GC-MS Spectrum Interpretation Guide for Litsea Cubeba Oil from HiSiaddi

For third-party testing institutions and purchasing laboratories, teaches buyers to read litsea cubeba oil chromatograms and identify adulteration (blending with lemongrass oil, synthetic citral mixing) discrimination methods.

Technical Guide for Citral Extraction from Litsea Cubeba Oil

I. General Provisions

1.1 Scope of Application

This guide standardizes the whole process of preparing crude litsea cubeba oil by steam distillation of fresh / dried litsea cubeba fruits, followed by three mainstream purification processes: vacuum rectification, molecular distillation and sodium bisulfite chemical addition for citral purification. Applicable to large-scale production of food-grade / daily chemical grade citral in flavor factories and forest chemical enterprises.

Applicable Standards:

- QB/T 1789-2014 Citral (Industrial / Daily Chemical Grade)
- GB 1886.191-2016 Food Additive Citral (Food Grade)

1.2 Basic Raw Material Parameters

- Litsea Cubeba Crude Oil: Citral content 55%～80%, containing light fractions (pinene, limonene, linalool), heavy fractions (caryophyllene, esters, high-boiling terpenes), trace moisture and free acids
- Citral: Mixture of Geranial (α) + Neral (β), atmospheric boiling point 228℃, heat-sensitive; prone to oxidation, polymerization and aroma deterioration above 135℃
- Target Product Indicators: First-grade citral ≥95%, high-purity citral ≥97.5%

1.3 Overall Process Framework

Raw Material Pretreatment → Steam Distillation for Crude Litsea Cubeba Oil → Crude Oil Drying & Dehydration Pretreatment → One of Three Purification Processes → Finished Product Filtration, Testing, Storage & Packaging

II. Preparation of Litsea Cubeba Crude Oil (Preceding Process)

2.1 Raw Material Pretreatment

1. Fresh Fruits: Process within 48h after picking, remove branches and leaves, slightly roll to break fruit peel; soak dried fruits in clean water for 2h for rehydration
2. Optional Enhancement: Soak in 1% NaCl solution for 90～120min to improve oil yield; microwave / ultrasonic auxiliary pretreatment for 20～30min to shorten distillation time
3. Feeding Limit: Distillation kettle filling volume ≤75% to prevent overflow

2.2 Negative Pressure Steam Distillation (Recommended Industrial Solution)

1. Process Conditions: Kettle negative pressure 0.03～0.06MPa, water temperature 75～85℃, low temperature reduces citral decomposition
2. Steam Control: Slowly feed saturated low-pressure steam, cooling water temperature ≤25℃ with full immersion coil / shell condenser
3. Oil-Water Separation: Stand for 30min in two-stage vertical oil-water separator, drain lower wastewater and collect upper crude oil; separately recover and re-distill oil sludge
4. Oil Yield Index: Fresh fruit oil yield 3%～4%, dried fruit 2%～6%; crude oil citral 60%～78%

2.3 Crude Oil Pretreatment (Mandatory Before Purification)

1. Drying & Dehydration: Stir with anhydrous sodium sulfate / magnesium sulfate for 30min, filter crystals to moisture ≤0.1% (moisture aggravates high-temperature oxidation during rectification)
2. Neutralization & Deacidification: Wash with a small amount of 5% sodium carbonate dilute solution to remove organic acids, separate liquid to neutral, dry again; acid value ≤1.0 mgKOH/g
3. Filtration: Precision filtration with 100-mesh screen to remove colloids and solid impurities

III. Three Core Citral Purification Processes (Equipment Selection, Standard Parameters, Operation Steps, Advantages & Disadvantages Separated)

Process 1: Intermittent Vacuum Rectification (Mainstream for 70% Small & Medium Domestic Enterprises, Moderate Investment, Stable Continuous Operation)

3.1 Equipment Composition

Rectification kettle, structured packing tower, condenser, vacuum unit (water ring + Roots vacuum pump), reflux distributor, multi-stage fraction storage tank

3.2 Standard Optimal Operating Parameters (Two-Stage Rectification)

Primary Rough Separation (Light Fraction Removal)

- Tower Top Vacuum: 2.66～4kPa (20～30mmHg)
- Kettle Temperature ≤130℃, Tower Top 78～80℃
- Reflux Ratio R=2:1, extract light fractions (pinene, limonene)
- Citral enriched fraction at kettle bottom (citral 85%～90%)

Secondary Rectification (Finished Product Purification)

- Tower Top Vacuum: 0.5～0.67kPa (4～5mmHg)
- Kettle Temperature ≤130℃, Tower Top 85～90℃
- Variable Reflux Ratio: Transition fraction R=5～6; finished product extraction R=3:1; side discharge to collect citral
- Intermittently discharge heavy fractions at kettle bottom for re-extraction in primary rectification

3.3 Complete Operation Flow

1. Feed pretreated litsea cubeba oil into rectification kettle, pump vacuum to target negative pressure, slowly heat with heat-conducting oil jacket
2. Full reflux stabilization for 30min, collect front light impurities after gas-liquid balance inside tower
3. Switch reflux ratio to collect main fraction citral, monitor purity via online GC; switch to transition tank for recovery if purity below 95%
4. Regularly collect kettle residual oil for centralized re-distillation to recover residual citral
5. Cool finished product below 40℃ before filtration and warehousing

3.4 Performance & Applicable Scenarios

- Purity: 95%～97.8%, Total Yield 72%～78%
- Advantages: Mature equipment, large processing capacity, low operation & maintenance cost, no three wastes; suitable for mass production of daily chemical grade products
- Disadvantages: Long heat exposure time, difficult stable production of ultra-high purity (＞98%), slight aroma loss

Process 2: Two-Stage Molecular Distillation (First Choice for High-End Food / Pharmaceutical Grade, Low Temperature Short Path to Protect Heat-Sensitive Substances)

3.1 Principle

Separation by molecular free path under extremely low vacuum, evaporation temperature 50～60℃, material residence time ＜10s, completely avoid citral high-temperature oxidation and discoloration

3.2 Standard Process Parameters (Wiped Film Molecular Distillation)

Primary Molecular Distillation (Light Removal)

- Vacuum: 0.18kPa, Evaporation Temperature 55℃, Cooling Water 12℃

- Wiping Speed 400r/min, Feed Flow Rate 15mL/min
- Distillate: Light terpene impurities; Residue: Citral enriched phase

Secondary Molecular Distillation (Finished Product Extraction)

- Vacuum: 0.05～0.1kPa, Evaporation Temperature 58～62℃
- Distillate: High-purity citral; Kettle Residue: High-boiling heavy fractions
- Orthogonal Optimal Result: Purity 97.88%, Comprehensive Yield 77.2%; Three-stage series reaches 99% purity

3.3 Operation Key Points

1. Preheat crude oil to 40℃ for uniform constant feeding to ensure even liquid film
2. Whole process micro nitrogen protection to isolate air and prevent oxidation
3. Sample GC test every 4h; reduce feed flow rate and increase reflux if light fractions exceed standard
4. Regularly send residual oil to vacuum rectification for citral recovery

3.4 Performance & Applicable Scenarios

- Purity: 97.5%～99.0%, Total Yield 80%～88%
- Advantages: Low temperature short contact, complete aroma retention, low acid value, special for food / pharmaceutical intermediates
- Disadvantages: High one-time equipment investment, small single batch processing capacity, slightly higher energy consumption

Process 3: Sodium Bisulfite Chemical Addition Method (Laboratory / Small-Scale Ultra-High Purity, Gradually Phased Out)

3.1 Reaction Principle

Citral aldehyde group undergoes addition reaction with saturated $NaHSO_3$ to form white crystalline sulfonate salt, filter to separate impurities then hydrolyze with alkali to release free citral

3.2 Operation Steps

1. Prepare saturated sodium bisulfite solution, adjust weak acidity with a small amount of glacial acetic acid
2. Litsea cubeba oil : saturated solution = 1:3 (volume) stir at low temperature for 2～4h to precipitate addition crystals
3. Suction filter, wash crystals with cold water to remove terpene impurities
4. Heat and hydrolyze crystals with 10% sodium carbonate lye, separate layers to obtain crude citral
5. Wash with water, dry, short-path vacuum rectification for refining

3.3 Advantages & Disadvantages

- Advantages: Single-pass purity over 99%
- Disadvantages: Long process, large chemical consumption, high salt-containing wastewater output, yield only 60%～70%, high environmental protection cost; rarely used in large-scale industrial production

IV. Whole Process Quality Control Specifications

4.1 Central Control Test Nodes

1. Warehousing of crude litsea cubeba oil: GC test citral content, moisture, acid value
2. Online gas phase monitoring every 2h during rectification / molecular distillation:
   GC Chromatography Conditions (GB 1886.191): 60m capillary column, programmed temperature rise 80～230℃, area normalization method for citral quantification (sum of geranial + neral)
3. Full-item finished product testing:
   Appearance: Colorless to pale yellow transparent oily liquid
   Odor: Pure lemon fruity aroma, no burnt or oxidized peculiar odor
   Purity: ≥95% (Industrial Grade) / ≥97.5% (Food Grade)
   Refractive Index (20℃): 1.4860～1.4900; Relative Density: 0.888～0.894
   Acid Value, Moisture, Heavy Metals (Lead ≤2mg/kg for Food Grade)

4.2 Key Anti-Oxidation Control Points (Core Control Node)

1. Whole system vacuum sealing, fill nitrogen in rectification / molecular distillation kettles and tanks for protection
2. Strict upper temperature limit for all sections: kettle temperature ≤130℃, molecular distillation ≤65℃
3. Cool finished product to room temperature before filling, light-proof sealed storage below 25℃
4. Add a small amount of food-grade antioxidant (Vitamin E / rosemary extract) to storage tanks

V. Safety Production & Environmental Protection Technical Requirements

5.1 Safety Specifications

1. Litsea cubeba oil and citral are flammable; explosion-proof electrical equipment in workshop, no open flame, full ventilation
2. Regular vacuum equipment leak detection to prevent air infiltration leading to aldehyde spontaneous oxidation

3. Heat-conducting oil system temperature interlock, automatic heating cut-off for over-temperature; equipped with foam fire extinguisher and sand
4. Wear acid and alkali resistant protective gear in chemical addition section, store sodium bisulfite and lye separately

5.2 Three Wastes Treatment

1. Distillation Wastewater: Recover trace residual oil via oil-water separator, biochemical treatment after precipitation to reach discharge standard
2. Rectification Residual Oil: Centralized recovery and re-distillation, no random dumping; can be sold externally as low-cost fragrance raw material
3. High-Salt Wastewater from Chemical Method: Neutralization + membrane desalination, direct discharge prohibited (vacuum distillation process without chemical agents preferred)
4. Residue (Dried Fruit Slag): Fermented organic fertilizer, biomass fuel resource utilization

VI. Equipment Selection Process Comparison Table

表格

Comparison Item	**Vacuum Rectification**	**Two-Stage Molecular Distillation**	**Sodium Bisulfite Chemical Method**
Finished Product Purity	95%～97.8%	97.5%～99%	98.5%～99.5%
Comprehensive Yield	72%～78%	80%～88%	60%～70%
Equipment Investment	Low	High	Medium
Processing Scale	Large-Scale Continuous	Small & Medium Batch High-End	Laboratory Small Trial
Aroma Retention	Good	Optimal	General (Aroma Damaged by Acid & Alkali)
Three Wastes Output	Minimal	No Wastewater	High Salt Wastewater

Comparison Item	Vacuum Rectification	Two-Stage Molecular Distillation	Sodium Bisulfite Chemical Method
Applicable Products	Daily Chemicals, Ordinary Fragrances	Food, Pharmaceutical Intermediates, High-End Fragrances	Special Ultra-High Purity Laboratory Reagents

VII. Finished Product Storage, Packaging & Shelf Life

1. Packaging: Food-grade stainless steel drums / light-proof brown plastic drums, nitrogen sealed, labeled with GB/QB standards
2. Storage Conditions: Cool light-proof warehouse, temperature ≤25℃, air isolation, avoid long-term metal contact
3. Shelf Life: 12 months for original sealed packaging; use within 3 months after opening, regularly recheck purity and acid value

VIII. Process Troubleshooting Guide

1. Low Citral Purity

- Causes: Insufficient vacuum, too small reflux ratio, excessive kettle temperature, incomplete light fraction removal
- Countermeasures: Inspect vacuum pump, increase reflux ratio, reduce kettle temperature, extend light removal time

1. Yellow Finished Product & Sharply Rising Acid Value

- Causes: High-temperature oxidation, air leakage in system, excessive raw material moisture
- Countermeasures: Full system nitrogen protection, dry pretreatment of raw materials, strict temperature control

1. Sharp Drop in Yield

- Causes: Vacuum leakage, insufficient condenser cooling, unrecovered residual oil, excessive molecular distillation feed flow rate
- Countermeasures: Leak detection of equipment, lower cooling water temperature, centralized re-distillation of residual oil, reduce feed flow rate

Would you like me to sort this guide into a printable simplified workshop SOP operation version?