92% | 0.762% |
| 27 | 10.251 | 1709 | 1718 | 1738 | VV 2 | 4588389 | 129009170 | 6.10% | 0.945% |
| 28 | 10.583 | 1762 | 1775 | 1784 | VV | 2709713 | 61363472 | 2.90% | 0.450% |
| 29 | 10.692 | 1784 | 1793 | 1800 | VV | 1221287 | 33534404 | 1.59% | 0.246% |
| 30 | 10.771 | 1800 | 1807 | 1819 | VV | 1909805 | 41427984 | 1.96% | 0.304% |
| 31 | 10.987 | 1837 | 1843 | 1862 | VV | 1856110 | 36423709 | 1.72% | 0.267% |
| 32 | 11.674 | 1944 | 1960 | 1977 | BV 4 | 453094 | 27264782 | 1.29% | 0.200% |
| 33 | 11.865 | 1977 | 1992 | 2009 | VV 5 | 516685 | 30559188 | 1.45% | 0.224% |
| 34 | 12.410 | 2064 | 2084 | 2105 | VV | 12191544 | 595147292 | 28.15% | 4.361% |
| 35 | 12.575 | 2105 | 2112 | 2152 | VV | 3513832 | 201140565 | 9.51% | 1.474% |
| 6 | 12.862 | 2152 | 2161 | 2170 | VV 2 | 2112372 | 84249067 | 3.98% | 0.617% |
| 7 | 13.014 | 2170 | 2186 | 2208 | VV 3 | 12799629 | 994825840 | 47.05% | 7.290% |
| 8 | 13.193 | 2208 | 2217 | 2252 | VV 5 | 3064288 | 260781435 | 12.33% | 1.911% |
| 9 | 13.660 | 2252 | 2296 | 2319 | VV 10 | 9679373 | 985001730 | 46.59% | 7.218% |
| 0 | 13.901 | 2319 | 2337 | 2347 | VV 6 | 6792051 | 517666458 | 24.49% | 3.793% |

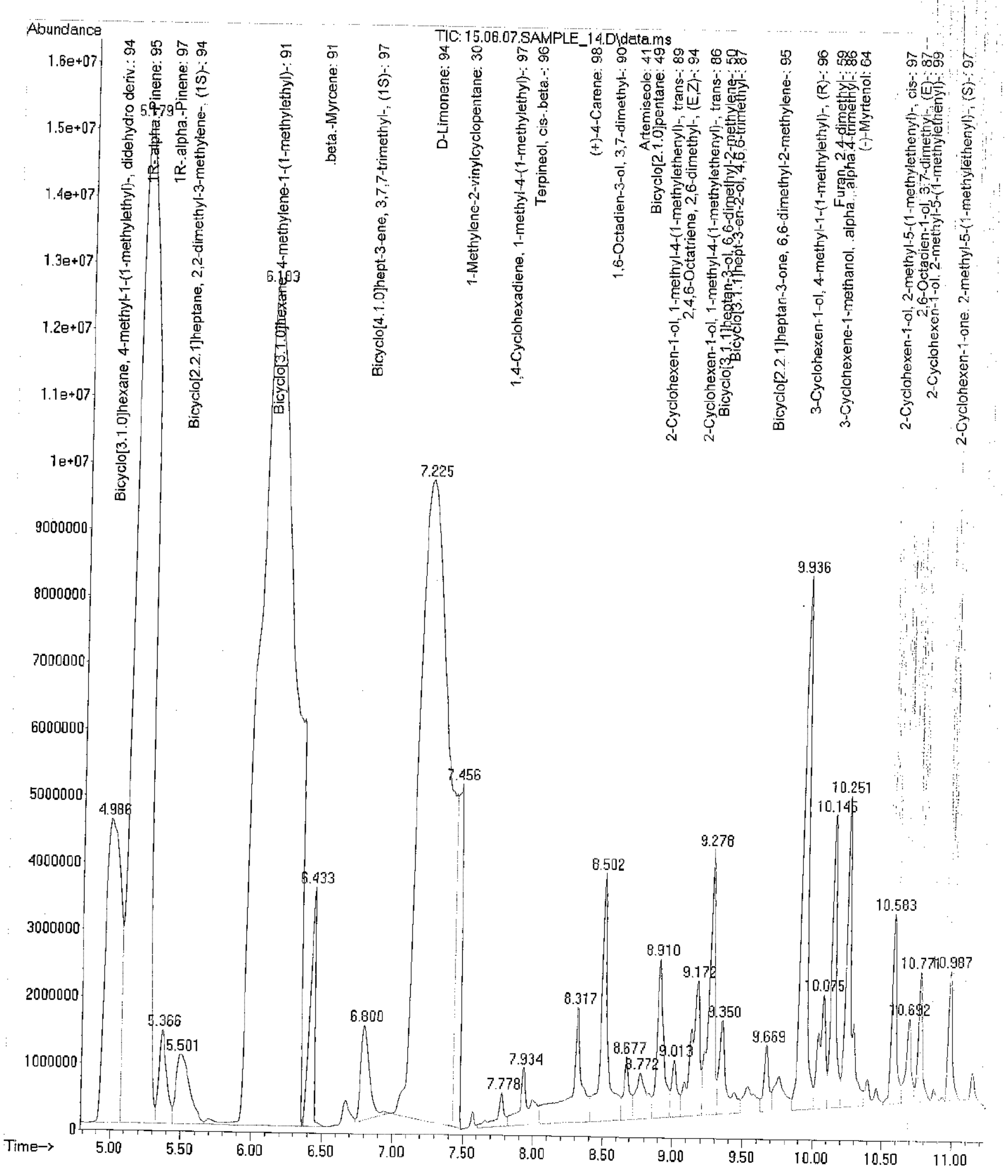
| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 14.003 | 2347 | 2354 | 2361 | VV | | 1109193 | 18798757 | 0.89% | 0.138% |
| 42 | 14.170 | 2361 | 2382 | 2396 | PV | | 4819990 | 161290883 | 7.63% | 1.182% |
| 43 | 14.357 | 2396 | 2414 | 2424 | VV | | 1247827 | 59395631 | 2.81% | 0.435% |
| 44 | 14.440 | 2424 | 2428 | 2434 | VV | | 703638 | 17255458 | 0.82% | 0.126% |
| 45 | 14.532 | 2434 | 2444 | 2449 | VV | | 3166222 | 74585505 | 3.53% | 0.547% |
| 46 | 14.644 | 2449 | 2463 | 2469 | VV | 8 | 4027554 | 173862346 | 8.22% | 1.274% |
| 47 | 14.768 | 2469 | 2484 | 2495 | VV | 5 | 4835158 | 328705485 | 15.55% | 2.409% |
| 48 | 14.992 | 2495 | 2522 | 2531 | VV | 3 | 2981696 | 157332454 | 7.44% | 1.153% |
| 49 | 15.363 | 2573 | 2584 | 2591 | VV | | 2540694 | 50821863 | 2.40% | 0.372% |
| 50 | 15.806 | 2605 | 2659 | 2672 | VV | 10 | 5914500 | 437304039 | 20.68% | 3.204% |
| 51 | 16.039 | 2672 | 2699 | 2706 | VV | 4 | 1236261 | 48276112 | 2.28% | 0.354% |
| 52 | 16.125 | 2706 | 2714 | 2718 | VV | | 678053 | 15453997 | 0.73% | 0.113% |
| 53 | 16.224 | 2718 | 2730 | 2739 | VV | 6 | 2336078 | 87197219 | 4.12% | 0.639% |
| 54 | 16.446 | 2739 | 2768 | 2776 | VV | 2 | 4378100 | 206048974 | 9.75% | 1.510% |
| 55 | 16.561 | 2776 | 2787 | 2795 | PV | | 650967 | 13722176 | 0.65% | 0.101% |
| 56 | 16.693 | 2795 | 2810 | 2822 | VV | 4 | 659947 | 23872517 | 1.13% | 0.175% |
| 57 | 16.827 | 2822 | 2832 | 2840 | VV | 7 | 456161 | 15038702 | 0.71% | 0.110% |
| 58 | 17.227 | 2885 | 2900 | 2905 | VV | 7 | 407051 | 16878980 | 0.80% | 0.124% |
| 59 | 17.398 | 2917 | 2929 | 2945 | VV | 2 | 1033106 | 33355613 | 1.58% | 0.244% |
| 60 | 17.604 | 2945 | 2964 | 2980 | VV | 4 | 573901 | 34158945 | 1.62% | 0.250% |
| 61 | 17.811 | 2980 | 2999 | 3011 | VV | | 1387701 | 54968907 | 2.60% | 0.403% |
| 62 | 17.926 | 3011 | 3018 | 3029 | VV | 3 | 981190 | 31427366 | 1.49% | 0.230% |
| 63 | 18.097 | 3029 | 3048 | 3056 | VV | 8 | 870604 | 38260209 | 1.81% | 0.280% |
| 64 | 18.216 | 3056 | 3068 | 3085 | VV | 6 | 730942 | 37218328 | 1.76% | 0.273% |
| 65 | 18.553 | 3116 | 3125 | 3138 | VV | | 1156249 | 35651180 | 1.69% | 0.261% |
| 66 | 19.306 | 3246 | 3252 | 3266 | VV | | 572630 | 12563550 | 0.59% | 0.092% |
| 67 | 20.670 | 3454 | 3483 | 3499 | VV | 2 | 434645 | 13604585 | 0.64% | 0.100% |
| 68 | 20.962 | 3522 | 3533 | 3548 | VV | | 617647 | 12006382 | 0.57% | 0.088% |
| 69 | 22.462 | 3779 | 3787 | 3801 | PV | 5 | 444839 | 11421267 | 0.54% | 0.084% |
| 70 | 24.687 | 4151 | 4164 | 4170 | VV | 5 | 396039 | 7890206 | 0.37% | 0.058% |

Sum of corrected areas: 13647220887

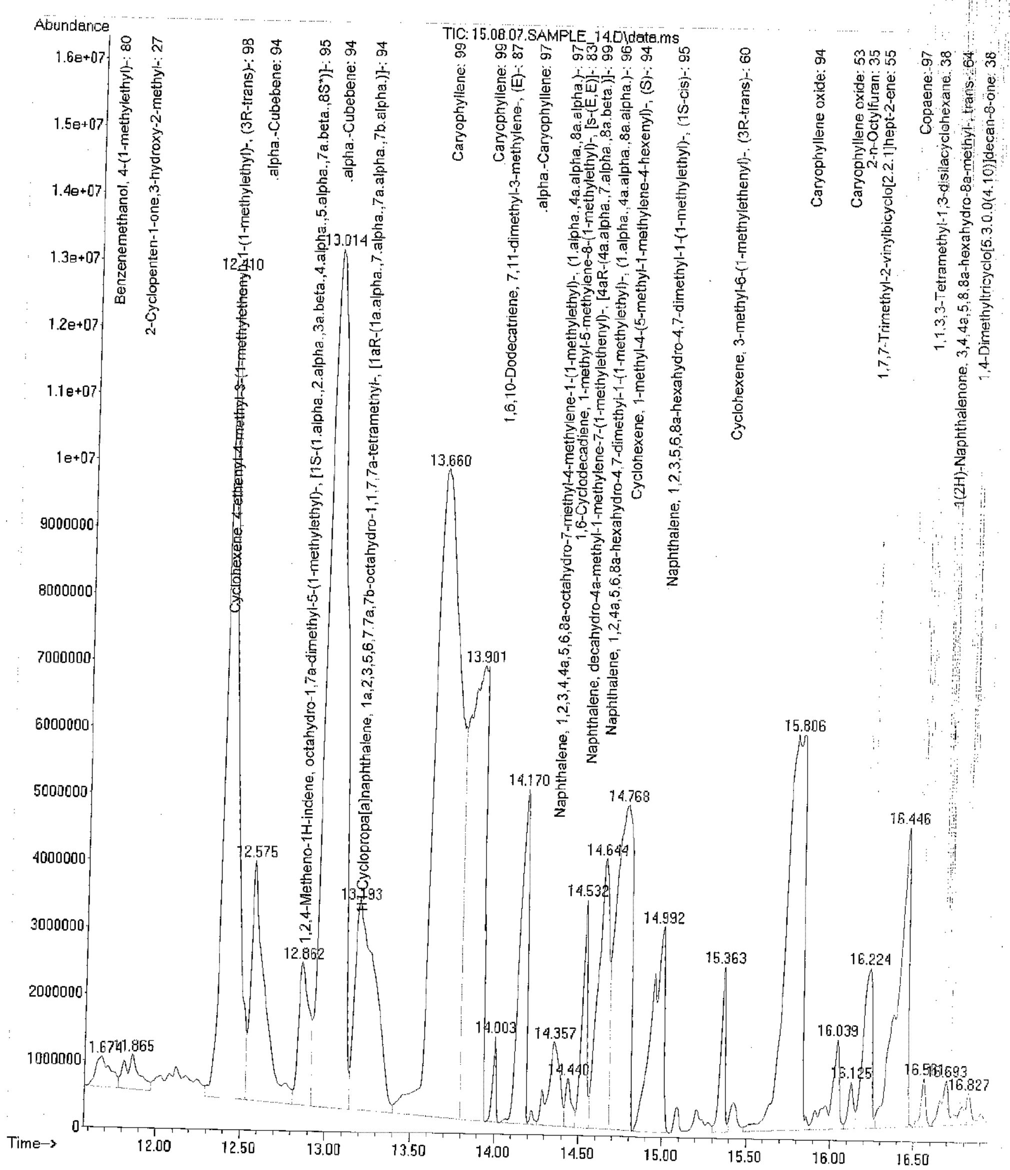
SMART.M Fri Sep 11 11:13:07 2015

File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_14.D
Operator    :
Acquired    :  7 Aug 2015  14:42      using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number:  2

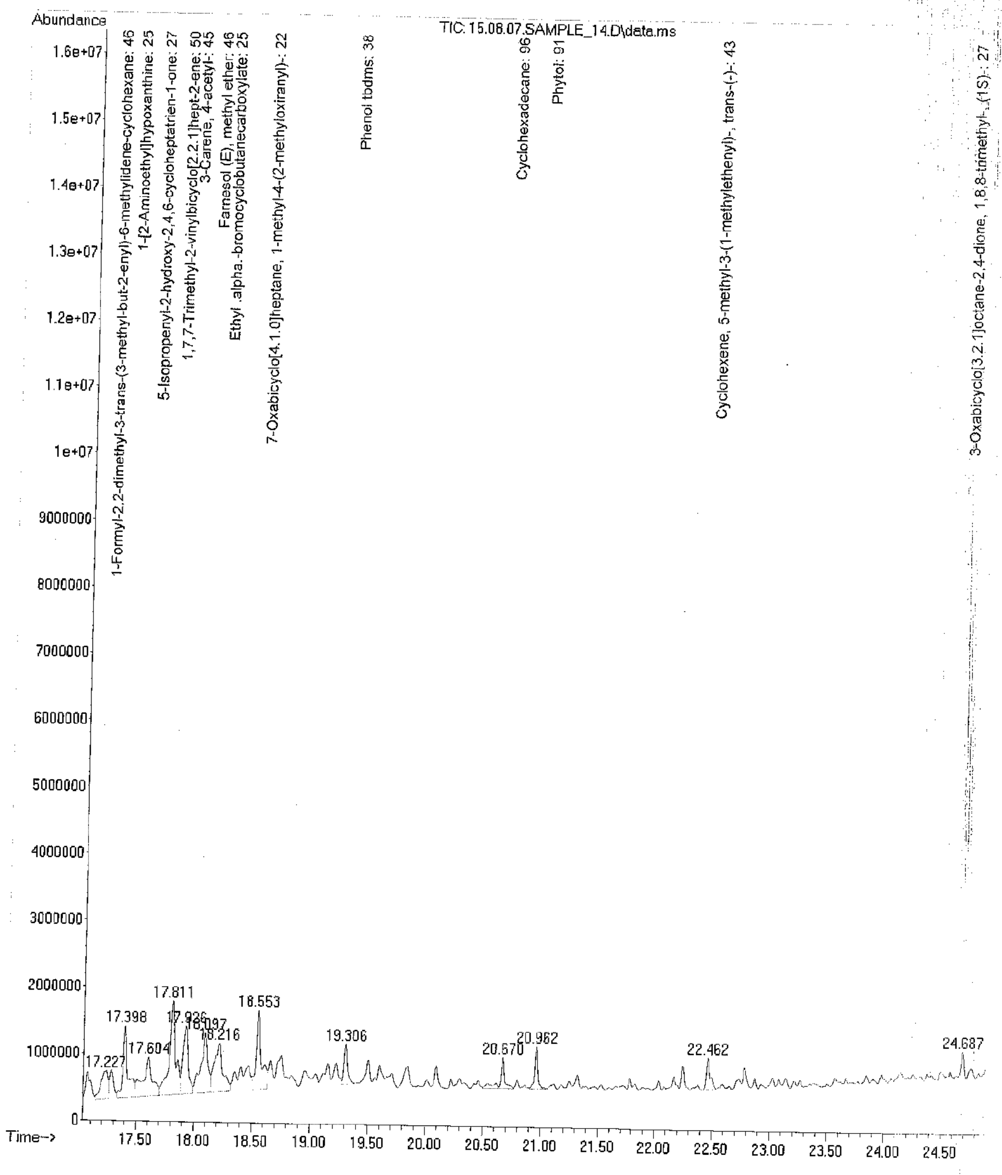
ERR



```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_14.D
Operator    :
Acquired    :  7 Aug 2015  14:42      using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 2                                              ERR
```



```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_14.D
Operator    :
Acquired    :  7 Aug 2015  14:42      using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 2                                         ERR
```



## Sample No: 15

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.09.01.SAMPLE_15.D
Acq On : 1 Sep 2015 14:15
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.09.01.SAMPLE_15.D\data.ms

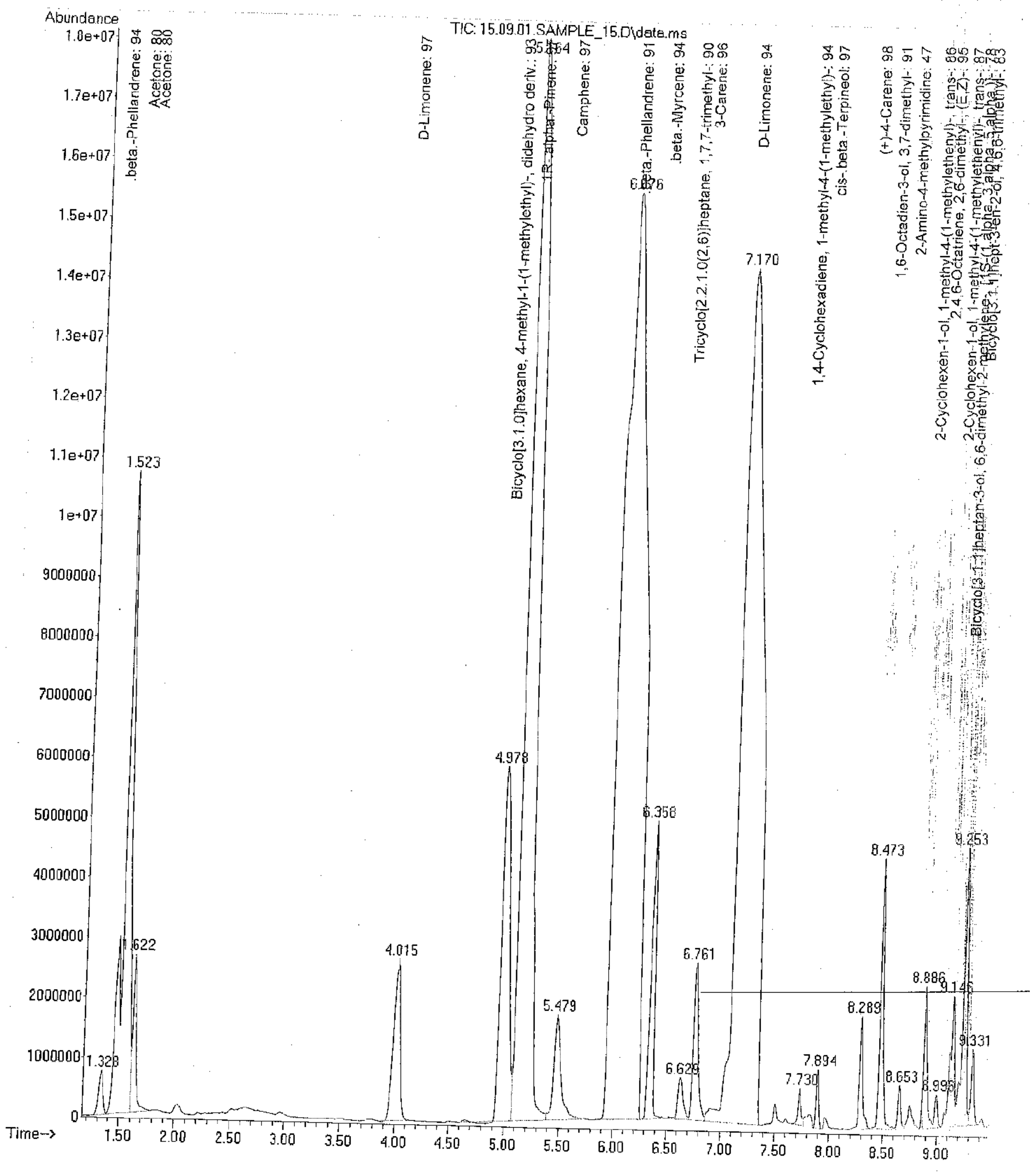
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.328 | 193 | 210 | 220 | BV | 720254 | 20906172 | 0.97% | 0.167% |
| 2 | 1.523 | 220 | 243 | 256 | VV 2 | 10565895 | 401393614 | 18.69% | 3.205% |
| 3 | 1.622 | 256 | 260 | 289 | VB | 2594421 | 64024826 | 2.98% | 0.511% |
| 4 | 4.015 | 633 | 665 | 692 | BB | 2540280 | 114561442 | 5.34% | 0.915% |
| 5 | 4.978 | 765 | 828 | 845 | BV | 5888879 | 294562289 | 13.72% | 2.352% |
| 6 | 5.164 | 845 | 860 | 898 | VV 2 | 18027246 | 1230151821 | 57.29% | 9.823% |
| 7 | 5.479 | 898 | 913 | 955 | VB | 1706493 | 79429202 | 3.70% | 0.634% |
| 8 | 6.076 | 970 | 1015 | 1048 | BV 4 | 15429358 | 2147182629 | 100.00% | 17.146% |
| 9 | 6.358 | 1048 | 1062 | 1087 | PB | 4630964 | 115267314 | 5.37% | 0.920% |
| 10 | 6.629 | 1089 | 1108 | 1122 | BV 2 | 686758 | 22334437 | 1.04% | 0.178% |
| 11 | 6.761 | 1122 | 1130 | 1147 | VV | 2589304 | 85901332 | 4.00% | 0.686% |
| 12 | 7.170 | 1147 | 1200 | 1236 | VV 4 | 14196725 | 1689729894 | 78.70% | 13.493% |
| 13 | 7.730 | 1282 | 1295 | 1301 | BV | 600729 | 12054797 | 0.56% | 0.096% |
| 14 | 7.894 | 1317 | 1322 | 1330 | PV | 945976 | 15429899 | 0.72% | 0.123% |
| 15 | 8.289 | 1355 | 1389 | 1405 | BV | 1819331 | 37857937 | 1.76% | 0.302% |
| 16 | 8.473 | 1405 | 1420 | 1444 | VV | 4383070 | 91801770 | 4.28% | 0.733% |
| 17 | 8.653 | 1444 | 1451 | 1459 | VV | 712852 | 12991032 | 0.61% | 0.104% |
| 18 | 8.886 | 1482 | 1490 | 1503 | PV 4 | 2298735 | 55857864 | 2.60% | 0.446% |
| 19 | 8.996 | 1503 | 1509 | 1517 | VV | 543732 | 10507044 | 0.49% | 0.084% |
| 20 | 9.146 | 1517 | 1535 | 1540 | VV 6 | 2143703 | 66042184 | 3.08% | 0.527% |
| 21 | 9.253 | 1540 | 1553 | 1560 | VV | 4660241 | 110737566 | 5.16% | 0.884% |
| 22 | 9.331 | 1560 | 1566 | 1575 | VV | 1262560 | 26214507 | 1.22% | 0.209% |
| 23 | 9.655 | 1613 | 1621 | 1628 | PV 2 | 712309 | 13830203 | 0.64% | 0.110% |
| 24 | 9.910 | 1650 | 1664 | 1677 | PV | 9207795 | 211060315 | 9.83% | 1.685% |
| 25 | 10.058 | 1677 | 1689 | 1694 | VV 4 | 1604055 | 48678558 | 2.27% | 0.389% |
| 26 | 10.123 | 1694 | 1700 | 1710 | VV | 4519949 | 86820652 | 4.04% | 0.693% |
| 27 | 10.230 | 1710 | 1718 | 1737 | VV 2 | 4703924 | 104661565 | 4.87% | 0.836% |
| 28 | 10.568 | 1766 | 1775 | 1784 | BV | 3091144 | 57905249 | 2.70% | 0.462% |
| 9 | 10.679 | 1784 | 1794 | 1802 | VV | 1220188 | 28490599 | 1.33% | 0.228% |
| 0 | 10.757 | 1802 | 1807 | 1820 | VV | 2199422 | 39738320 | 1.85% | 0.317% |
| 1 | 10.974 | 1837 | 1844 | 1857 | BV | 1899342 | 32988922 | 1.54% | 0.263% |
| 2 | 12.398 | 2065 | 2085 | 2099 | PV | 12341190 | 328565381 | 15.30% | 2.624% |
| 3 | 12.564 | 2099 | 2113 | 2140 | VV 4 | 3447447 | 113481835 | 5.29% | 0.906% |
| 4 | 12.756 | 2140 | 2146 | 2154 | VV | 916108 | 16061672 | 0.75% | 0.128% |
| 5 | 12.853 | 2154 | 2162 | 2173 | VV | 2083925 | 63610332 | 2.96% | 0.508% |
| 6 | 13.008 | 2173 | 2189 | 2206 | VV 3 | 15158948 | 723410009 | 33.69% | 5.777% |
| 7 | 13.173 | 2206 | 2217 | 2249 | VB 3 | 5000636 | 233687688 | 10.88% | 1.866% |
| 8 | 13.439 | 2251 | 2262 | 2280 | BV | 4099567 | 97551326 | 4.54% | 0.779% |
| 9 | 13.643 | 2280 | 2296 | 2336 | VV 4 | 13204197 | 1356461342 | 63.17% | 10.832% |
| 0 | 13.945 | 2336 | 2347 | 2354 | PV | 744983 | 11684715 | 0.54% | 0.093% |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 41 | 14.103 | 2354 | 2374 | 2381 | VV | 4296953 | 108835025 | 5.07% | 0.869% |
| 42 | 14.323 | 2381 | 2412 | 2421 | VV 6 | 1067266 | 51408106 | 2.39% | 0.411% |
| 43 | 14.404 | 2421 | 2425 | 2433 | VV 2 | 603733 | 15638875 | 0.73% | 0.125% |
| 44 | 14.492 | 2433 | 2440 | 2446 | VV | 3321772 | 64487040 | 3.00% | 0.515% |
| 45 | 14.605 | 2446 | 2459 | 2465 | VV 7 | 3989633 | 169429267 | 7.89% | 1.353% |
| 46 | 14.724 | 2465 | 2479 | 2487 | VV 2 | 7151692 | 337423451 | 15.71% | 2.694% |
| 47 | 14.933 | 2487 | 2515 | 2526 | VV 3 | 4519822 | 202211214 | 9.42% | 1.615% |
| 48 | 15.058 | 2526 | 2536 | 2545 | PV 3 | 515826 | 11924737 | 0.56% | 0.095% |
| 49 | 15.174 | 2545 | 2556 | 2570 | VV | 490676 | 16931184 | 0.79% | 0.135% |
| 50 | 15.322 | 2570 | 2581 | 2587 | VV | 2685915 | 51365809 | 2.39% | 0.410% |
| 51 | 15.395 | 2587 | 2593 | 2604 | VV 3 | 496339 | 14036857 | 0.65% | 0.112% |
| 52 | 15.755 | 2604 | 2654 | 2669 | VV 2 | 8511036 | 464212369 | 21.62% | 3.707% |
| 53 | 15.931 | 2669 | 2684 | 2689 | VV 8 | 443614 | 22042826 | 1.03% | 0.176% |
| 54 | 16.008 | 2689 | 2697 | 2706 | VV | 1774300 | 41198409 | 1.92% | 0.329% |
| 55 | 16.100 | 2706 | 2712 | 2717 | VV 2 | 922223 | 18839824 | 0.88% | 0.150% |
| 56 | 16.194 | 2717 | 2728 | 2735 | VV | 3874196 | 107821643 | 5.02% | 0.861% |
| 57 | 16.405 | 2735 | 2764 | 2774 | VV 2 | 7017461 | 278153725 | 12.95% | 2.221% |
| 58 | 16.530 | 2774 | 2785 | 2794 | VV | 1061112 | 25993557 | 1.21% | 0.208% |
| 59 | 16.670 | 2794 | 2809 | 2822 | VV 5 | 1030216 | 39350251 | 1.83% | 0.314% |
| 60 | 16.810 | 2822 | 2833 | 2841 | VV 5 | 610281 | 21630592 | 1.01% | 0.173% |
| 61 | 17.381 | 2918 | 2929 | 2954 | PB | 892117 | 20861566 | 0.97% | 0.167% |
| 62 | 17.794 | 2982 | 3000 | 3012 | PV | 1246466 | 34033284 | 1.59% | 0.272% |
| 63 | 17.914 | 3012 | 3020 | 3031 | VV 2 | 738674 | 20388162 | 0.95% | 0.163% |
| 64 | 18.086 | 3031 | 3049 | 3057 | PV 7 | 615105 | 22255146 | 1.04% | 0.178% |
| 65 | 18.203 | 3057 | 3069 | 3086 | VV 7 | 507412 | 20805771 | 0.97% | 0.166% |
| 66 | 18.543 | 3121 | 3126 | 3150 | VV 2 | 635724 | 21345698 | 0.99% | 0.170% |
| 67 | 20.667 | 3403 | 3486 | 3502 | BV 4 | 378196 | 16784002 | 0.78% | 0.134% |
| 68 | 20.960 | 3502 | 3536 | 3552 | VV | 485714 | 15431576 | 0.72% | 0.123% |
| 69 | 24.682 | 4130 | 4166 | 4173 | PV 4 | 372223 | 14764637 | 0.69% | 0.118% |

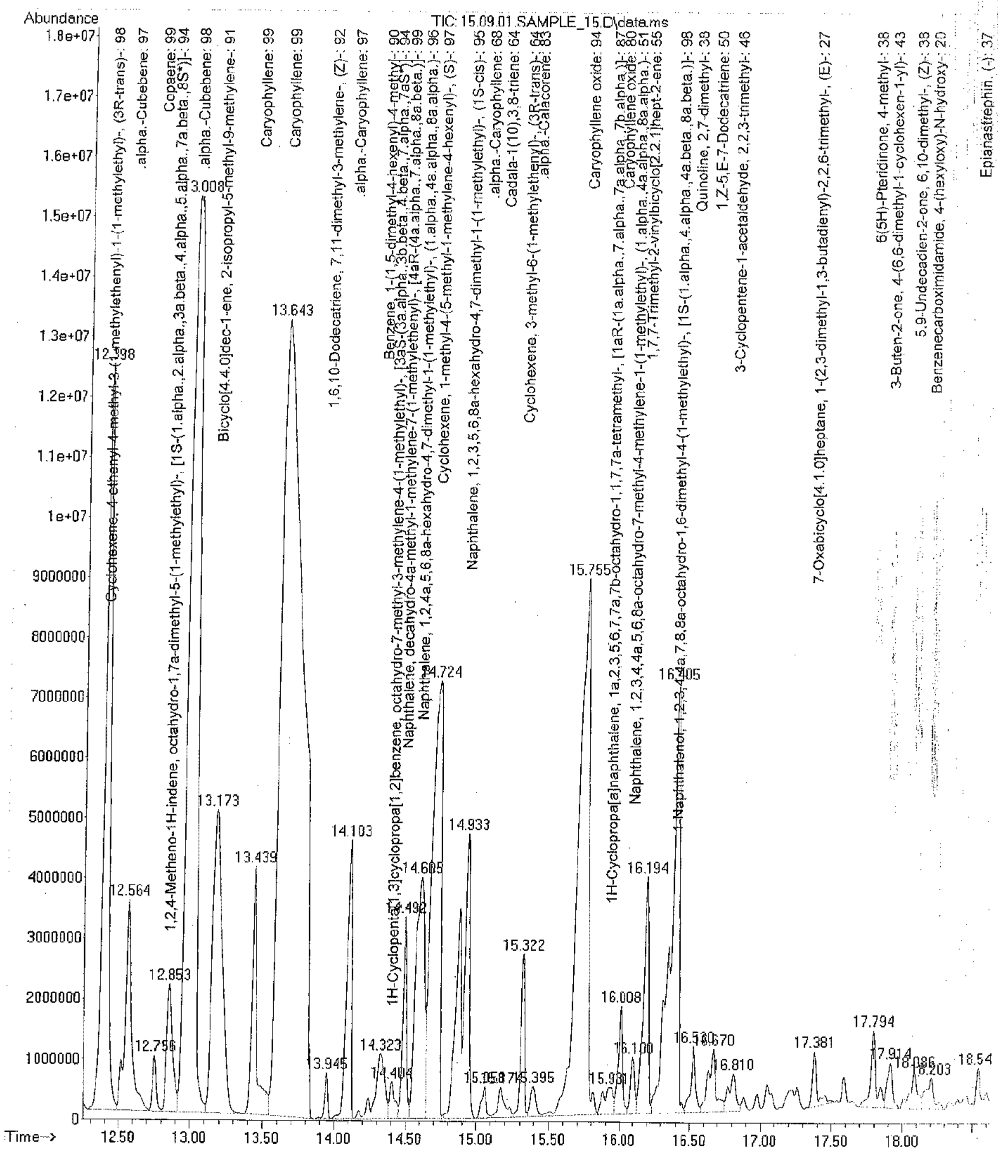
Sum of corrected areas: 12523232857

MART.M Fri Sep 11 11:17:11 2015

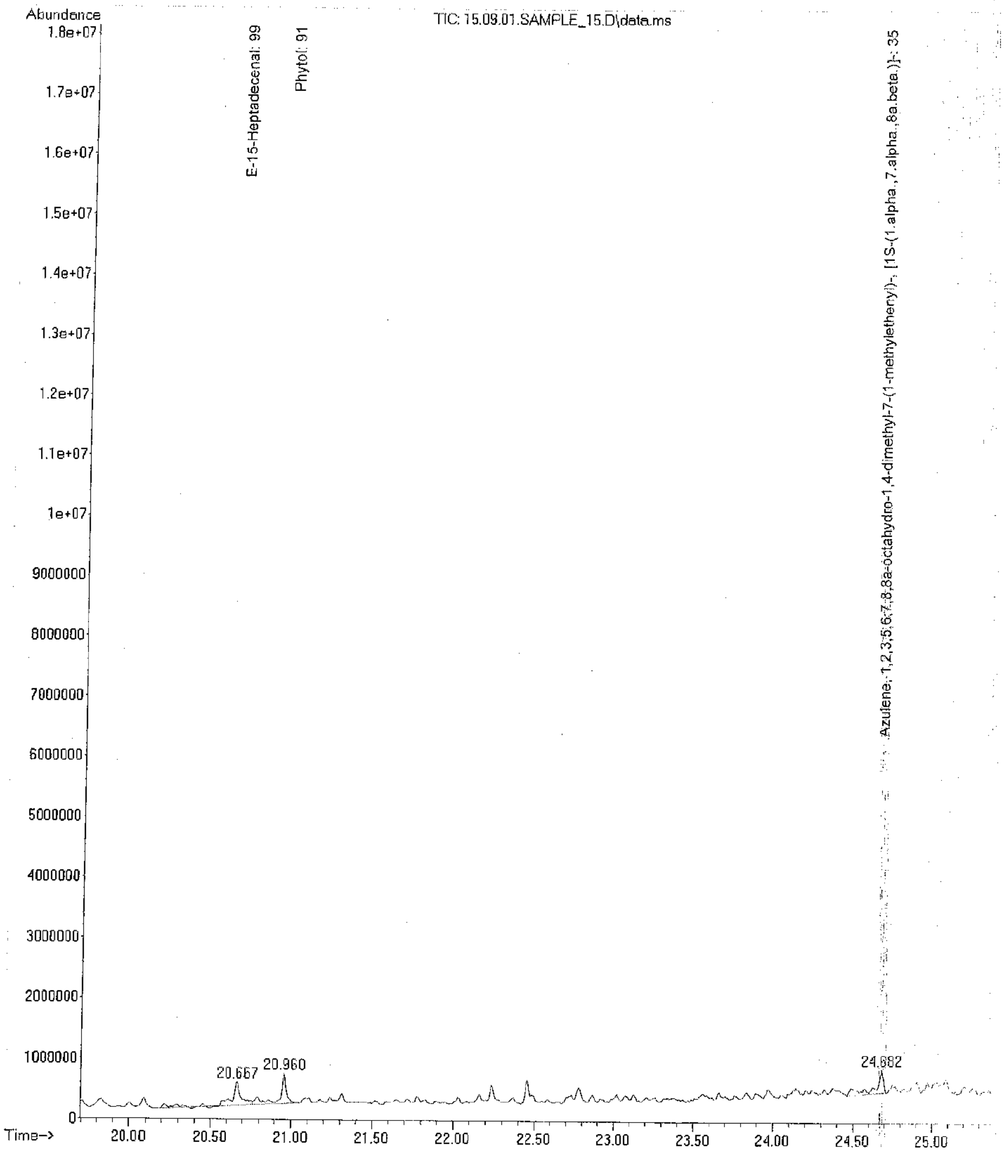
```
File          :C:\msdchem\1\data\Commercial 2015.08.07\15.09.01.SAMPLE_15.D
Operator      :
Acquired      :  1 Sep 2015  14:15      using AcqMethod PLANT EXTRACTS.M
Instrument    :   UOSJP GCMSD
Sample Name:
Misc Info     :
Vial Number:  1                                    ERR
```



```
File       :C:\msdchem\1\data\Commercial 2015.08.07\15.09.01.SAMPLE_15.D
Operator   :
Acquired   :  1 Sep 2015  14:15      using AcqMethod PLANT EXTRACTS.M
Instrument :   UOSJP GCMSD
Sample Name:
Misc Info  :                                          ERR
Vial Number: 1
```



```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.09.01.SAMPLE_15.D
Operator    :
Acquired    :  1 Sep 2015  14:15      using AcqMethod PLANT EXTRACTS.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :                                          ERR
Vial Number: 1
```



**Sample No: 16**

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.25.SAMPLE_16.D
Acq On : 25 Aug 2015 13:27
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.08.25.SAMPLE_16.D\data.ms

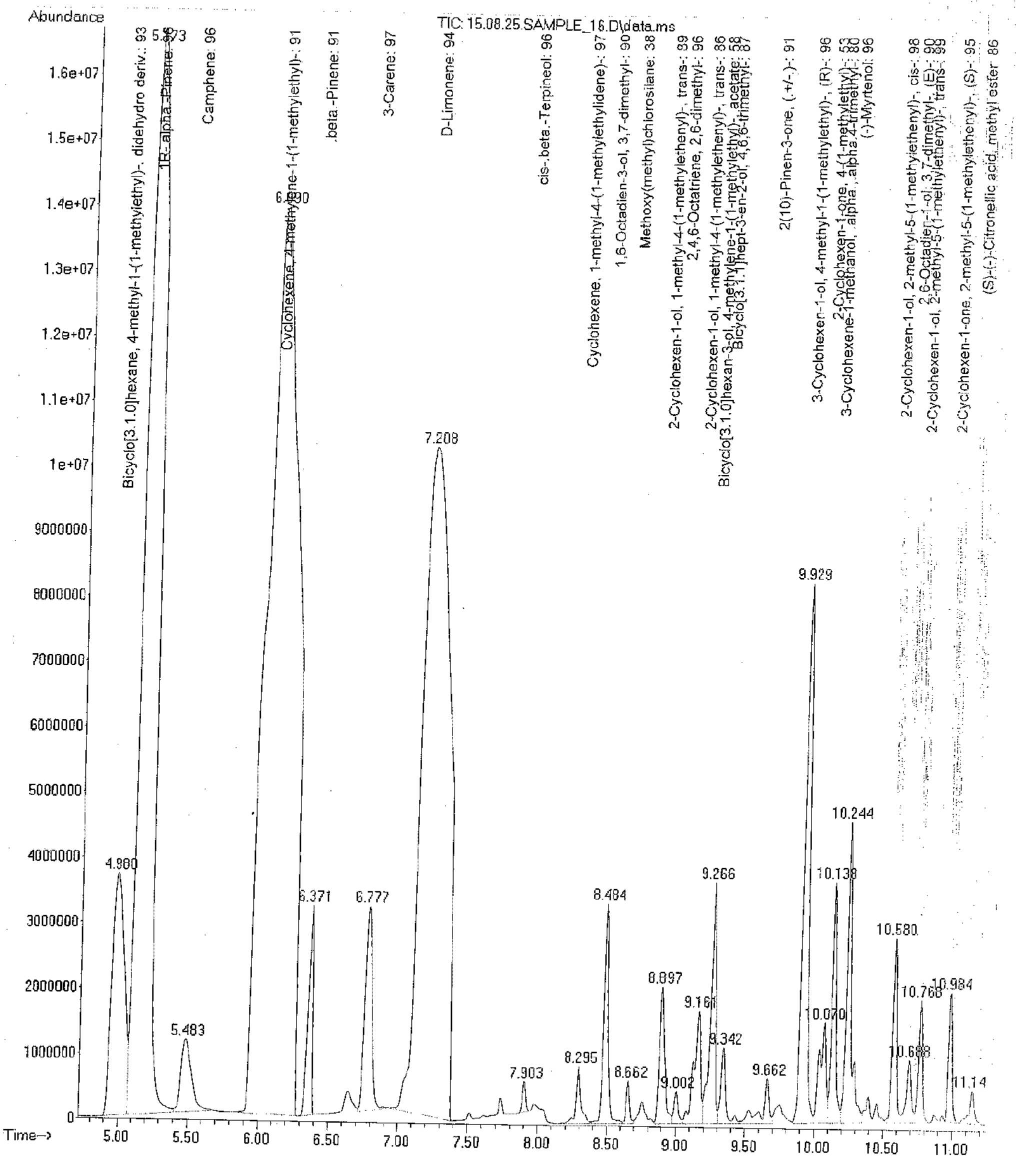
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.507 | 208 | 241 | 283 | BB | 8268532 | 300625704 | 15.34% | 2.670% |
| 2 | 4.980 | 800 | 829 | 845 | BV | 3696791 | 240062564 | 12.25% | 2.132% |
| 3 | 5.173 | 845 | 862 | 900 | VV 2 | 16648296 | 1211719576 | 61.81% | 10.760% |
| 4 | 5.483 | 900 | 914 | 947 | VB 2 | 1104605 | 56548605 | 2.88% | 0.502% |
| 5 | 6.090 | 970 | 1017 | 1052 | BV 3 | 13901653 | 1960348224 | 100.00% | 17.409% |
| 6 | 6.371 | 1052 | 1064 | 1074 | PB | 3040841 | 66995316 | 3.42% | 0.595% |
| 7 | 6.777 | 1122 | 1133 | 1160 | VB | 3108450 | 111362531 | 5.68% | 0.989% |
| 8 | 7.208 | 1160 | 1206 | 1238 | BV 5 | 10217339 | 1312118465 | 66.93% | 11.652% |
| 9 | 7.903 | 1306 | 1324 | 1331 | BV | 466313 | 7660003 | 0.39% | 0.068% |
| 10 | 8.295 | 1364 | 1390 | 1407 | BV 3 | 858732 | 22898263 | 1.17% | 0.203% |
| 11 | 8.484 | 1407 | 1422 | 1445 | VV | 3315441 | 73636410 | 3.76% | 0.654% |
| 12 | 8.662 | 1445 | 1452 | 1459 | VV | 633639 | 11474536 | 0.59% | 0.102% |
| 13 | 8.897 | 1484 | 1492 | 1505 | VV 3 | 2029275 | 51990207 | 2.65% | 0.462% |
| 14 | 9.002 | 1505 | 1510 | 1518 | VV | 489067 | 10484375 | 0.53% | 0.093% |
| 15 | 9.161 | 1518 | 1537 | 1543 | VV 4 | 1685117 | 56381045 | 2.88% | 0.501% |
| 16 | 9.266 | 1543 | 1555 | 1562 | VV | 3642095 | 94458119 | 4.82% | 0.839% |
| 17 | 9.342 | 1562 | 1568 | 1588 | VV 2 | 1153342 | 27662408 | 1.41% | 0.246% |
| 18 | 9.662 | 1588 | 1622 | 1628 | VV 5 | 679617 | 24725301 | 1.26% | 0.220% |
| 19 | 9.929 | 1653 | 1667 | 1678 | VV 2 | 7874542 | 221208928 | 11.28% | 1.964% |
| 20 | 10.070 | 1678 | 1691 | 1696 | VV 5 | 1500357 | 52063477 | 2.66% | 0.462% |
| 21 | 10.138 | 1696 | 1703 | 1712 | VV | 3663641 | 78032642 | 3.98% | 0.693% |
| 22 | 10.244 | 1712 | 1720 | 1738 | VV 2 | 4557143 | 112875514 | 5.76% | 1.002% |
| 23 | 10.580 | 1767 | 1777 | 1787 | VV | 2803087 | 55553082 | 2.83% | 0.493% |
| 24 | 10.688 | 1787 | 1796 | 1803 | VV | 949403 | 23834503 | 1.22% | 0.212% |
| 25 | 10.768 | 1803 | 1809 | 1821 | VV | 1821692 | 34353493 | 1.75% | 0.305% |
| 26 | 10.984 | 1839 | 1846 | 1857 | BV | 1963363 | 34562525 | 1.76% | 0.307% |
| 27 | 11.148 | 1857 | 1874 | 1887 | PV 5 | 489023 | 12650944 | 0.65% | 0.112% |
| 28 | 11.679 | 1943 | 1964 | 1980 | BV 8 | 408327 | 20720685 | 1.06% | 0.184% |
| 29 | 11.869 | 1980 | 1996 | 2008 | VV 4 | 498710 | 17245270 | 0.88% | 0.153% |
| 30 | 12.407 | 2069 | 2087 | 2101 | BV | 13145143 | 411705158 | 21.00% | 3.656% |
| 31 | 12.572 | 2101 | 2115 | 2144 | VV 3 | 3634605 | 160836131 | 8.20% | 1.428% |
| 32 | 12.860 | 2144 | 2164 | 2175 | VV 2 | 2100872 | 81428808 | 4.15% | 0.723% |
| 33 | 13.011 | 2175 | 2189 | 2208 | VV 3 | 14735699 | 815887653 | 41.62% | 7.245% |
| 34 | 13.181 | 2208 | 2218 | 2249 | VV 3 | 4014769 | 226163930 | 11.54% | 2.008% |
| 35 | 13.651 | 2249 | 2298 | 2339 | VV 5 | 11781114 | 1354944029 | 69.12% | 12.032% |
| 36 | 13.964 | 2339 | 2351 | 2357 | PV | 611501 | 9197203 | 0.47% | 0.082% |
| 37 | 14.128 | 2357 | 2378 | 2394 | VV | 4074231 | 113380802 | 5.78% | 1.007% |
| 38 | 14.337 | 2394 | 2414 | 2435 | VV 9 | 968916 | 55896424 | 2.85% | 0.496% |
| 39 | 14.508 | 2435 | 2443 | 2449 | VV | 2780262 | 57007233 | 2.91% | 0.506% |
| 40 | 14.617 | 2449 | 2461 | 2468 | VV 7 | 3607648 | 144099226 | 7.35% | 1.280% |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 14.748 | 2468 | 2483 | 2492 | VV | | 5587663 | 290847004 | 14.84% | 2.583% |
| 42 | 14.902 | 2492 | 2510 | 2513 | VV | | 2383584 | 69719548 | 3.56% | 0.619% |
| 43 | 14.957 | 2513 | 2519 | 2530 | VV | 2 | 3344353 | 79203656 | 4.04% | 0.703% |
| 44 | 15.189 | 2548 | 2558 | 2574 | VV | | 454947 | 14800234 | 0.75% | 0.131% |
| 45 | 15.344 | 2574 | 2584 | 2591 | VV | | 2795419 | 53265124 | 2.72% | 0.473% |
| 46 | 15.419 | 2591 | 2597 | 2607 | VV | 2 | 523373 | 13610842 | 0.69% | 0.121% |
| 47 | 15.791 | 2607 | 2660 | 2673 | VV | 8 | 6769265 | 473217162 | 24.14% | 4.202% |
| 48 | 16.028 | 2692 | 2700 | 2708 | VV | 2 | 1389216 | 31889736 | 1.63% | 0.283% |
| 49 | 16.114 | 2708 | 2715 | 2720 | VV | | 586553 | 12434357 | 0.63% | 0.110% |
| 50 | 16.213 | 2720 | 2732 | 2739 | VV | 5 | 2372752 | 78196463 | 3.99% | 0.694% |
| 51 | 16.346 | 2739 | 2754 | 2759 | VV | 6 | 1648094 | 71426914 | 3.64% | 0.634% |
| 52 | 16.427 | 2759 | 2768 | 2778 | VV | | 4475437 | 129143652 | 6.59% | 1.147% |
| 53 | 16.552 | 2778 | 2789 | 2797 | PV | | 1169649 | 21451260 | 1.09% | 0.190% |
| 54 | 16.691 | 2797 | 2813 | 2824 | VV | | 1186665 | 34170051 | 1.74% | 0.303% |
| 55 | 16.823 | 2824 | 2835 | 2844 | VV | 5 | 443011 | 13598963 | 0.69% | 0.121% |
| 56 | 17.393 | 2919 | 2932 | 2948 | PB | 2 | 726344 | 15931056 | 0.81% | 0.141% |
| 57 | 17.806 | 2983 | 3001 | 3014 | PV | 3 | 1116567 | 32514049 | 1.66% | 0.289% |
| 58 | 17.919 | 3014 | 3021 | 3033 | VV | 5 | 746776 | 22485211 | 1.15% | 0.200% |
| 59 | 18.095 | 3033 | 3050 | 3059 | PV | 3 | 614398 | 21815229 | 1.11% | 0.194% |
| 60 | 18.213 | 3059 | 3070 | 3088 | VV | 9 | 584144 | 22527900 | 1.15% | 0.200% |
| 61 | 18.551 | 3122 | 3128 | 3152 | VV | 3 | 717188 | 23764556 | 1.21% | 0.211% |

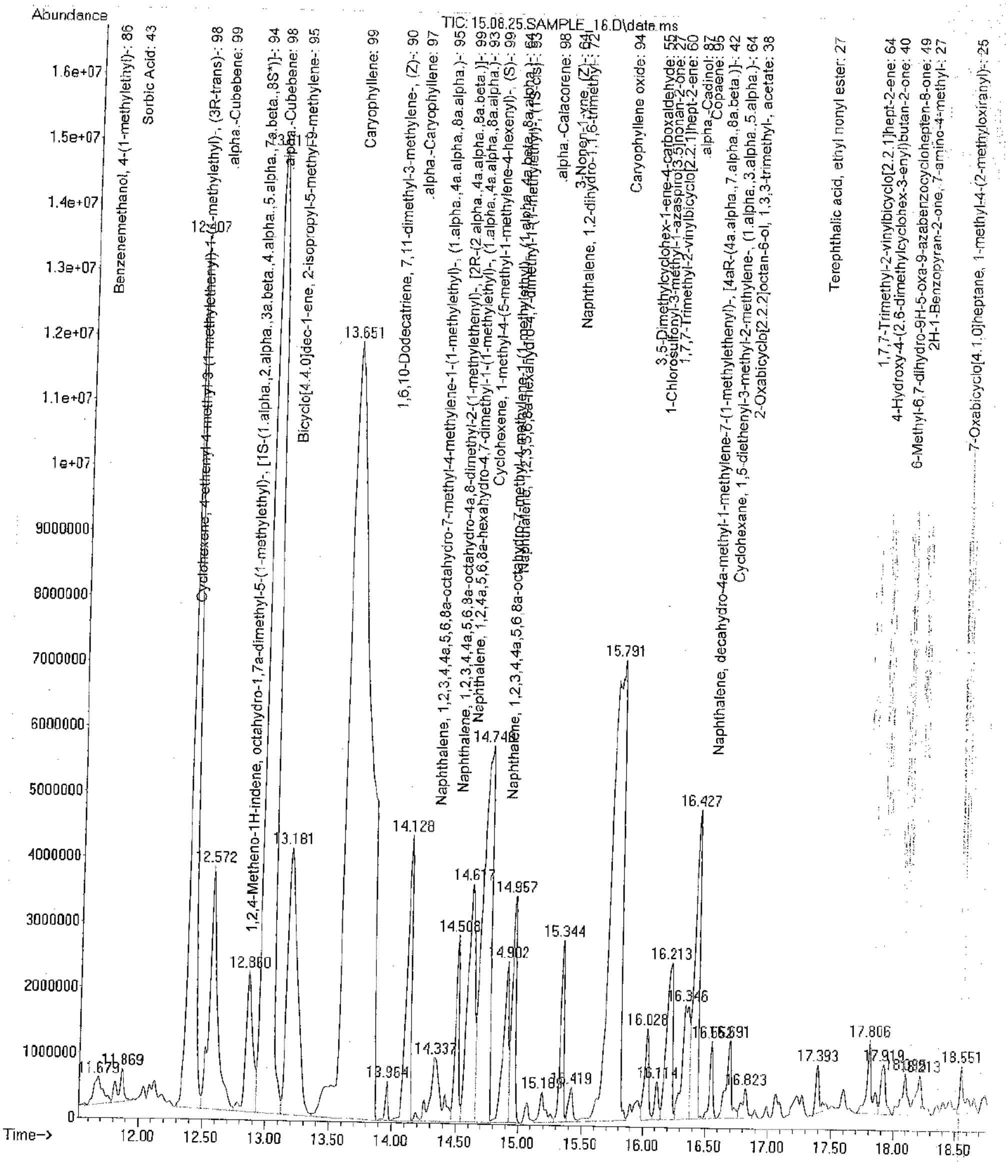
Sum of corrected areas: 11260812283

MART.M Fri Sep 11 11:23:56 2015

File : C:\msdchem\1\data\Commercial 2015.08.07\15.08.25.SAMPLE_16.D
Operator :
Acquired : 25 Aug 2015 13:27 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1



File :C:\msdchem\1\data\Commercial 2015.08.07\15.08.25.SAMPLE_16.D
Operator :
Acquired : 25 Aug 2015 13:27 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 1



**Sample No: 17**

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.25.SAMPLE_8.D
Acq On : 25 Aug 2015 11:04
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.08.25.SAMPLE_8.D\data.ms

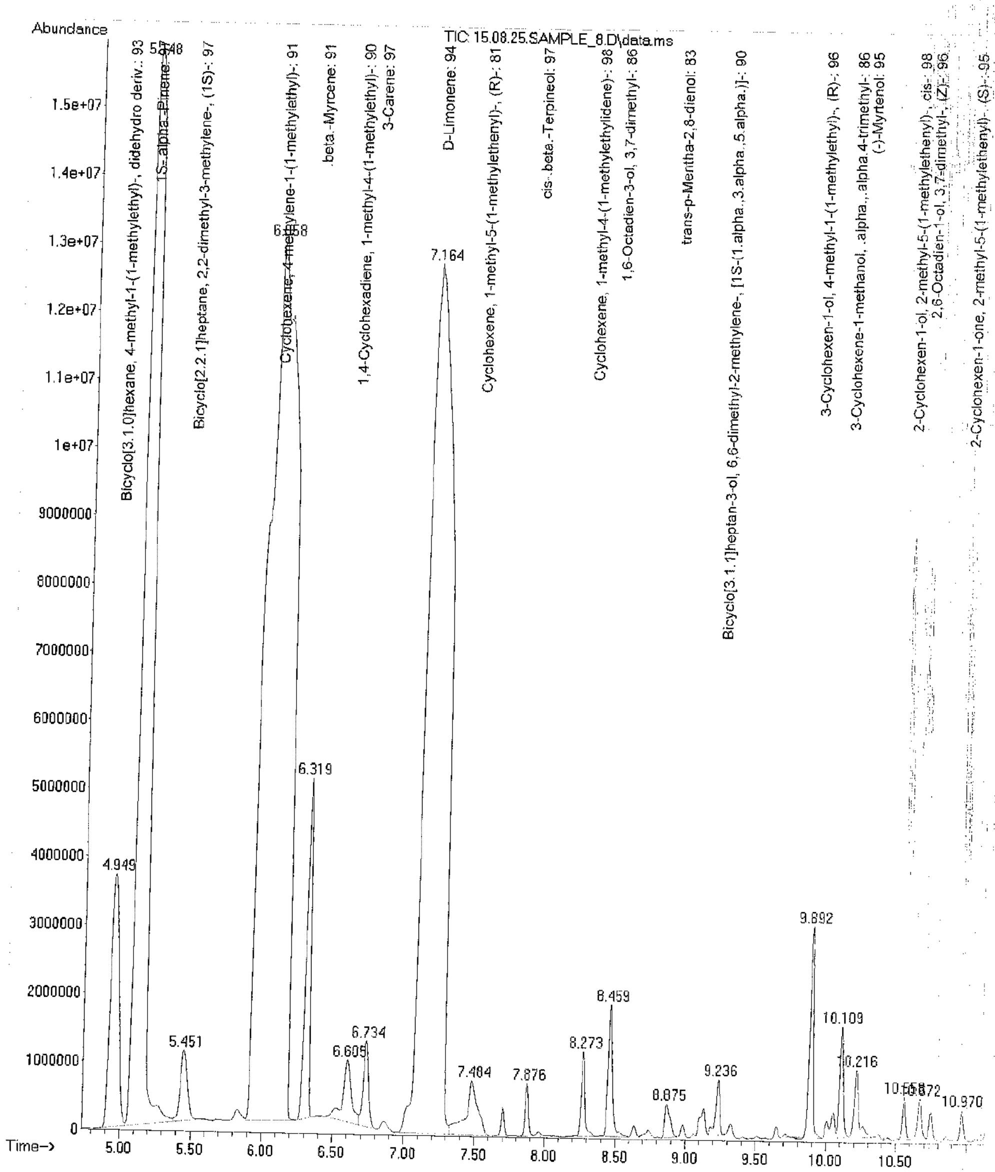
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.485 | 208 | 237 | 289 | BB | 12952997 | 714576402 | 43.85% | 7.607% |
| 2 | 4.949 | 800 | 824 | 839 | BV | 3669912 | 149765020 | 9.19% | 1.594% |
| 3 | 5.148 | 839 | 857 | 896 | VV 3 | 15811472 | 836533317 | 51.33% | 8.906% |
| 4 | 5.451 | 896 | 909 | 927 | VB | 1015610 | 34337079 | 2.11% | 0.366% |
| 5 | 6.058 | 983 | 1011 | 1045 | VV 3 | 12895591 | 1629690064 | 100.00% | 17.350% |
| 6 | 6.319 | 1045 | 1056 | 1062 | PB | 4677798 | 105222457 | 6.46% | 1.120% |
| 7 | 6.605 | 1081 | 1104 | 1117 | BV 3 | 897832 | 37744758 | 2.32% | 0.402% |
| 8 | 6.734 | 1117 | 1126 | 1140 | VV | 1245148 | 33589245 | 2.06% | 0.358% |
| 9 | 7.164 | 1165 | 1199 | 1226 | BV 3 | 12690457 | 1319151710 | 80.94% | 14.044% |
| 10 | 7.484 | 1226 | 1253 | 1279 | VV 2 | 779054 | 47618031 | 2.92% | 0.507% |
| 11 | 7.876 | 1310 | 1319 | 1328 | BV | 745995 | 12712222 | 0.78% | 0.135% |
| 12 | 8.273 | 1328 | 1387 | 1404 | VV | 1207478 | 24269924 | 1.49% | 0.258% |
| 13 | 8.459 | 1404 | 1418 | 1443 | VB 2 | 1886596 | 40170164 | 2.46% | 0.428% |
| 14 | 8.875 | 1481 | 1489 | 1502 | BV 5 | 470054 | 12051200 | 0.74% | 0.128% |
| 15 | 9.236 | 1538 | 1550 | 1558 | VV 2 | 823324 | 17556451 | 1.08% | 0.187% |
| 16 | 9.892 | 1631 | 1661 | 1674 | BV | 3034933 | 55733241 | 3.42% | 0.593% |
| 17 | 10.109 | 1693 | 1698 | 1708 | VV | 1594152 | 27586756 | 1.69% | 0.294% |
| 18 | 10.216 | 1708 | 1716 | 1735 | VB | 974005 | 23236421 | 1.43% | 0.247% |
| 19 | 10.558 | 1749 | 1774 | 1782 | BV | 595824 | 9203226 | 0.56% | 0.098% |
| 20 | 10.672 | 1782 | 1793 | 1801 | PV | 575204 | 10734888 | 0.66% | 0.114% |
| 21 | 10.970 | 1837 | 1843 | 1853 | BV | 428134 | 6970348 | 0.43% | 0.074% |
| 22 | 12.396 | 2066 | 2085 | 2099 | BV | 13061272 | 332871882 | 20.43% | 3.544% |
| 23 | 12.560 | 2099 | 2113 | 2142 | PV 4 | 2681001 | 71207589 | 4.37% | 0.758% |
| 24 | 12.850 | 2142 | 2162 | 2172 | VV | 1776092 | 47755347 | 2.93% | 0.508% |
| 25 | 12.997 | 2172 | 2187 | 2206 | VV 2 | 15725656 | 600076486 | 36.82% | 6.388% |
| 26 | 13.165 | 2206 | 2215 | 2246 | VB 6 | 5299795 | 198628278 | 12.19% | 2.115% |
| 27 | 13.636 | 2280 | 2295 | 2331 | VV 5 | 14434826 | 1270990754 | 77.99% | 13.531% |
| 28 | 13.935 | 2331 | 2346 | 2352 | PV | 1059234 | 17098402 | 1.05% | 0.182% |
| 29 | 14.083 | 2352 | 2371 | 2378 | VV | 5041466 | 117512436 | 7.21% | 1.251% |
| 30 | 14.311 | 2378 | 2410 | 2419 | VV 8 | 1008308 | 48120605 | 2.95% | 0.512% |
| 31 | 14.397 | 2419 | 2424 | 2432 | VV | 1110388 | 23133224 | 1.42% | 0.246% |
| 32 | 14.482 | 2432 | 2438 | 2445 | VV | 3968254 | 71957274 | 4.42% | 0.766% |
| 33 | 14.605 | 2445 | 2459 | 2464 | VV 8 | 4088019 | 185862436 | 11.40% | 1.979% |
| 34 | 14.703 | 2464 | 2476 | 2484 | VV | 8091428 | 315400428 | 19.35% | 3.358% |
| 35 | 14.856 | 2484 | 2502 | 2506 | VV | 4368089 | 111145309 | 6.82% | 1.183% |
| 36 | 14.915 | 2506 | 2512 | 2525 | VV 2 | 4869079 | 103578244 | 6.36% | 1.103% |
| 37 | 15.048 | 2525 | 2534 | 2542 | PV 2 | 638190 | 14649828 | 0.90% | 0.156% |
| 38 | 15.305 | 2566 | 2578 | 2585 | PV 4 | 1001316 | 23113145 | 1.42% | 0.246% |
| 39 | 15.708 | 2602 | 2646 | 2667 | BV | 6853847 | 221120120 | 13.57% | 2.354% |
| 40 | 15.912 | 2667 | 2681 | 2687 | VV 3 | 469741 | 17346179 | 1.06% | 0.185% |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 15.992 | 2687 | 2694 | 2704 | VV 4 | 880641 | 24332019 | 1.49% | 0.259% |
| 42 | 16.092 | 2704 | 2711 | 2716 | VV | 1298790 | 22512940 | 1.38% | 0.240% |
| 43 | 16.179 | 2716 | 2726 | 2734 | VV 3 | 4228035 | 96836753 | 5.94% | 1.031% |
| 44 | 16.390 | 2734 | 2762 | 2772 | VV | 8594298 | 269698625 | 16.55% | 2.871% |
| 45 | 16.519 | 2772 | 2784 | 2792 | PV 4 | 389304 | 10068343 | 0.62% | 0.107% |
| 46 | 17.372 | 2918 | 2928 | 2939 | PV 2 | 419472 | 7475976 | 0.46% | 0.080% |
| 47 | 17.787 | 2974 | 2998 | 3004 | BV | 469254 | 7385843 | 0.45% | 0.079% |
| 48 | 18.540 | 3082 | 3126 | 3150 | BB 2 | 422455 | 14751677 | 0.91% | 0.157% |

Sum of corrected areas: 9393083064

SMART.M Fri Sep 11 10:47:06 2015

```
File          :C:\msdchem\1\data\Commercial 2015.08.07\15.08.25.SAMPLE_8.D
Operator      :
Acquired      : 25 Aug 2015  11:04      using AcqMethod Plant Extracts.M
Instrument :    UOSJP GCMSD
Sample Name:
Misc Info  :
Vial Number: 1
```



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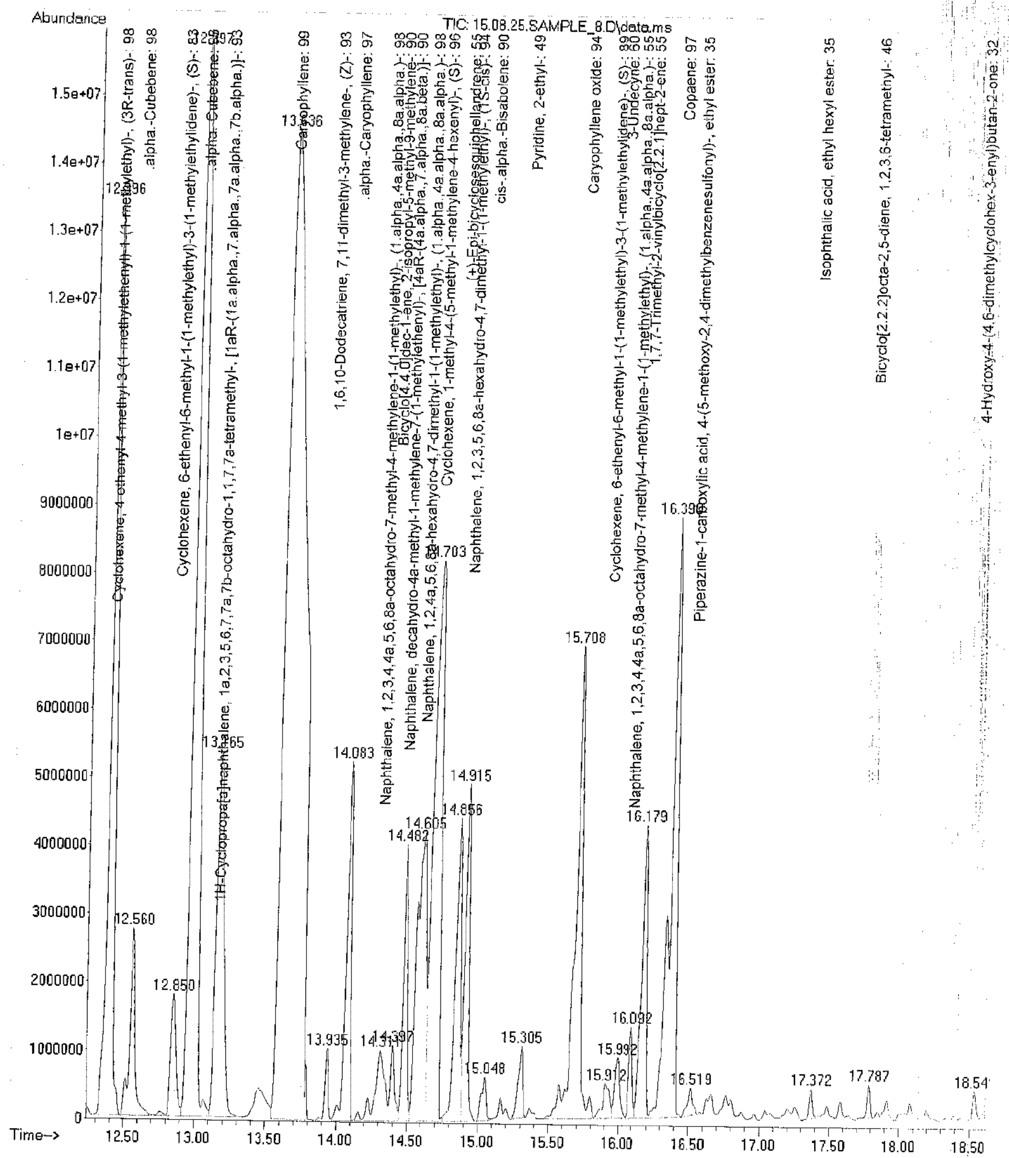
File         :C:\msdchem\1\data\Commercial 2015.08.07\15.08.25.SAMPLE_8.D
Operator     :
Acquired     : 25 Aug 2015  11:04      using AcqMethod Plant Extracts.M
Instrument   :   UOSJP GCMSD
Sample Name:
Misc Info    :
Vial Number: 1
```



## Sample No : 18

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.08.07.SAMPLE_10.D
Acq On : 7 Aug 2015 13:24
Operator :
Sample :
Misc :
ALS Vial : 2 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.08.07.SAMPLE_10.D\data.ms

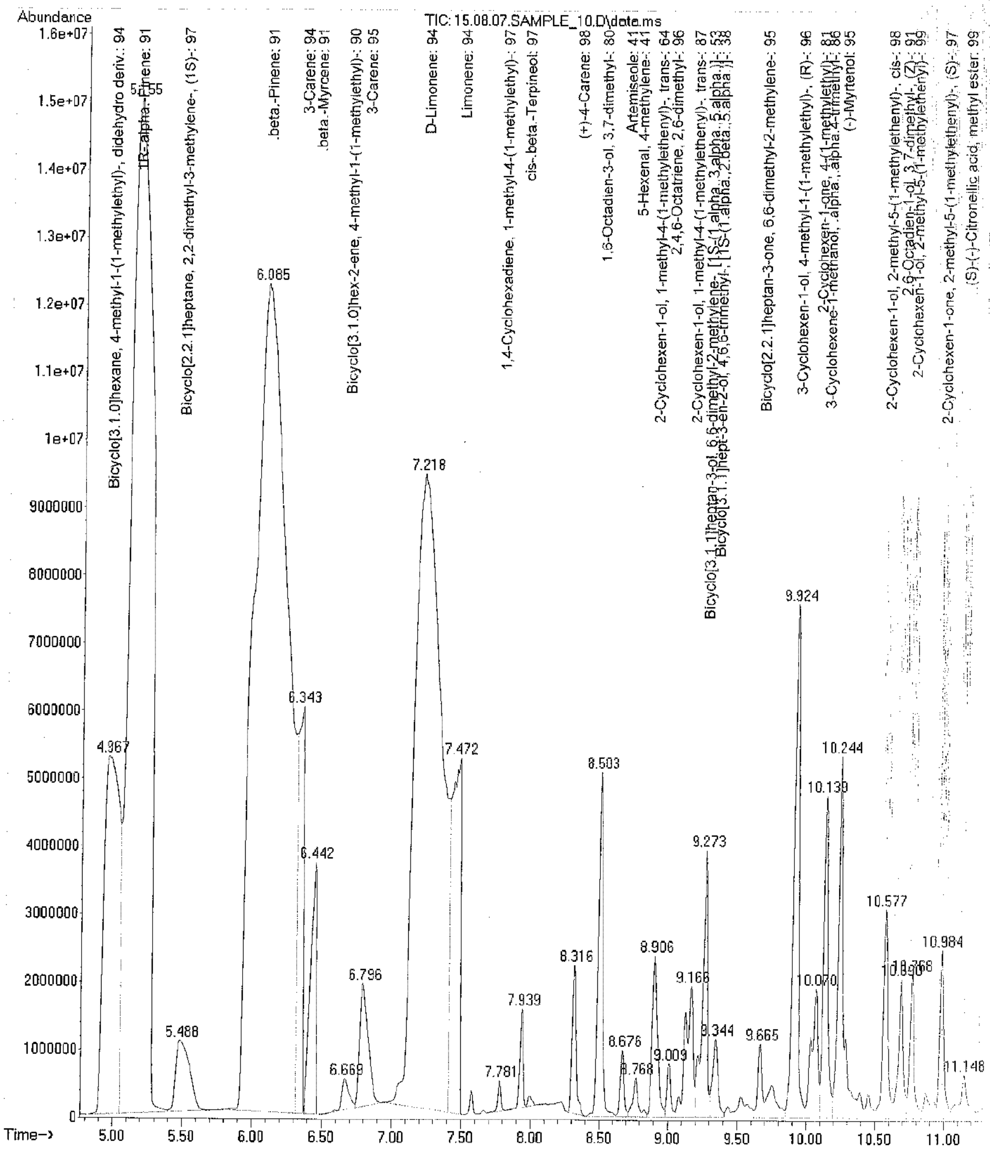
| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.478 | 205 | 231 | 261 | BV | 12273964 | 458763387 | 23.02% | 3.178% |
| 2 | 4.967 | 796 | 822 | 837 | BV 2 | 5260361 | 400311743 | 20.09% | 2.773% |
| 3 | 5.155 | 837 | 854 | 896 | VV 2 | 14948334 | 1556075360 | 78.09% | 10.779% |
| 4 | 5.488 | 896 | 910 | 945 | VB 3 | 1030953 | 72169729 | 3.62% | 0.500% |
| 5 | 6.085 | 964 | 1012 | 1050 | BV 2 | 12198358 | 1992657117 | 100.00% | 13.803% |
| 6 | 6.343 | 1050 | 1055 | 1062 | VV | 5813790 | 176470703 | 8.86% | 1.222% |
| 7 | 6.442 | 1062 | 1072 | 1080 | VV | 3509396 | 103690173 | 5.20% | 0.718% |
| 8 | 6.669 | 1080 | 1111 | 1123 | PV | 451031 | 15001215 | 0.75% | 0.104% |
| 9 | 6.796 | 1123 | 1132 | 1155 | VB | 1776600 | 75689858 | 3.80% | 0.524% |
| 10 | 7.218 | 1162 | 1204 | 1236 | BV 5 | 9301447 | 1232149457 | 61.83% | 8.535% |
| 11 | 7.472 | 1236 | 1247 | 1254 | VV | 5108701 | 246692269 | 12.38% | 1.709% |
| 12 | 7.781 | 1284 | 1299 | 1306 | PV | 452982 | 7344328 | 0.37% | 0.051% |
| 13 | 7.939 | 1306 | 1326 | 1345 | PB 2 | 1447807 | 27190565 | 1.36% | 0.188% |
| 14 | 8.316 | 1382 | 1390 | 1404 | PV | 2105024 | 41930317 | 2.10% | 0.290% |
| 15 | 8.503 | 1404 | 1421 | 1442 | PV | 4831494 | 110733559 | 5.56% | 0.767% |
| 16 | 8.676 | 1442 | 1451 | 1458 | VV | 948156 | 16834099 | 0.84% | 0.117% |
| 17 | 8.768 | 1458 | 1466 | 1480 | VV 4 | 548987 | 15899263 | 0.80% | 0.110% |
| 18 | 8.906 | 1480 | 1489 | 1502 | VV 3 | 2285892 | 60073035 | 3.01% | 0.416% |
| 19 | 9.009 | 1502 | 1507 | 1516 | VV | 775186 | 15652746 | 0.79% | 0.108% |
| 20 | 9.166 | 1516 | 1534 | 1539 | VV 6 | 1931385 | 71558077 | 3.59% | 0.496% |
| 21 | 9.273 | 1539 | 1552 | 1558 | VV 2 | 3977126 | 104630296 | 5.25% | 0.725% |
| 22 | 9.344 | 1558 | 1564 | 1574 | VV 5 | 1140818 | 29269026 | 1.47% | 0.203% |
| 23 | 9.665 | 1610 | 1618 | 1649 | VV 7 | 1033464 | 45693149 | 2.29% | 0.317% |
| 24 | 9.924 | 1649 | 1662 | 1673 | VV 2 | 7546000 | 198606599 | 9.97% | 1.376% |
| 25 | 10.070 | 1673 | 1687 | 1691 | VV 4 | 1880409 | 62119084 | 3.12% | 0.430% |
| 26 | 10.139 | 1691 | 1698 | 1707 | VV | 4763020 | 105997425 | 5.32% | 0.734% |
| 27 | 10.244 | 1707 | 1716 | 1747 | VV 2 | 4955507 | 149683550 | 7.51% | 1.037% |
| 28 | 10.577 | 1760 | 1773 | 1782 | VV | 2979307 | 67833100 | 3.40% | 0.470% |
| 29 | 10.690 | 1782 | 1792 | 1799 | VV | 2036598 | 51857327 | 2.60% | 0.359% |
| 30 | 10.768 | 1799 | 1805 | 1816 | VV | 2089993 | 46062855 | 2.31% | 0.319% |
| 31 | 10.984 | 1835 | 1842 | 1853 | VV | 2333012 | 49929916 | 2.51% | 0.346% |
| 32 | 11.148 | 1853 | 1869 | 1884 | VV 3 | 617099 | 25898134 | 1.30% | 0.179% |
| 33 | 11.669 | 1932 | 1958 | 1975 | VV 8 | 725946 | 63028288 | 3.16% | 0.437% |
| 34 | 11.812 | 1975 | 1982 | 2009 | VV 2 | 610232 | 40213327 | 2.02% | 0.279% |
| 35 | 12.420 | 2064 | 2085 | 2105 | VV | 15060210 | 823868199 | 41.35% | 5.707% |
| 36 | 12.580 | 2105 | 2112 | 2150 | VV | 3922667 | 227159316 | 11.40% | 1.574% |
| 37 | 12.867 | 2150 | 2161 | 2170 | VV | 2481573 | 105046569 | 5.27% | 0.728% |
| 38 | 13.011 | 2170 | 2185 | 2211 | VV 4 | 13067049 | 1144318896 | 57.43% | 7.927% |
| 39 | 13.197 | 2211 | 2216 | 2258 | VV 4 | 2898213 | 278280250 | 13.97% | 1.928% |
| 40 | 13.663 | 2258 | 2295 | 2319 | VV 6 | 9013088 | 921874081 | 46.26% | 6.386% |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 13.954 | 2319 | 2345 | 2353 | VV 5 | 7115978 | 722816830 | 36.27% | 5.007% |
| 42 | 14.037 | 2353 | 2359 | 2365 | VV | 1717479 | 32229839 | 1.62% | 0.223% |
| 43 | 14.203 | 2365 | 2387 | 2400 | VV 2 | 5237864 | 205232189 | 10.30% | 1.422% |
| 44 | 14.375 | 2400 | 2416 | 2425 | VV 2 | 1385672 | 68775451 | 3.45% | 0.476% |
| 45 | 14.460 | 2425 | 2430 | 2437 | VV | 1192379 | 26599250 | 1.33% | 0.184% |
| 46 | 14.553 | 2437 | 2446 | 2452 | VV | 3999114 | 93514141 | 4.69% | 0.648% |
| 47 | 14.668 | 2452 | 2466 | 2472 | VV 4 | 4274294 | 208775241 | 10.48% | 1.446% |
| 48 | 14.779 | 2472 | 2484 | 2500 | VV 7 | 4271532 | 338763218 | 17.00% | 2.347% |
| 49 | 15.024 | 2500 | 2526 | 2534 | VV 8 | 2540953 | 164752968 | 8.27% | 1.141% |
| 50 | 15.108 | 2534 | 2540 | 2552 | PV | 486235 | 7492709 | 0.38% | 0.052% |
| 51 | 15.373 | 2573 | 2585 | 2605 | VV | 1465916 | 39908805 | 2.00% | 0.276% |
| 52 | 15.802 | 2605 | 2658 | 2672 | VV 5 | 5772207 | 361455922 | 18.14% | 2.504% |
| 53 | 15.958 | 2672 | 2684 | 2690 | VV 7 | 484020 | 19433791 | 0.98% | 0.135% |
| 54 | 16.040 | 2690 | 2698 | 2706 | VV 3 | 1236777 | 34207669 | 1.72% | 0.237% |
| 55 | 16.132 | 2706 | 2714 | 2718 | VV 2 | 1068844 | 24836820 | 1.25% | 0.172% |
| 56 | 16.228 | 2718 | 2730 | 2740 | VV 5 | 2692672 | 108956220 | 5.47% | 0.755% |
| 57 | 16.460 | 2740 | 2769 | 2778 | VV 2 | 5027015 | 258208370 | 12.96% | 1.789% |
| 58 | 16.568 | 2778 | 2788 | 2795 | VV 3 | 553188 | 12685206 | 0.64% | 0.088% |
| 59 | 16.692 | 2795 | 2808 | 2815 | VV 4 | 468356 | 18418117 | 0.92% | 0.128% |
| 60 | 16.827 | 2815 | 2831 | 2839 | VV 5 | 537999 | 22660611 | 1.14% | 0.157% |
| 61 | 17.226 | 2883 | 2899 | 2903 | VV 5 | 474843 | 17518710 | 0.88% | 0.121% |
| 62 | 17.280 | 2903 | 2908 | 2916 | VV 2 | 606583 | 16182851 | 0.81% | 0.112% |
| 63 | 17.399 | 2916 | 2928 | 2943 | VV 2 | 1305417 | 38735265 | 1.94% | 0.268% |
| 64 | 17.603 | 2956 | 2963 | 2979 | VV | 575200 | 23691226 | 1.19% | 0.164% |
| 65 | 17.807 | 2979 | 2997 | 3010 | VV 4 | 1125401 | 49388957 | 2.48% | 0.342% |
| 66 | 17.927 | 3010 | 3018 | 3027 | VV 3 | 1208388 | 31598003 | 1.59% | 0.219% |
| 67 | 18.096 | 3027 | 3046 | 3056 | VV 6 | 907561 | 44148462 | 2.22% | 0.306% |
| 68 | 18.215 | 3056 | 3066 | 3083 | VV | 730074 | 28218366 | 1.42% | 0.195% |
| 69 | 18.554 | 3113 | 3124 | 3147 | VV 2 | 1892566 | 62841670 | 3.15% | 0.435% |
| 70 | 19.220 | 3229 | 3237 | 3244 | VV 2 | 504137 | 14351329 | 0.72% | 0.099% |
| 71 | 19.306 | 3244 | 3251 | 3263 | VV 2 | 1011102 | 21034575 | 1.06% | 0.146% |
| 72 | 19.502 | 3263 | 3285 | 3291 | PV | 427405 | 9247917 | 0.46% | 0.064% |
| 73 | 20.093 | 3358 | 3385 | 3400 | BV 2 | 1181052 | 21816473 | 1.09% | 0.151% |
| 74 | 20.670 | 3453 | 3482 | 3499 | VV | 723758 | 19782651 | 0.99% | 0.137% |
| 75 | 20.962 | 3499 | 3532 | 3547 | VV | 665149 | 17698156 | 0.89% | 0.123% |
| 76 | 22.462 | 3778 | 3786 | 3799 | PV 4 | 465185 | 11838070 | 0.59% | 0.082% |

Sum of corrected areas: 14436072433

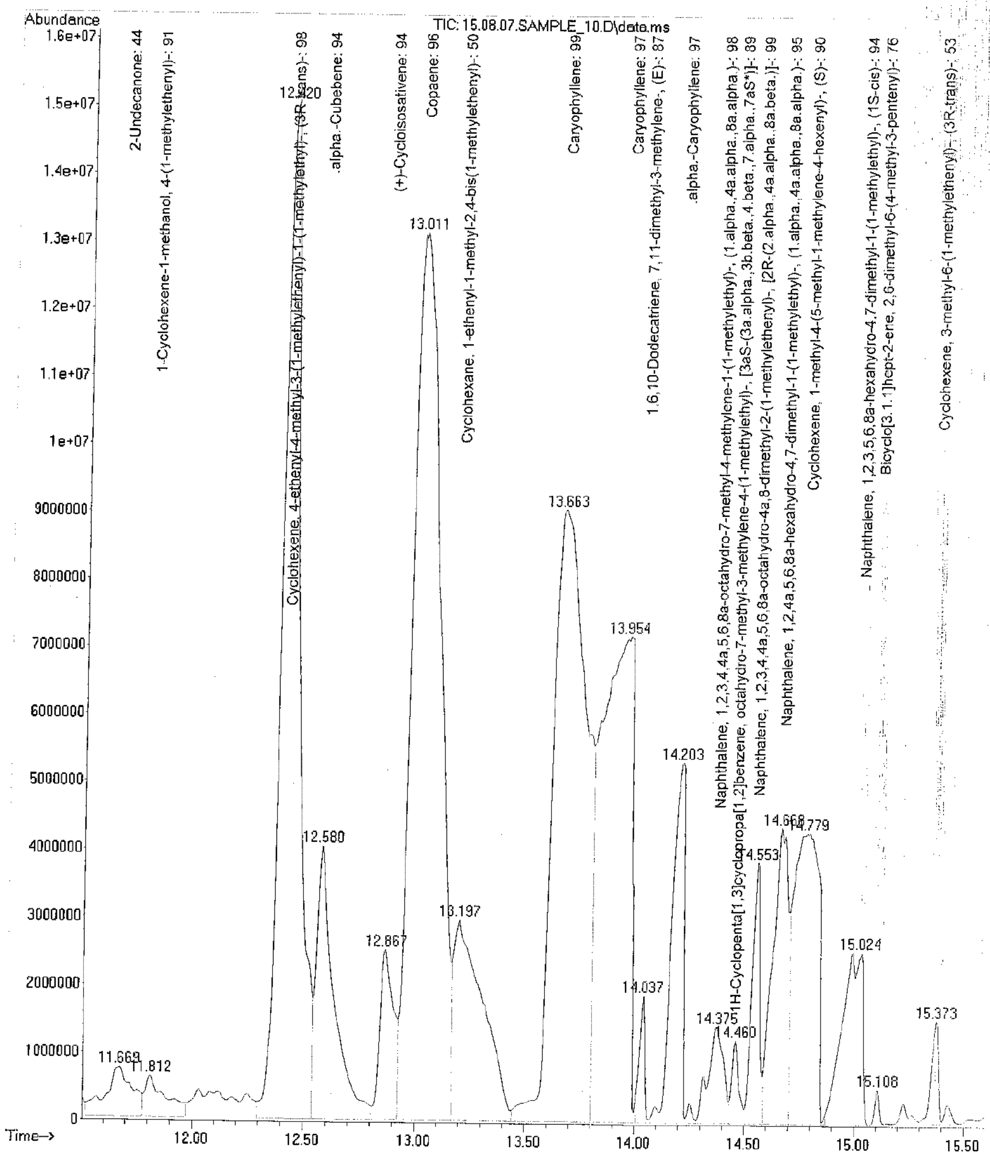
SMART.M Fri Sep 11 10:51:47 2015

```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_10.D
Operator    :
Acquired    :  7 Aug 2015  13:24      using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :                                              ERR
Vial Number:  2
```



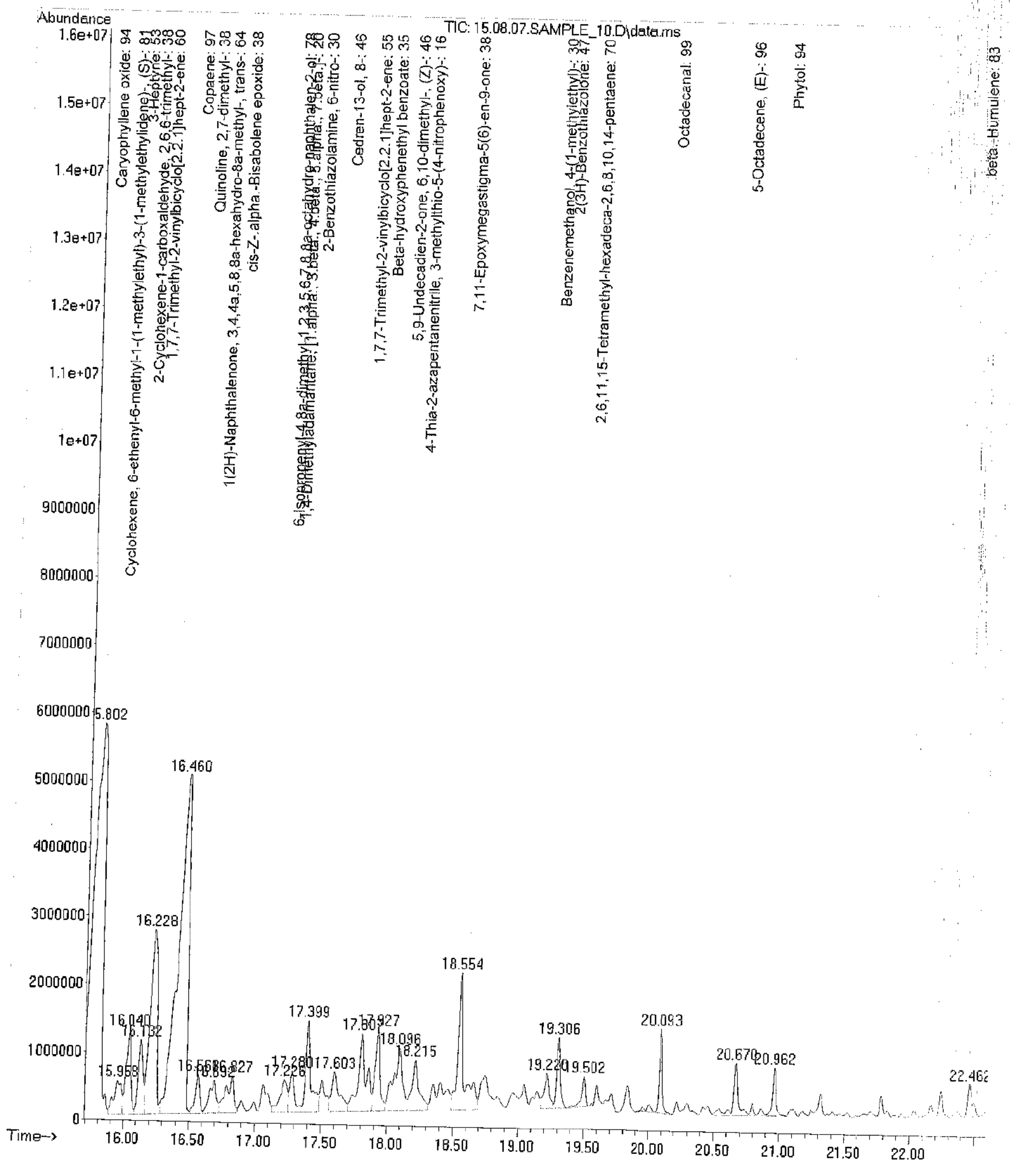
```
File        :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_10.D
Operator    :
Acquired    :  7 Aug 2015  13:24      using AcqMethod Plant Extracts.M
Instrument  :   UOSJP GCMSD
Sample Name:
Misc Info   :
Vial Number: 2
```

ERR



File :C:\msdchem\1\data\Commercial 2015.08.07\15.08.07.SAMPLE_10.D
Operator :
Acquired : 7 Aug 2015 13:24 using AcqMethod Plant Extracts.M
Instrument : UOSJP GCMSD
Sample Name:
Misc Info :
Vial Number: 2

ERR



**Sample No : 19**

Area Percent Report

Data Path : C:\msdchem\1\data\Commercial 2015.08.07\
Data File : 15.09.07.SAMPLE_F.D
Acq On : 7 Sep 2015 14:33
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\SMART.M
Title : autoint1.e

Signal : TIC: 15.09.07.SAMPLE_F.D\data.ms

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.500 | 230 | 239 | 278 | BB | 6951457 | 347271456 | 47.22% | 9.577% |
| 2 | 4.970 | 796 | 827 | 843 | BV | 1438494 | 67687662 | 9.20% | 1.867% |
| 3 | 5.165 | 843 | 860 | 876 | VB 3 | 6462380 | 372454496 | 50.64% | 10.272% |
| 4 | 6.087 | 968 | 1016 | 1045 | BV 2 | 5636920 | 735426029 | 100.00% | 20.282% |
| 5 | 6.350 | 1045 | 1061 | 1070 | PB | 2046302 | 43679370 | 5.94% | 1.205% |
| 6 | 7.187 | 1127 | 1203 | 1234 | BB 4 | 5240131 | 580469344 | 78.93% | 16.009% |
| 7 | 8.285 | 1365 | 1389 | 1404 | BV | 504251 | 8980229 | 1.22% | 0.248% |
| 8 | 8.470 | 1404 | 1420 | 1444 | VB | 722897 | 13528278 | 1.84% | 0.373% |
| 9 | 9.901 | 1600 | 1662 | 1675 | BV | 988405 | 18981065 | 2.58% | 0.523% |
| 10 | 10.116 | 1675 | 1699 | 1708 | PV | 501143 | 10043045 | 1.37% | 0.277% |
| 11 | 12.404 | 2053 | 2086 | 2099 | BV | 4582408 | 115058662 | 15.65% | 3.173% |
| 12 | 12.562 | 2099 | 2113 | 2142 | VB 2 | 697126 | 20396366 | 2.77% | 0.563% |
| 13 | 12.853 | 2143 | 2162 | 2173 | BV 4 | 441911 | 12768380 | 1.74% | 0.352% |
| 14 | 13.007 | 2173 | 2189 | 2206 | VV | 5560677 | 210924519 | 28.68% | 5.817% |
| 15 | 13.170 | 2206 | 2216 | 2246 | VB 6 | 1479353 | 61331133 | 8.34% | 1.691% |
| 16 | 13.659 | 2246 | 2299 | 2333 | BV 6 | 5447363 | 559198979 | 76.04% | 15.422% |
| 17 | 14.096 | 2353 | 2373 | 2389 | VV | 1544671 | 35345699 | 4.81% | 0.975% |
| 18 | 14.489 | 2433 | 2440 | 2446 | VV | 955233 | 17243872 | 2.34% | 0.476% |
| 19 | 14.615 | 2446 | 2461 | 2466 | VV 5 | 1224075 | 51396910 | 6.99% | 1.417% |
| 20 | 14.717 | 2466 | 2478 | 2485 | VV | 3128166 | 125584499 | 17.08% | 3.464% |
| 21 | 14.868 | 2485 | 2504 | 2508 | VV | 1388347 | 37532912 | 5.10% | 1.035% |
| 22 | 14.926 | 2508 | 2514 | 2526 | VV 2 | 1811349 | 39158185 | 5.32% | 1.080% |
| 23 | 15.711 | 2598 | 2647 | 2667 | BV | 1534058 | 45443076 | 6.18% | 1.253% |
| 24 | 16.182 | 2717 | 2726 | 2733 | VV | 917853 | 21280197 | 2.89% | 0.587% |
| 25 | 16.397 | 2733 | 2763 | 2773 | VV | 2527706 | 74734741 | 10.16% | 2.061% |

Sum of corrected areas: 3625919104

SMART.M Fri Sep 11 11:43:18 2015

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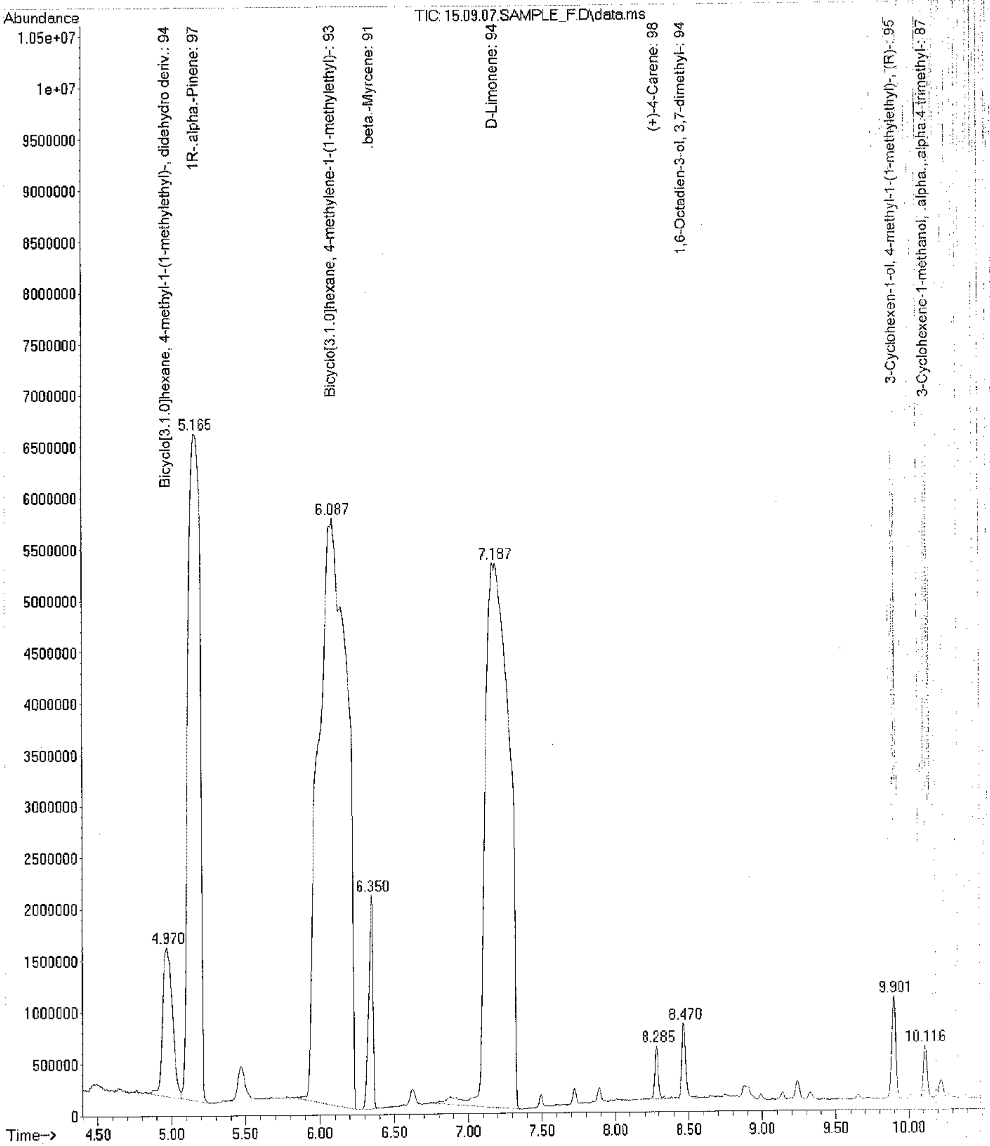

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Misc Info   :                                              ERR
Vial Number: 1
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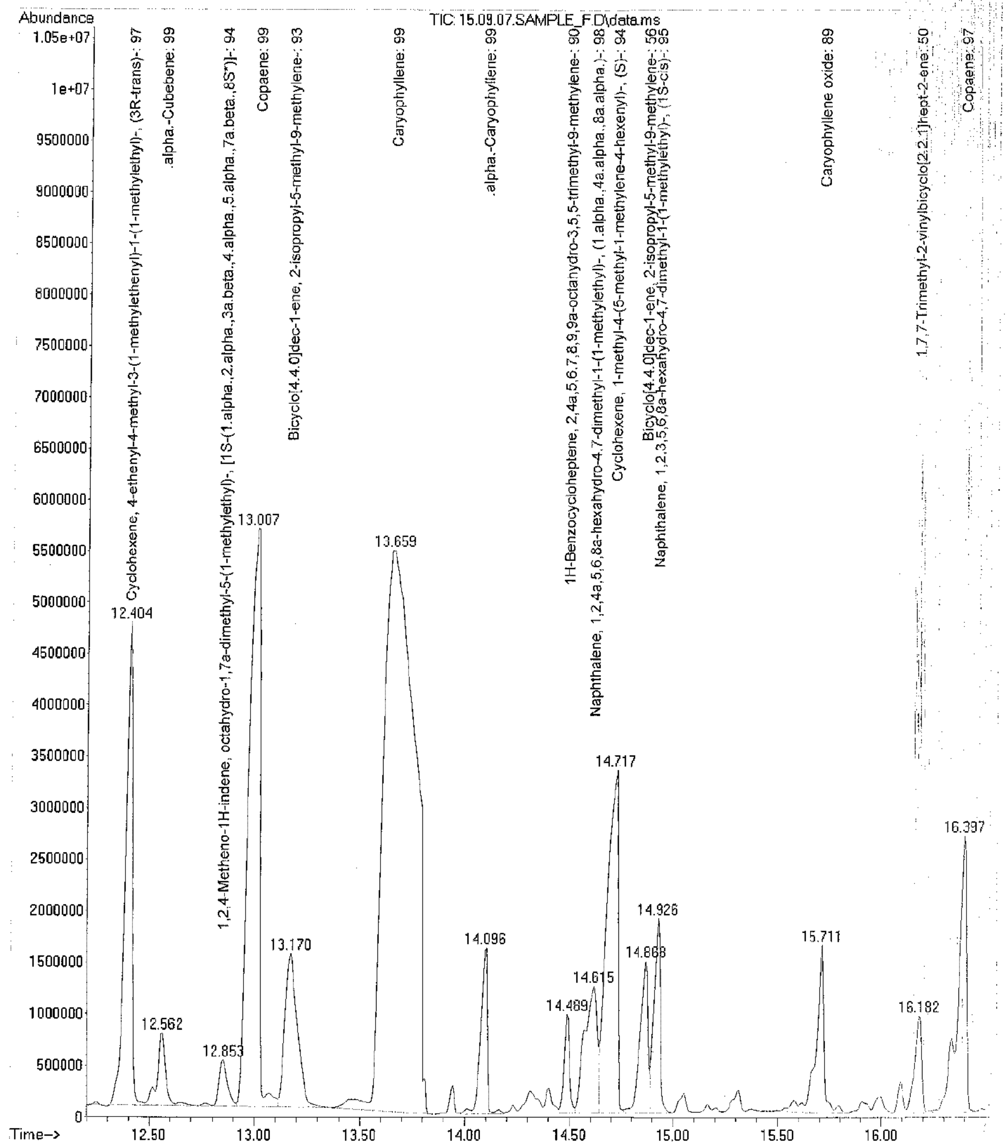

## Sample No :20

Area Percent Report

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Sample :
Misc :
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Integrator: ChemStation

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Title : autoint1.e

Signal : TIC: 15.09.03.SAMPLE_A.D\data.ms

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.228 | 162 | 193 | 213 | BB 2 | 7153110 | 264252008 | 50.05% | 7.212% |
| 2 | 4.935 | 805 | 821 | 843 | BB | 5530559 | 184712737 | 34.98% | 5.041% |
| 3 | 5.968 | 955 | 996 | 1020 | BV 4 | 6642487 | 495201504 | 93.78% | 13.514% |
| 4 | 6.146 | 1020 | 1026 | 1052 | VB | 453750 | 9039382 | 1.71% | 0.247% |
| 5 | 7.056 | 1163 | 1180 | 1207 | VB | 5744841 | 258787786 | 49.01% | 7.063% |
| 6 | 8.403 | 1389 | 1409 | 1431 | BV | 1211740 | 27590079 | 5.23% | 0.753% |
| 7 | 8.843 | 1472 | 1483 | 1507 | PV 7 | 695558 | 25579089 | 4.84% | 0.698% |
| 8 | 9.202 | 1533 | 1544 | 1553 | VV 5 | 1280500 | 36935608 | 7.00% | 1.008% |
| 9 | 9.914 | 1642 | 1665 | 1673 | BV 2 | 4668306 | 169377312 | 32.08% | 4.622% |
| 10 | 10.029 | 1673 | 1684 | 1690 | VV 4 | 429913 | 15732414 | 2.98% | 0.429% |
| 11 | 10.127 | 1690 | 1701 | 1708 | VV | 2576568 | 72469253 | 13.72% | 1.978% |
| 12 | 10.220 | 1708 | 1716 | 1734 | VV 2 | 1509101 | 32980608 | 6.25% | 0.900% |
| 13 | 10.550 | 1759 | 1772 | 1781 | BV 2 | 622737 | 11153929 | 2.11% | 0.304% |
| 14 | 10.957 | 1819 | 1841 | 1852 | BV | 534300 | 10085401 | 1.91% | 0.275% |
| 15 | 12.403 | 2064 | 2086 | 2099 | BV | 5456602 | 171201658 | 32.42% | 4.672% |
| 16 | 12.559 | 2099 | 2113 | 2126 | VV 2 | 1259973 | 40196182 | 7.61% | 1.097% |
| 17 | 12.846 | 2141 | 2161 | 2171 | VV 3 | 721207 | 23901103 | 4.53% | 0.652% |
| 18 | 13.012 | 2171 | 2189 | 2206 | VV 2 | 5541972 | 255322901 | 48.35% | 6.968% |
| 19 | 13.173 | 2206 | 2217 | 2246 | VB 4 | 1514028 | 66476446 | 12.59% | 1.814% |
| 20 | 13.661 | 2279 | 2299 | 2331 | VV 5 | 5158028 | 528023608 | 100.00% | 14.410% |
| 21 | 14.100 | 2361 | 2374 | 2381 | BV | 1778753 | 40912562 | 7.75% | 1.117% |
| 22 | 14.327 | 2381 | 2412 | 2432 | PV 5 | 547527 | 27903543 | 5.28% | 0.762% |
| 23 | 14.500 | 2432 | 2441 | 2447 | VV | 1242574 | 26416372 | 5.00% | 0.721% |
| 24 | 14.616 | 2447 | 2461 | 2466 | VV 3 | 1672426 | 58936664 | 11.16% | 1.608% |
| 25 | 14.738 | 2466 | 2482 | 2494 | VV 4 | 3136859 | 170054429 | 32.21% | 4.641% |
| 26 | 14.946 | 2494 | 2517 | 2530 | VV 2 | 1572196 | 54447800 | 10.31% | 1.486% |
| 27 | 15.190 | 2530 | 2558 | 2572 | PV | 401499 | 13802168 | 2.61% | 0.377% |
| 28 | 15.353 | 2572 | 2586 | 2593 | PV | 1812502 | 42800977 | 8.11% | 1.168% |
| 29 | 15.798 | 2625 | 2661 | 2699 | BV 9 | 3459696 | 346589164 | 65.64% | 9.459% |
| 30 | 16.077 | 2699 | 2709 | 2724 | VV 2 | 639990 | 15763681 | 2.99% | 0.430% |
| 31 | 16.232 | 2724 | 2735 | 2745 | PV 2 | 833220 | 24050405 | 4.55% | 0.656% |
| 32 | 16.472 | 2745 | 2775 | 2784 | VV 2 | 1565449 | 93284144 | 17.67% | 2.546% |
| 33 | 16.601 | 2784 | 2797 | 2804 | VV 2 | 747424 | 15323631 | 2.90% | 0.418% |
| 34 | 16.746 | 2804 | 2822 | 2834 | PV 4 | 685430 | 22498119 | 4.26% | 0.614% |
| 35 | 17.941 | 3016 | 3024 | 3037 | VV | 427373 | 12440316 | 2.36% | 0.340% |

Sum of corrected areas: 3664242982

MART.M Fri Sep 11 11:28:57 2015

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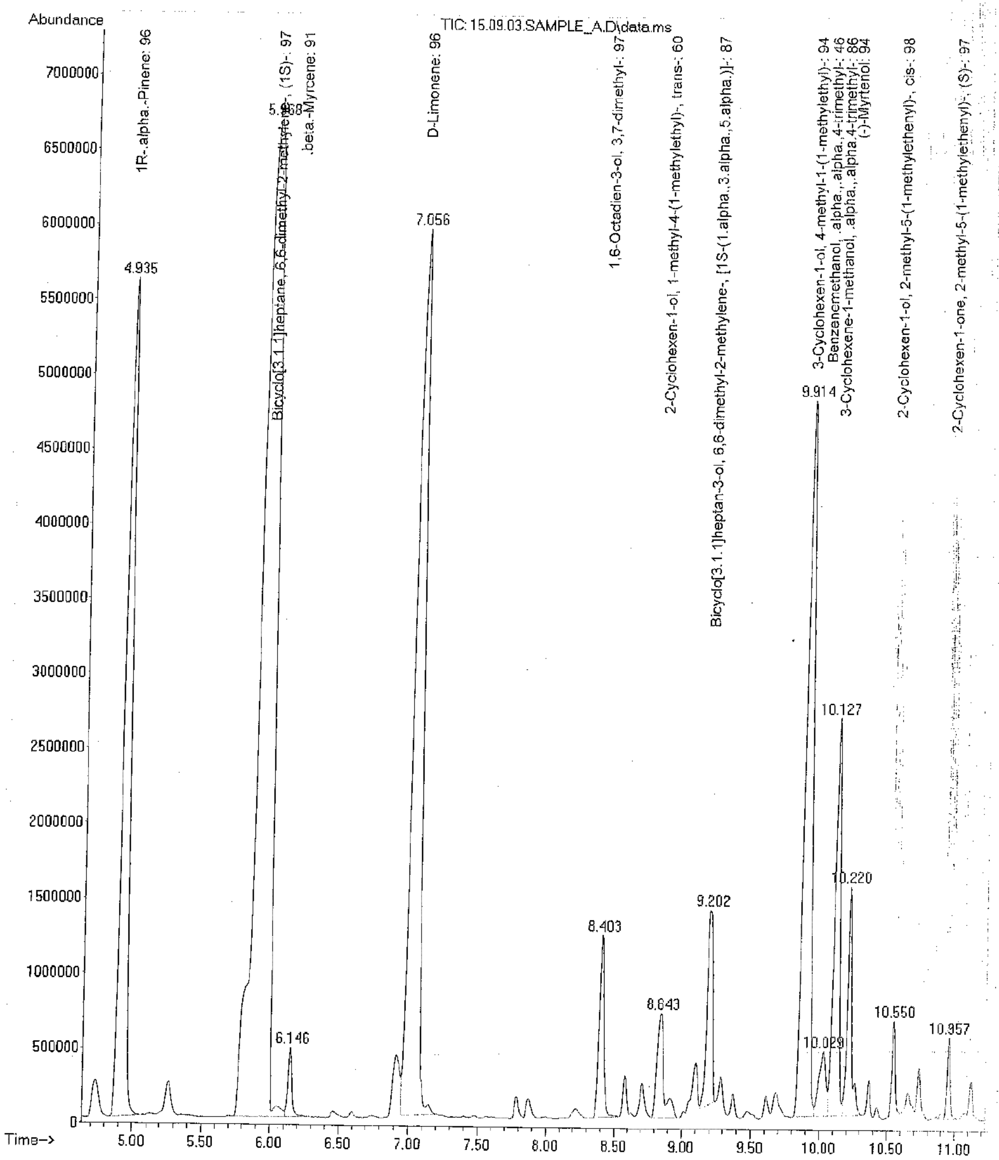

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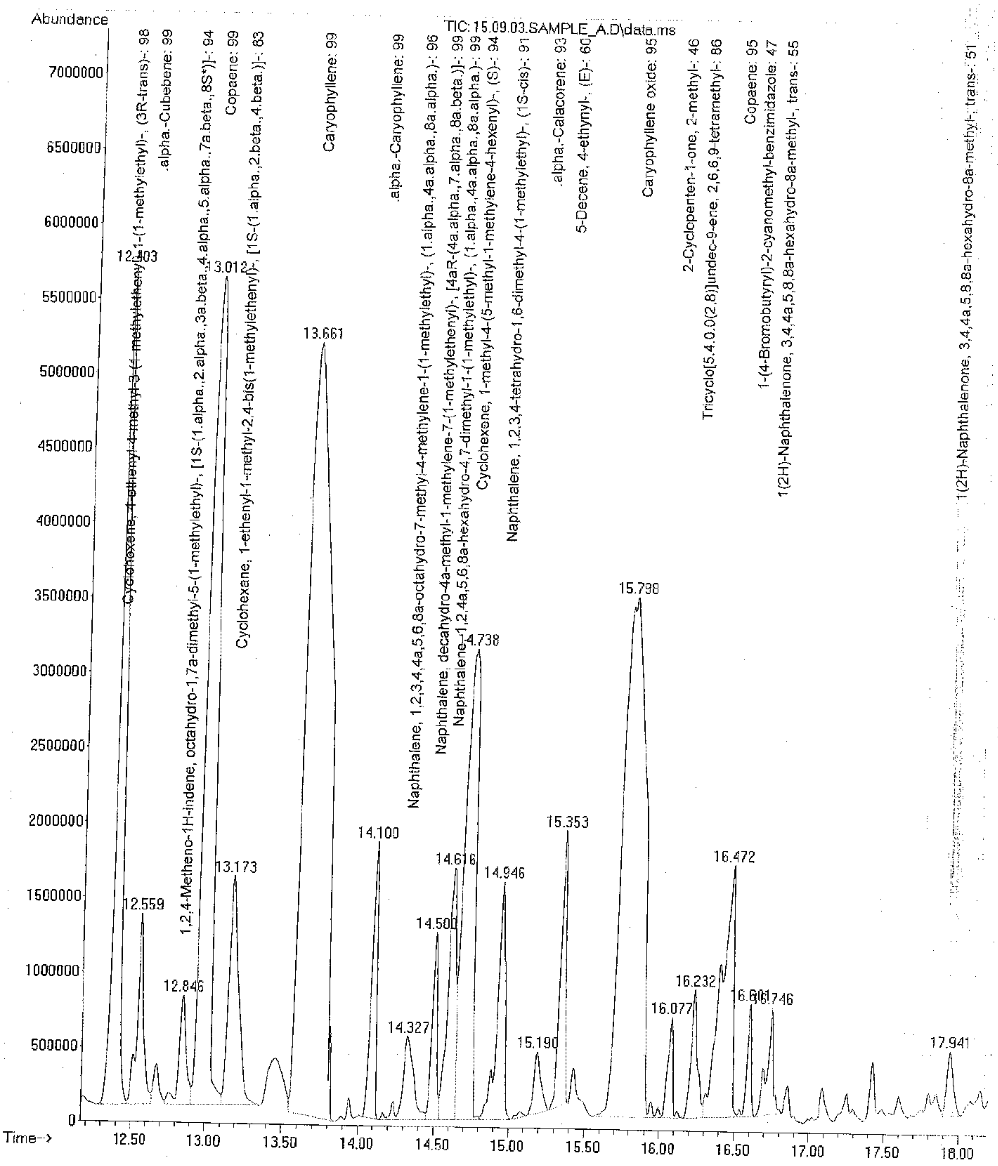


# APPENDIX E

Table 1: Mean composition of essential oil derived from black pepper dried at different conditions

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | | Spouted bed dried | | | |
| | | Sun -dried | 45°C | 55°C | 65°C | 75°C |
| 1 | Cada-1,4-diene | 0.026 | - | - | - | - |
| 2 | cis β-Famesene | 0.016 | - | - | - | - |
| 3 | cis-Limonene oxide | - | - | 0.101 | - | - |
| 4 | cis-β-Terpineol | 0.192 | - | - | 0.017 | - |
| 5 | E-Piperitol | 0.134 | - | - | - | - |
| 6 | L-4-terpineol | 2.830 | 0.381 | 0.509 | 0.457 | 0.662 |
| 7 | α-Terpinolene | 0.221 | - | - | - | - |
| 8 | β-Phorone | - | - | 0.153 | - | - |
| 9 | β-Sabinyl acetate | - | - | - | 0.216 | - |
| 10 | (E)-p-2,8-Menthadien-1-ol | - | - | 0.337 | - | - |
| 11 | 3-p-Menthene | - | - | 3.398 | - | - |
| 12 | cis-Geraniol | - | - | 0.052 | 0.059 | - |
| 13 | Cyclene | - | - | - | 0.046 | - |
| 14 | Cyclosativene | - | - | 0.078 | - | - |
| 15 | E,Z Ocimene | 0.075 | - | - | - | - |
| 16 | Geraniol | - | - | 0.043 | - | - |
| 17 | Limonene-1,2-diol | - | 1.246 | - | - | - |
| 18 | m-Toluquinaldine | - | - | - | 0.054 | - |
| 19 | Myrtenal | - | 0.975 | - | - | - |
| 20 | Ocimene | - | - | 0.045 | 0.046 | - |
| 21 | α- Terpinolen | - | - | 0.163 | - | - |
| 22 | α-Elemene | 0.252 | - | - | - | - |

Table 1. Continued

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | | Spouted bed dried | | | |
| | | Sun -dried | 45°C | 55°C | 65°C | 75°C |
| 23 | α-Gurjunene | - | - | 0.064 | - | - |
| 24 | β-Farnesene | - | - | - | 0.021 | - |
| 25 | β-Selinene | 0.103 | 0.089 | 0.162 | 0.256 | - |
| 26 | β-Thujene; | - | 0.129 | - | - | - |
| 27 | δ-Elemene | 1.651 | 1.411 | 1.978 | 3.213 | 4.580 |
| 28 | (-)-4-Terpineol | - | - | - | 0.504 | - |
| 29 | (-)-beta-Pinene | - | - | - | - | - |
| 30 | (-)-Carvone | - | 0.149 | 0.208 | - | - |
| 31 | (-)-cis-Sabinol | 0.120 | - | - | - | - |
| 32 | (-)-Myrtenol | 0.647 | 0.523 | 1.378 | 0.643 | 0.578 |
| 33 | (-)-Terpinen-4-ol | - | - | 0.931 | - | - |
| 34 | (+)-3-Carene | - | 1.532 | - | 0.115 | - |
| 35 | (+)-4-Carene | 4.712 | 0.114 | 0.065 | 0.272 | 0.143 |
| 36 | (+)-cycloisosativene | - | 0.128 | - | - | - |
| 37 | (+)-Cyclosativene | - | - | - | - | 0.188 |
| 38 | (+)epi-Bicyclosesquiphellandrene | 0.173 | 0.099 | 0.190 | 0.165 | - |
| 39 | (1R)-alpha-Pinene | 5.216 | 4.097 | 2.507 | 5.608 | 6.982 |
| 40 | (Cyclopropyl)trivinylsilane | - | - | 0.065 | - | - |
| 41 | (E)-p-2-Menthen-1-ol | - | - | - | 0.247 | - |
| 42 | (E)-p-Menth-2,8-dien-1-ol | 0.233 | 0.167 | 0.608 | 0.560 | 0.235 |
| 43 | (E)-β-Famesene | - | - | 0.033 | - | 0.050 |
| 44 | (R)-α-Pinene | - | - | - | 2.541 | - |
| 45 | (S)-cis-Verbenol | - | - | - | - | 0.052 |
| 46 | [1.2.4]Triazolo [1,5-a]pyrimidine-6-carboxylic acid, 7 amino-, ethyl ester | - | 0.465 | - | - | - |
| 47 | 1, 5-cyclooctadiene 1,2 -dimethyl | - | - | 0.107 | - | - |
| 48 | 1,3,5-Hexatriene,3-methyl | 0.146 | - | - | - | - |

Table 1. Continued

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | | Spouted bed dried | | | |
| | | Sun -dried | 45°C | 55°C | 65°C | 75°C |
| 49 | 1,5-di(ethenyl)-3-methyl-2-methylidenecyclohexane | - | - | - | 0.078 | - |
| 50 | 1,7,7-Trimethyl-2-vinylbicyclo [2.2.1]hept-2-ene | 0.516 | 0.231 | - | 0.223 | - |
| 51 | 10,10-dimethyl-2,6-dimethyl bicyclo [7.2.0]undecane-5.beta.-ol | 0.181 | 0.186 | - | - | - |
| 52 | 10,10-Dimethyl-2,6-dimethylenebicyclo [7.2.0]undecan-5β-ol | 0.324 | 0.498 | - | - | - |
| 53 | 1-Allyl-2-hydroxy-6-methyl-cyclohexanecarboxylic acid | - | 0.000 | - | - | - |
| 54 | 1-Chlorosulfonyl-3-methyl-1-azaspiro [3.5]nonan-2-one | - | - | - | 0.028 | - |
| 55 | 1-Ethenyl-1-methyl-2,4-bis-(1-methylethenyl)cyclohexane | - | - | 0.028 | - | - |
| 56 | 1-Methylene-2-vinylcyclopentane | - | - | - | 0.276 | - |
| 57 | 1-Naphthalenol, 1,2,3,4,4a,7,8,8a-octahydro-1,6-dimethyl-4-(1-methylethyl)-, [1R-(1α,4β,4aβ,8aβ)]- | - | - | - | 0.575 | - |
| 58 | 1S -camphene | 0.190 | - | - | 0.134 | 0.229 |
| 59 | 1S-α-Pinene | 1.906 | 0.236 | 6.349 | - | 2.436 |
| 60 | 2,3-Dimethyl-cyclohexa-1,3-diene | 0.309 | - | - | - | - |
| 61 | 2,4,6-Octatriene, 2,6-dimethyl- | - | - | - | - | 0.028 |
| 62 | 2,4-Cycloheptadien-1-one, 2,6,6-trimethyl- | 0.212 | - | - | - | - |
| 63 | 2,4-Dimethylfuran | - | - | - | 0.113 | - |
| 64 | 2,6-Octadien-1-ol, 3,7-dimethyl-, (Z)- | - | - | 0.047 | - | 0.093 |
| 65 | 2-Acetylcyclopentanone | 0.218 | - | - | - | - |
| 66 | 2-Amino-4-methylpyrimidine | - | - | - | 0.027 | - |
| 67 | 2-Carene | 0.318 | - | 0.056 | - | - |
| 68 | 2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-, (s) | - | - | - | - | 0.020 |
| 69 | 2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-, cis- | - | - | - | - | 0.121 |
| 70 | 2-cyclohexen-1-one 2-methyl-5-(1-methylethenyl)-(R)- | - | - | - | 0.070 | - |
| 71 | 2-Cyclopenten-1-one, 2-methyl- | - | - | - | - | 0.116 |
| 72 | 2-Oxabicyclo [2.2.2]octan-6-ol, 1,3,3-trimethyl-, acetate | - | - | - | 0.031 | - |
| 73 | 2-Pinen-10-ol | - | - | - | 0.116 | - |

Table 1. Continued

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | Sun -dried | Spouted bed dried | | | |
| | | | 45°C | 55°C | 65°C | 75°C |
| 74 | 3,5-Dimethyl cyclohex-1-ene-4-carboxaldehyde | - | - | - | 0.073 | - |
| 75 | 3-carene | 3.889 | - | 0.840 | 0.432 | 0.549 |
| 76 | 3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-, (R)- | 0.222 | - | - | 0.436 | - |
| 77 | 3-methylene-1 6-heptadiene | - | - | 0.211 | - | - |
| 78 | 3-Octyne, 7-methyl- | - | 0.075 | - | - | - |
| 79 | 3-p-Menthene | 1.887 | 3.533 | - | - | - |
| 80 | 4-ETHYNYL-5-DECENE; | - | - | - | - | - |
| 81 | 4-Hydroxy-4-(2,6-dimethyl cyclohex-3-enyl)butan-2-one | - | - | - | 0.051 | - |
| 82 | 4-hydroxy-4-(4 6-dimethyl cyclohex-3-enyl)butan-2-one | - | 0.061 | - | - | - |
| 83 | 5-Hexanal, 4-methylene | - | - | 0.067 | - | - |
| 84 | 5-Hexanal,4-methylene | - | - | 0.058 | - | - |
| 85 | 5-Hexenal, 4-methylene- | - | - | - | - | 0.028 |
| 86 | 5-methylene-1,3a,4,5,6,6a-hexahydropentalen-1-ol | - | - | 0.204 | - | - |
| 87 | 5-Octadecene, (E)- | - | - | 0.033 | - | - |
| 88 | 5-Oxatricyclo [8.2.0.0(4,6)-]dodecane, 4,12,12-trimethyl-9-methylene-, [1R-(1R*,4R*,6R*,10S*)]-; | 0.347 | - | - | - | - |
| 89 | 6,6-Dimethyl-2-methylenebicyclo [2.2.1]heptan-3-one | 0.119 | - | 0.111 | 0.076 | 0.082 |
| 90 | 6-Methyl-6,7 dihydro-9H-5-oxa-9-azabenzocyclohepten-8-one | - | - | - | 0.050 | - |
| 91 | 8a-Methyl-3,4,4a,5,8,8a-hexahydro-1(2H)-naphthalenone | - | - | - | - | 0.719 |
| 92 | Alloaromadendrene | 0.416 | 0.069 | - | - | - |
| 93 | alpha caryophyllene | 0.282 | - | - | - | - |
| 94 | Artemiseole | 0.030 | - | 0.135 | 0.054 | 0.030 |
| 95 | Benzene, (fluoromethyl)- | - | - | 0.054 | - | - |
| 96 | Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl- | - | - | 0.157 | 0.106 | - |
| 97 | Benzenemethanol, α,α,4-trimethyl- | - | - | - | - | 0.116 |
| 98 | Berbenone | - | - | - | 0.063 | - |

Table 1. Continued

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | Sun -dried | Spouted bed dried | | | |
| | | | 45°C | 55°C | 65°C | 75°C |
| 99 | bicyclo 3.1.0 hexane 4-methyl-1-(1-methylethyl)- didehydro deriv | 3.190 | 1.599 | 1.596 | 2.041 | 1.668 |
| 100 | bicyclo 4.4.0 dec-1-ene 2-isopropyl-5-methyl-9-methylene- | 0.503 | - | - | - | - |
| 101 | Bicyclo [3.1.0]hex-2-ene, 4,4,6,6-tetramethyl | - | - | 0.047 | - | - |
| 102 | Bicyclo [3.1.1]hept-3-en-2-ol, 4,6,6-trimethyl-; | 0.163 | - | - | - | - |
| 103 | Bicyclo [3.1.1]hept-3-en-2-one, 4,6,6-trimethyl-, (1S)- | - | - | 0.031 | - | - |
| 104 | Bicyclo [3.1.1]hept-3-ene, 2-formylmethyl-4,6,6-trimethyl- | - | 0.206 | - | - | - |
| 105 | Bicyclo [3.1.1]heptan-3-ol, 6,6-dimethyl-2-methylene-, [1S-(1α,3α,5α)]- | - | - | - | 0.157 | - |
| 106 | Bicyclo [3.2.0]heptan-3-ol, 2-methylene-6,6-dimethyl- | - | - | 0.067 | - | - |
| 107 | Bicyclo [3.3.0]oct-2-en-7-one, 6-methyl- | - | - | 0.051 | - | - |
| 108 | Bicyclo [4.4.0]dec-1-ene, 2-isopropyl-5-methyl-9-methylene- | 0.177 | 0.499 | 1.458 | 0.999 | 0.821 |
| 109 | Bicyclo [6.1.0]nonane, 9-(1-methylethylidene)- | - | 0.148 | - | - | - |
| 110 | Bicyclo [7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-, [1R-(1R*,4Z,9S*)]- | - | - | 0.520 | - | - |
| 111 | Bornylene | - | - | 0.280 | 0.253 | 0.444 |
| 112 | Cadala-1(10),3,8-triene | - | - | - | 0.035 | - |
| 113 | Calamenene | - | - | - | - | 0.401 |
| 114 | camphene | 0.337 | 0.356 | 0.468 | 0.293 | - |
| 115 | Carveol | - | - | 0.238 | 0.162 | 0.082 |
| 116 | Carvotanaceton | - | - | 0.197 | - | 0.074 |
| 117 | Carvotanacetone | - | 0.813 | - | - | - |
| 118 | Caryophylla-4(12),8(13)-dien-5β-ol | - | - | - | 0.269 | - |
| 119 | Caryophyllene | 9.305 | 11.391 | 9.998 | 12.574 | 14.792 |
| 120 | Caryophyllene oxide | 3.926 | 11.531 | 6.558 | 5.482 | 4.173 |
| 121 | cis -p-Mentha-2,8-dien-1-ol | 0.152 | - | 0.079 | - | - |
| 122 | cis-Carveol | 0.281 | 0.749 | 0.454 | 0.601 | 0.109 |
| 123 | cis-Geraniol | 0.120 | - | 0.078 | 0.065 | 0.031 |

Table 1. Continued

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | Sun -dried | Spouted bed dried | | | |
| | | | 45°C | 55°C | 65°C | 75°C |
| 124 | cis-Limonene oxide | - | - | 0.165 | - | - |
| 125 | cis-Linalool oxide; | 0.059 | - | - | - | - |
| 126 | cis-α-Bisabolene | - | - | 0.047 | - | - |
| 127 | cis-β-Farnesene | - | - | 0.074 | 0.024 | - |
| 128 | cis-β-Terpineol | - | - | 0.261 | 0.087 | 0.085 |
| 129 | Crypton | - | 0.128 | - | - | - |
| 130 | Cryptone | 0.199 | - | 0.278 | 0.219 | 0.111 |
| 131 | Curcumene | - | 0.117 | - | - | - |
| 132 | Cyclene | - | - | 0.053 | - | - |
| 133 | Cyclofenchene | 3.335 | - | - | - | - |
| 134 | Cyclohexane, 1,5-diethenyl-3-methyl-2-methylene-, (1.alpha.,3.alpha.,5.alpha | - | 0.346 | - | - | - |
| 135 | Cyclohexene, 1-methyl-4-(1-methylethylidene)- | - | - | - | - | 0.071 |
| 136 | Cyclohexene, 4-ethenyl-4-methyl-3-(1-methylethenyl)-1-(1-methylethyl)-, (3R-trans)- | - | - | 0.737 | - | - |
| 137 | Cyclohexene, 4-methyl-1-(1-methylethenyl)- | 0.174 | - | - | - | - |
| 138 | Cycloisosativene | - | - | - | - | 0.273 |
| 139 | Cyclopentane, 1,3-bis(methylene)- | 0.084 | - | - | - | - |
| 140 | cyclopropane 1 1-dimethyl-2-(3-methyl-1 3-butadienyl)- | 0.757 | - | - | - | - |
| 141 | Cyclosativene | 0.490 | - | 0.538 | 0.294 | - |
| 142 | Cymenene | - | - | 0.076 | - | - |
| 143 | D limonene | 8.009 | 11.051 | 12.750 | 13.724 | 12.817 |
| 144 | d-Camphene | 0.193 | - | - | - | - |
| 145 | D-Carvone | 0.082 | - | 0.188 | 0.138 | - |
| 146 | Di-epi-α-cedrene | - | - | 0.262 | 0.144 | - |
| 147 | dipropyl ester | 0.087 | - | - | - | - |
| 148 | E Geraniol | - | - | - | - | - |

Table 1. Continued

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | Sun -dried | Spouted bed dried | | | |
| | | | 45°C | 55°C | 65°C | 75°C |
| 149 | E-15-Heptadecenal | - | - | - | 0.035 | - |
| 150 | Elemene | - | - | - | - | 0.498 |
| 151 | Eucarvone | 0.130 | - | 0.063 | - | - |
| 152 | Germacrene D | - | - | - | 0.033 | - |
| 153 | Globulol | - | - | 0.048 | - | - |
| 154 | Hexanoic anhydride | - | - | 0.026 | - | - |
| 155 | Humulene epoxide 2 | - | 0.660 | - | 0.090 | - |
| 156 | Humulene epoxide II | - | - | 0.083 | - | - |
| 157 | Isogeraniol | - | - | 0.047 | - | - |
| 158 | Isolimonene | - | - | - | 0.204 | 0.071 |
| 159 | Limonene | 1.372 | - | 0.106 | - | - |
| 160 | Linalool | 1.487 | 0.338 | 0.903 | 0.595 | 0.621 |
| 161 | Longipinene | - | - | - | - | 0.177 |
| 162 | L-Pinocarveol | - | 0.871 | - | - | 0.459 |
| 163 | L-α-Terpineol | 0.121 | - | - | - | - |
| 164 | L-β-Pinene | 2.358 | 5.715 | 4.765 | 5.245 | - |
| 165 | methoxy methyl chlorosilane | - | - | 0.022 | - | - |
| 166 | Methoxy(methyl)chlorosilane | - | - | 0.132 | 0.026 | - |
| 167 | Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S-cis)- | - | - | 0.452 | - | - |
| 168 | Naphthalene, 1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)- | 0.053 | 0.262 | - | - | - |
| 169 | Naphthalene, 1,2-dihydro-1,1,6-trimethyl- | 0.046 | - | 0.129 | 0.031 | - |
| 170 | Neo-allo-ocimene | - | - | - | 0.217 | - |
| 171 | Ocimene | - | - | - | 0.024 | - |
| 172 | o-Cymene | 0.292 | - | - | - | - |
| 173 | p-Cymen-7-ol | 0.222 | - | - | 0.053 | - |
| 174 | p-Cymen-8-ol | 0.278 | - | - | - | - |

Table 1. Continued

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | Sun -dried | Spouted bed dried | | | |
| | | | 45°C | 55°C | 65°C | 75°C |
| 175 | Phytol | - | - | 0.031 | 0.032 | - |
| 176 | Pinocarveol | 0.248 | 0.089 | 1.305 | 0.453 | 0.051 |
| 177 | Pinocarvone | - | - | 0.066 | 0.057 | - |
| 178 | p-Mentha-6,8-dien-2-ol | - | 0.299 | - | - | - |
| 179 | Sabinene | 3.431 | 3.169 | 3.746 | 4.076 | 5.608 |
| 180 | Sabinyl acetate | - | 0.241 | - | - | - |
| 181 | Spiro [2.4]heptane, 1,5-dimethyl-6-methylene- | - | 0.112 | - | - | - |
| 182 | Spiro [5.6]dodecane | - | 0.000 | - | - | - |
| 183 | S-Verbenone | 0.232 | - | 0.277 | - | - |
| 184 | Sylvestrene | - | - | - | - | 0.139 |
| 185 | Terephthalic acid, ethyl nonyl ester | - | - | - | 0.036 | - |
| 186 | Terpinen-4-ol | - | 0.217 | - | - | 1.246 |
| 187 | Terpinenol | - | - | - | 0.268 | - |
| 188 | Tetracyclo [6.3.2.0(2,5).0(1,8)]tridecan-9-ol, 4,4-dimethyl- | 0.152 | - | - | - | - |
| 189 | trans-2,3-Epoxydecane | - | - | 0.063 | - | - |
| 190 | trans-3-methylpent-3-ene-5-ol | 0.063 | - | - | - | - |
| 191 | trans-Carveol | - | - | 0.114 | - | - |
| 192 | trans-Pinocarveol | - | 0.613 | - | - | - |
| 193 | trans-p-mentha-2 8-dienol | - | - | 0.321 | - | - |
| 194 | trans-p-Mentha-2 8-dienol | - | 0.099 | - | - | - |
| 195 | trans-p-Mentha-2,8-dienol | - | - | 0.281 | - | 0.035 |
| 196 | Tricyclo [7.2.0.0(2,6)]undecan-5-ol, 2,6,10,10-tetramethyl- (isomer 3) | 0.053 | - | - | - | - |
| 197 | Verbenol | 0.184 | 0.075 | 0.271 | 0.150 | - |
| 198 | α- Terpinolen | 0.134 | - | 0.073 | 0.052 | - |
| 199 | α-Cadinol | - | - | - | 0.163 | - |
| 200 | α-Calacorene | 0.075 | - | 0.180 | 0.063 | 0.102 |

Table 1. Continued

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | Sun -dried | Spouted bed dried | | | |
| | | | 45°C | 55°C | 65°C | 75°C |
| 201 | α-Caryophyllene | 2.810 | 0.868 | 1.093 | 1.117 | 1.280 |
| 202 | α-Copaene | 2.106 | 8.191 | 4.371 | 2.382 | 7.770 |
| 203 | α-Cubebene | 4.336 | 3.743 | 4.143 | 6.435 | 2.813 |
| 204 | α-Curcumene | - | - | 0.136 | - | - |
| 205 | α-Elemene | - | - | - | - | 0.139 |
| 206 | α-Farnesene | - | - | - | 0.130 | - |
| 207 | α-Gurjenene | - | - | 0.069 | - | - |
| 208 | α-Himachalene | - | - | - | - | 0.132 |
| 209 | α-Muurolene | 0.470 | 0.790 | 1.445 | 1.340 | 1.740 |
| 210 | α-Phellandrene | 0.134 | 0.184 | - | - | - |
| 211 | α-Pinene | - | 6.854 | 0.127 | 2.391 | - |
| 212 | α-Selinene | 0.073 | 0.271 | - | 0.130 | 0.167 |
| 213 | α-Terpinene | 0.296 | - | - | - | - |
| 214 | α-Terpineol | 0.429 | 0.090 | 0.880 | 0.520 | 0.880 |
| 215 | β-Bisabolene | 0.925 | 3.318 | 3.202 | 3.058 | 3.733 |
| 216 | β-cis-Caryophyllene | 0.781 | - | - | - | - |
| 217 | β-Cubebene | 0.561 | 0.384 | 0.520 | 0.032 | 0.048 |
| 218 | β-Elemene | - | - | - | - | 0.489 |
| 219 | β-Farnesene | - | - | 0.026 | 0.036 | 0.058 |
| 220 | β-Gurjenene | - | - | - | 0.860 | 0.579 |
| 221 | β-Myrcene | 0.919 | 0.620 | 0.969 | 0.618 | 0.892 |
| 222 | β-Phellandrene | 0.444 | - | - | 4.479 | - |
| 223 | β-Phorone | - | - | 0.179 | - | - |
| 224 | β-Pinene | 1.504 | 4.207 | - | 0.153 | 3.564 |
| 225 | β-Selinene | 0.117 | - | 0.159 | 0.182 | 0.404 |
| 226 | β-Terpinen | - | - | - | - | 4.746 |

Table 1. Continued

| No | Component | Mean composition % (w/w) | | | | |
|---|---|---|---|---|---|---|
| | | Sun -dried | Spouted bed dried | | | |
| | | | 45°C | 55°C | 65°C | 75°C |
| 227 | β-Terpinene | - | - | - | 4.472 | - |
| 228 | β-Thujene | - | - | - | - | 0.027 |
| 229 | γ-Cadinene | 0.107 | - | - | 0.159 | - |
| 230 | γ-Muurolene | 0.520 | - | 0.313 | 0.281 | 0.468 |
| 231 | γ-Terpinene | 0.387 | - | 0.025 | 0.060 | 0.123 |
| 232 | δ3-p-Menthene | 4.827 | - | 4.102 | - | - |
| 233 | δ-Cadinene | 1.192 | 0.882 | 0.628 | 1.166 | 0.895 |
| 234 | ε-Cyclogeraniolene | 0.021 | - | - | - | - |
| 235 | τ-Cadinol | 0.134 | 0.432 | - | - | - |
| | Trace compounds | 5.079 | 0.583 | 5.048 | 2.407 | 1.911 |
| | Total | 98.84 | 99.50 | 100.0 | 99.92 | 95.99 |

Table 2: Percentage of Constituents of essential oil extracted from black pepper dried at different drying conditions

| Sample No | Drying condition | % percentage of components | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Monoterpene | | | Oxygenated monoterpene | | | sesquiterpene | Oxygenated sesquiterpene | |
| | | $C_{10}H_{16}$ | $C_{10}H_{18}$ | $C_{10}H_{12}$ | $C_{10}H_{14}O$ | $C_{10}H_{16}O$ | $C_{10}H_{18}O$ | $C_{15}H_{24}$ | $C_{15}H_{24}O$ | $C_{15}H_{26}O$ |
| 1 | Sun dried | 41.79 | - | - | 1.83 | 6.67 | 6.62 | 30.89 | 5.60 | - |
| 2 | Sun dried | 50.56 | - | - | 0.13 | 2.30 | 4.79 | 32.69 | 4.56 | - |
| 3 | Sun dried | 29.56 | 7.55 | - | 2.67 | 0.64 | 10.71 | 24.36 | 8.17 | - |
| 4 | Sun dried | 64.39 | 7.08 | - | | | 1.48 | 25.15 | 1.25 | 0.54 |
| 5 | 45°C | 29.09 | 14.13 | - | 0.60 | 4.19 | 1.69 | 37.90 | 5.64 | - |
| 6 | 45°C | 66.27 | | - | | | 1.95 | 27.78 | 0.74 | 0.45 |
| 7 | 45°C | 13.33 | 0.00 | - | 3.90 | 12.18 | 0.00 | 24.73 | 39.03 | 0.00 |
| 8 | 45°C | 50.76 | - | - | | 0.82 | 0.47 | 39.16 | 6.09 | 1.28 |
| 9 | 55°C | 24.65 | - | 0.30 | 0.38 | 9.93 | 5.01 | 27.51 | 9.59 | - |
| 10 | 55°C | 40.49 | - | - | 1.26 | 6.63 | 2.74 | 33.38 | 4.91 | - |
| 11 | 55°C | 48.59 | - | - | 0.19 | 2.50 | 3.37 | 38.84 | 5.07 | 0.19 |
| 12 | 55°C | 25.73 | 16.41 | - | 0.57 | 6.07 | 3.05 | 32.53 | 7.00 | - |
| 13 | 65°C | 49.96 | - | - | | | 1.63 | 34.69 | 11.13 | - |
| 14 | 65°C | 43.82 | - | - | 0.49 | 4.70 | 4.06 | 37.30 | 3.74 | - |
| 15 | 65°C | 49.64 | - | - | 0.27 | 4.64 | 2.87 | 32.73 | 4.18 | 2.30 |
| 16 | 65°C | 46.56 | - | - | 2.24 | 1.99 | 1.73 | 36.82 | 4.32 | 0.65 |
| 17 | 75°C | 50.26 | - | - | - | 0.80 | 1.71 | 42.80 | 2.58 | - |
| 18 | 75°C | 42.75 | - | - | - | 4.23 | 3.54 | 39.20 | 2.59 | - |
| 19 | 75°C | 55.81 | - | - | - | - | 1.30 | 41.40 | 1.38 | - |
| 20 | 75°C | 27.89 | - | - | 0.46 | 2.68 | 8.68 | 46.94 | 10.15 | - |

Table 3: Information of five most abundant sesquiterpene in black pepper essential oil under investigation [120]

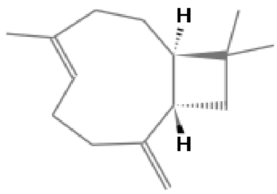
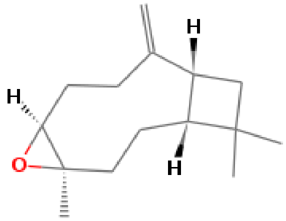
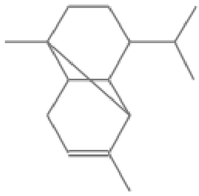
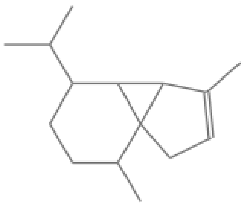
| **Component** | **Concentration (% w/w)** | **Formula and structure** | **Molecular weight** |
|---|---|---|---|
| Caryophyllene | 14.792 | $C_{15}H_{24}$   | 204.3511 |
| Caryophyllene oxide | 11.531 | $C_{15}H_{24}O$   | 220.3505 |
| α-Copaene | 8.191 | $C_{15}H_{24}$  | 204.3511 |
| α-Cubebene | 6.435 | $C_{15}H_{24}$  | 204.3511 |

Table 4: Information of six most abundant monoterpene in black pepper essential oil under investigation [120]

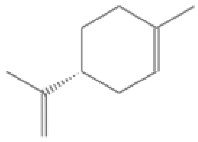
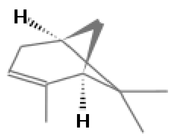
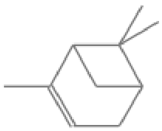
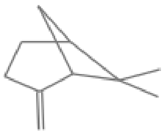
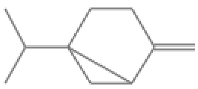
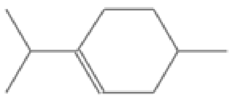
| Component | Percentage | Formula and structure | Molecular weight |
|---|---|---|---|
| D limonene | 13.724 | $C_{10}H_{16}$  | 136.2340 |
| (1R)- α -Pinene | 6.982 | $C_{10}H_{16}$  | 136.2340 |
| α-Pinene | 6.854 | $C_{10}H_{16}$  | 136.2340 |
| L-β-Pinene | 5.715 | $C_{10}H_{16}$  | 136.2340 |
| Sabinene | 5.608 | $C_{10}H_{16}$  | 136.2340 |
| δ3-p-Menthene | 4.827 | $C_{10}H_{18}$  | 138.2499 |

Table 5: ANOVA table for comparative study of sesquiterpenes, monoterpenes and oxygenated terpenes with drying temperature

| ANOVA Table | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | Sum of Squares | df | Mean Square | F | Sig. |
| C10H16 * Dry_temperature | Between Groups | (Combined) | 436.641 | 4 | 109.160 | .519 | .723 |
| | Within Groups | | 3153.769 | 15 | 210.251 | | |
| | Total | | 3590.409 | 19 | | | |
| C15H24 * Dry_temperature | Between Groups | (Combined) | 446.632 | 4 | 111.658 | 5.282 | .007 |
| | Within Groups | | 317.070 | 15 | 21.138 | | |
| | Total | | 763.702 | 19 | | | |
| oxides * Dry_temperature | Between Groups | (Combined) | 186.821 | 4 | 46.705 | 1.102 | .394 |
| | Within Groups | | 593.603 | 14 | 42.400 | | |
| | Total | | 780.424 | 18 | | | |

Table 6: ANOVA table for Caryophyllene with drying temperature

| ANOVA Table | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | Sum of Squares | df | Mean Square | F | Sig. |
| Caryophyllene * dry_temp | Between Groups | (Combined) | 107.132 | 4 | 26.783 | 1.722 | .201 |
| | Within Groups | | 217.711 | 14 | 15.551 | | |
| | Total | | 324.842 | 18 | | | |

Table 7: ANOVA table for oil yield vs. drying temperature

| ANOVA Table | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | Sum of Squares | df | Mean Square | F | Sig. |
| oil_yield * Dry_conditions | Between Groups | (Combined) | 1.558 | 4 | .390 | 3.148 | .046 |
| | Within Groups | | 1.856 | 15 | .124 | | |
| | Total | | 3.414 | 19 | | | |

## APPENDIX F

Table 1: Operating conditions, heat transfer coefficient, important non-dimensional numbers of heat transfer process of black pepper drying in conventional spouted bed.

| Run | Operating conditions | | | Properties of air | | | $h_p$ (W/m$^{2°}$C) | Dimensionless numbers | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | H (cm) | $T_{gi}$ (°C) | U (m/s) | ρ (kg/m$^3$) | μ x $10^{-5}$ (Ns/m$^2$) | $k_g$ (W/mK) | | Nu | Re | Gu | H/dp |
| 0 | 14 | 45 | 2.37 | 1.1095 | 1.9307 | 0.0276 | 49.00 | 9.25 | 708.07 | 0.3111 | 26.90 |
| 1 | 14 | 55 | 2.37 | 1.0757 | 1.9763 | 0.0283 | 45.00 | 8.27 | 670.65 | 0.4273 | 26.90 |
| 2 | 14 | 65 | 2.37 | 1.0439 | 2.0212 | 0.0291 | 54.67 | 9.79 | 636.35 | 0.4846 | 26.90 |
| 3 | 14 | 75 | 2.37 | 1.0139 | 2.0655 | 0.0298 | 57.24 | 9.99 | 604.82 | 0.5667 | 26.90 |
| 4 | 14 | 65 | 1.60 | 1.0439 | 2.0212 | 0.0291 | 51.69 | 9.25 | 429.71 | 0.4846 | 26.90 |
| 5 | 14 | 65 | 1.97 | 1.0439 | 2.0212 | 0.0291 | 59.09 | 10.58 | 530.73 | 0.4846 | 26.90 |
| 6 | 7 | 65 | 2.37 | 1.0439 | 2.0212 | 0.0291 | 65.93 | 11.80 | 636.35 | 0.5000 | 13.45 |
| 7 | 18 | 65 | 2.37 | 1.0439 | 2.0212 | 0.0291 | 51.09 | 9.15 | 636.35 | 0.4877 | 34.59 |
| 8 | 20 | 65 | 2.37 | 1.0439 | 2.0212 | 0.0291 | 46.96 | 8.41 | 636.35 | 0.5538 | 38.43 |

Table 1. Continued

| Run | H (cm) | $T_{gi}$ (°C) | U (m/s) | ρ (kg/m$^3$) | μ x $10^{-5}$ (Ns/m$^2$) | $k_g$ (W/mK) | $h_p$ (W/m$^2$°C) | Nu | Re | Gu | H/dp |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 20 | 55 | 2.37 | 1.0139 | 2.0655 | 0.0298 | 47.16 | 8.67 | 670.65 | 0.4091 | 38.43 |
| 11 | 22 | 75 | 2.37 | 1.0757 | 1.9763 | 0.0283 | 45.64 | 7.97 | 604.82 | 0.4923 | 42.28 |
| 12 | 20 | 45 | 2.37 | 1.0139 | 2.0655 | 0.0298 | 40.80 | 7.70 | 708.07 | 0.3000 | 38.43 |
| 13 | 14 | 45 | 2.37 | 1.1095 | 1.9307 | 0.0276 | 51.09 | 9.64 | 708.07 | 0.3111 | 26.90 |
| 14 | 18 | 45 | 2.37 | 1.1095 | 1.9307 | 0.0276 | 53.82 | 10.16 | 708.07 | 0.3444 | 34.59 |
| 15 | 18 | 55 | 2.37 | 1.1095 | 1.9307 | 0.0276 | 43.50 | 7.99 | 670.65 | 0.5455 | 34.59 |
| 16 | 18 | 55 | 2.37 | 1.0757 | 1.9763 | 0.0283 | 53.68 | 9.86 | 670.65 | 0.4545 | 34.59 |
| 17 | 14 | 45 | 1.60 | 1.0757 | 1.9763 | 0.0283 | 47.09 | 8.89 | 478.14 | 0.3111 | 26.90 |
| 18 | 14 | 60 | 2.37 | 1.1095 | 1.9307 | 0.0276 | 57.50 | 10.43 | 653.13 | 0.5417 | 26.90 |
| 19 | 18 | 75 | 2.37 | 1.0595 | 1.9988 | 0.0287 | 56.29 | 9.83 | 604.82 | 0.6000 | 34.59 |
| 20 | 18 | 75 | 1.60 | 1.0139 | 2.0655 | 0.0298 | 53.51 | 9.34 | 408.42 | 0.5933 | 34.59 |
| 21 | 22 | 55 | 2.37 | 1.0139 | 2.0655 | 0.0298 | 45.28 | 8.32 | 670.65 | 0.4273 | 42.28 |
| 22 | 22 | 45 | 2.37 | 1.0757 | 1.9763 | 0.0283 | 40.86 | 7.71 | 708.07 | 0.3444 | 42.28 |

Table 1. Continued

| Run | H (cm) | $T_{gi}$ (°C) | U (m/s) | ρ ($kg/m^3$) | μ x $10^{-5}$ ($Ns/m^2$) | $k_g$ (W/mK) | $h_p$ ($W/m^{2}$°C) | Nu | Re | Gu | H/dp |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 23 | 22 | 60 | 1.60 | 1.1095 | 1.9307 | 0.0298 | 40.18 | 7.29 | 441.04 | 0.5500 | 42.28 |
| 24 | 14 | 35.3 | 2.37 | 1.0595 | 1.9988 | 0.0283 | 34.50 | 6.69 | 747.74 | 0.0935 | 26.90 |
| 25 | 24 | 75 | 2.37 | 1.1444 | 1.8857 | 0.0298 | 52.40 | 9.15 | 604.82 | 0.5840 | 46.12 |
| 26 | 24 | 65 | 2.37 | 1.0139 | 2.0655 | 0.0276 | 48.37 | 8.66 | 636.35 | 0.5200 | 46.12 |
| 27 | 22 | 65 | 1.60 | 1.0439 | 2.0212 | 0.0276 | 44.86 | 8.03 | 429.71 | 0.5200 | 42.28 |
| 28 | 24 | 65 | 2.57 | 1.0439 | 2.0212 | 0.0276 | 48.95 | 8.76 | 691.39 | 0.5200 | 46.12 |
| 29 | 24 | 55 | 2.57 | 1.0439 | 2.0212 | 0.0283 | 47.27 | 8.69 | 728.66 | 0.4327 | 46.12 |
| 30 | 24 | 55 | 2.37 | 1.0757 | 1.9763 | 0.0283 | 47.91 | 8.80 | 670.65 | 0.4327 | 46.12 |
| 31 | 7 | 65 | 1.60 | 1.0757 | 1.9763 | 0.0276 | 65.10 | 11.65 | 429.71 | 0.5200 | 13.45 |
| 32 | 7 | 75 | 2.37 | 1.0439 | 2.0212 | 0.0287 | 67.18 | 11.73 | 604.82 | 0.6000 | 13.45 |
| 33 | 7 | 45 | 2.06 | 1.0139 | 2.0655 | 0.0298 | 58.14 | 10.98 | 616.10 | 0.3067 | 13.45 |
| 34 | 7 | 55 | 2.33 | 1.1095 | 1.9307 | 0.0298 | 63.93 | 11.75 | 660.97 | 0.4327 | 13.45 |
| 35 | 7 | 55 | 1.72 | 1.0757 | 1.9763 | 0.0283 | 61.80 | 11.36 | 486.74 | 0.4364 | 13.45 |

Table 1. Continued

| Run | H (cm) | $T_{gi}$ (°C) | U (m/s) | ρ ($kg/m^3$) | μ x $10^{-5}$ ($Ns/m^2$) | $k_g$ (W/mK) | $h_p$ ($W/m^2$°C) | Nu | Re | Gu | H/dp |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 36 | 7 | 65 | 1.72 | 1.0757 | 1.9763 | 0.0291 | 63.14 | 11.31 | 461.85 | 0.5200 | 13.45 |
| 37 | 7 | 65 | 2.54 | 1.0439 | 2.0212 | 0.0291 | 67.60 | 12.10 | 682.27 | 0.5200 | 13.45 |
| 38 | 7 | 75 | 2.49 | 1.0439 | 2.0212 | 0.0298 | 69.47 | 12.13 | 635.37 | 0.5840 | 13.45 |
| 39 | 7 | 65 | 2.06 | 1.0139 | 2.0655 | 0.0291 | 67.75 | 12.13 | 553.69 | 0.5200 | 13.45 |
| 40 | 14 | 60 | 1.60 | 1.0439 | 2.0212 | 0.0287 | 51.49 | 9.34 | 441.04 | 0.4800 | 26.90 |
| 41 | 14 | 60 | 2.54 | 1.0595 | 1.9988 | 0.0287 | 54.99 | 9.97 | 700.26 | 0.4800 | 26.90 |
| 42 | 14 | 65 | 2.59 | 1.0595 | 2.0212 | 0.0291 | 56.80 | 10.17 | 696.04 | 0.4923 | 26.90 |
| 43 | 7 | 36 | 1.68 | 1.0439 | 1.8890 | 0.0269 | 49.64 | 9.61 | 529.79 | 0.1333 | 13.45 |
| 44 | 7 | 40 | 2.15 | 1.1418 | 1.9076 | 0.0272 | 57.13 | 10.93 | 659.78 | 0.2200 | 13.45 |
| 45 | 14 | 40 | 2.20 | 1.1272 | 1.9076 | 0.0272 | 45.60 | 8.73 | 675.54 | 0.2200 | 26.90 |
| 46 | 18 | 65 | 2.49 | 1.1272 | 2.0212 | 0.0291 | 57.65 | 10.32 | 668.49 | 0.5200 | 34.59 |
| 47 | 18 | 65 | 2.06 | 1.0439 | 2.0212 | 0.0291 | 48.91 | 8.76 | 553.69 | 0.5200 | 34.59 |

# APPENDIX G

Table 1: Summary of model for heat transfer

| **Model Summary**[b] | | | | | |
|---|---|---|---|---|---|
| Model | R | R Square | Adjusted R Square | Std. Error of the Estimate | Durbin-Watson |
| 1 | .889[a] | .791 | .777 | .0299600 | 1.981 |
| a. Predictors: (Constant), LogGu, LogHbydp, LogRe | | | | | |
| b. Dependent Variable: logNu | | | | | |

Table 2: ANOVA Table for model for heat transfer

| **ANOVA**[a] | | | | | | |
|---|---|---|---|---|---|---|
| Model | | Sum of Squares | df | Mean Square | F | Sig. |
| 1 | Regression | .150 | 3 | .050 | 55.524 | .000[b] |
| | Residual | .039 | 44 | .001 | | |
| | Total | .189 | 47 | | | |
| a. Dependent Variable: logNu | | | | | | |
| b. Predictors: (Constant), LogGu, LogHbydp, LogRe | | | | | | |

Table 3: Coefficients for model for heat transfer

| **Coefficients**[a] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Model | Unstandardized Coefficients | | Standardized Coefficients | t | Sig. | Collinearity Statistics | |
| | B | Std. Error | Beta | | | Tolerance | VIF |
| (Constant) | 1.081 | .170 | | 6.363 | .000 | | |
| LogRe | .137 | .064 | .158 | 2.154 | .037 | .886 | 1.128 |
| LogHbydp | -.293 | .024 | -.881 | -12.274 | .000 | .922 | 1.085 |
| LogGu | .180 | .028 | .463 | 6.329 | .000 | .886 | 1.129 |
| a. Dependent Variable: logNu | | | | | | | |

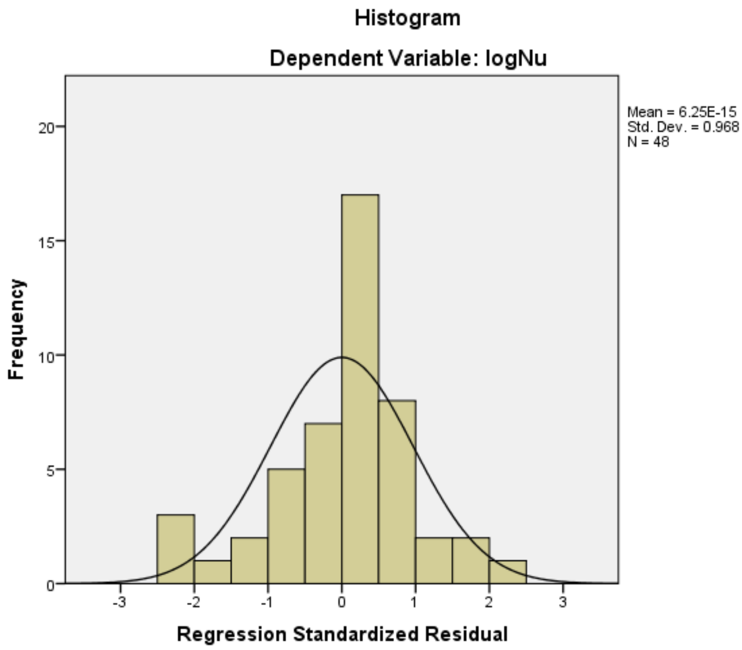



Figure 1 : Model for heat transfer

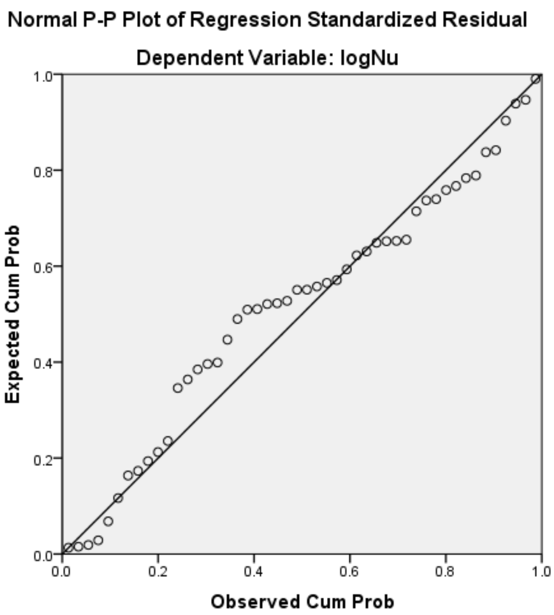



Figure 2: Model for heat transfer

# APPENDIX H

1. **Terminal velocity of a particle**

- Terminal falling velocity corresponding to a value of Re′ lies between 0.2 to 500 [12]:

$$u_t = \frac{g{d_p}^2}{18\mu}(\rho_s - \rho_f)$$

- Terminal falling velocity corresponds to a value of Re′ greater than about 500 [12]:

$$u_t^2 = \frac{3gd_p}{\rho_f}(\rho_s - \rho_f)$$

$u_t -$ terminal velocity (m/s)

$g - gravity\ accelaration\ (m/s^2)$

$d_p -$ particle diameter (m)

$\mu -$ viscosity of medium ($Ns/m^2$)

$\rho_s -$ density of solid particle ($kg/m^3$)

$\rho_f -$ density of fluid ($kg/m^3$)

Re′- particle Reynolds number

**2. Calculation of dimensionless numbers** [104]

**1 Reynolds (Re) number**

$$Re = \frac{d_p U \rho}{\mu}$$

$d_p -$ particle diameter (m)

U- Superficial air velocity (m/s)

$\rho$ − density of medium at dryng temperature (kg/m$^3$)

$\mu$ − viscosity of medium (Ns/m$^2$)

**2 Nusselt (Nu) number**

$$\mathrm{Nu} = \frac{\mathrm{h_p d_p}}{\mathrm{k_g}}$$

$\mathrm{h_p}$ − heat transfer coefficient of air to particle (W/m$^2$K)

$\mathrm{d_p}$ − particle diameter (m)

$\mathrm{k_g}$ − conductivity of medium (W/mK)

**3 Gukhman Number**

$$Gu = \frac{T_{gi} - T_{gi,w}}{T_{gi}}$$

$T_{gi}$ −Air inlet temperature (K)

$T_{gi,w}$ − gas inlet wet bulb temperature (K)

**3. Air thermo physical properties were calculated as function of the temperature** [132]

- Kinematic viscosity of air ($\upsilon$)

$$\upsilon = -1.155 \times 10^{-14}\mathrm{T}^3 + 9.572 \times 10^{-11}\mathrm{T}^2 + 3.760 \times 10^{-8}T - 3.448 \times 10^{-6}$$

- Thermal conductivity of air ($k_g$)

$$k_g = -1.5207 \times 10^{-11}\mathrm{T}^3 + 4.8574 \times\times 10^{-8}\mathrm{T}^2 + 1.0184 \times 10^{-4}T - 3.933 \times 10^{-4}$$

- Humid volume is the volume of the unit mass of dry air and its associated water vapour at that temperature and pressure [12].

$$V_h = \frac{22.4}{29}\left(\frac{T}{273}\right) + \frac{22.4H}{18}\left(\frac{T}{273}\right)$$

$$V_h = (0.00283 + 0.00456H)T$$

- Humid heat is the heat required to raise the temperature of unit mass of dry air and its associated vapour one degree K at constant pressure [12]

$$C_s = C_{air} + HC_{vapour}$$
$$C_s = 1.005 + 1.88\,H$$

- Average particle diameter ($d_p$) of black pepper were measured and was taken as 0.005204 m or 5.204 mm.
- True density of raw black pepper was measured using a densometer and the true density is 747.696 kg/m3. True density value was not used in any calculation of this study.

Where

$k_g$ - Thermal conductivity of air (W/mK

$V_h$ - humid volume (m3/kg) of dry air)

T- Temperature (K)

H - Humidity ( kg of moisture/ kg of dry air)

Cs - humid heat (kJ/kg K)

$C_{vapour}$ - heat capacity of water vapour

υ- kinematic viscosity ($m^2$/s)

## List of Publications

| No | Description | Category |
|---|---|---|
| 1 | G. K. Jayatunga and B. M. W. P. K. Amarasinghe, Drying Kinetics, Quality and Moisture Diffusivity of Spouted Bed Dried Sri Lankan Black Pepper. *Journal of Food Engineering*., vol. 263, pp. 38–45, Dec. 2019. | Index Journal<br><br>SCI/Scopus |
| 2 | Jayatunga G.K, Amarasinghe B.M.W.P.K., Drying Kinetics of Black Pepper Dried in A Spouted Bed Dryer with or without Draft Tubes. International Journal of Manufacturing & Industrial Engineering – IJMIE , Volume 1: Issue 2, pp. 6–10, Publication Date : 25 June 2014 | Refereed Journal |
| 3 | G.K. Jayatunga, S.M.N.D Martino and B.M.W. P.K. Amarasinghe, Thin Layer Drying Models for Drying of Black Pepper in Spouted Bed Dryer with Internal Devices. Transaction of IESL annual session. October 2016. Sri Lanka | Refereed Conference |
| 4 | Jayatunga G.K, Amarasinghe B.M.W.P.K.,Mathematical Modeling of Drying Kinetics of Black Pepper in a Spouted Bed Dryer with and without Non Porous Draft Tubes. International Conference on "Trends in Multidisciplinary Business and Economic Research (TMBER 25-26 March 2015). © 2015 Global Illuminators, Bangkok, Thailand | |
| 5 | Jayatunga G.K, Amarasinghe B.M.W.P.K., Effect of Configuration of Draft Tubes on Drying Kinetics of Black Pepper Dried in a Spouted Bed Dryer. Transaction of IESL annual session. October 2014. Sri Lanka | |
| 6 | Jayatunga G.K And Amarasinghe B.M.W.P.K, Effect of drying temperature in spouted bed drying on quality of black pepper, ITUM Symposium 2018, Sri Lanka | Extended Abstract - Conference proceeding |
| 7 | Jayatunga G.K And Amarasinghe B.M.W.P.K, Determination of moisture diffusivity of black pepper drying in conventional spouted bed, ITUM Symposium 2017, Sri Lanka | |
| 8 | Jayatunga G.K And Amarasinghe B.M.W.P.K, Influence of Internal Device on Drying Rate of Black Pepper In Spouted Bed, ITUM Symposium 2016, Sri Lanka | |
| 9 | Drying Kinetics of Black Pepper in Spouted Bed Dryer. Proceeding of the HETC Symposium, July 2014, Colombo Sri Lanka | |