

Characterization and Identification of Essential Oil Components by GC-MS

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Overview

Purpose: Determine the chemical profile for characterization of cinnamon oil, eucalyptus oil, lemongrass oil, peppermint oil, citronella oil, turpentine oil and standard components such as camphor, menthol, thymol, methyl salicylate by examination of TIC and EI / Mass spectral data using the capillary columns and GC/MS.

Methods: Essential oils were analyzed by GC-MS using a split injection onto a capillary column with a stationary phase containing Poly Ethylene Glycol (PEG).

Results: Several oils were analyzed on a quadrupole mass spectrometer. The mass spectrometer was able to provide structural information, matching library spectra for identification. Retention times were stable in TIC, and important active components were identified.

Introduction

Essential oils are fragrant essences of plants, usually volatile oils obtained from an odoriferous, single species of plant. Most essential oils are primarily composed of terpenes and their oxygenated derivatives and are obtained by steam distillation or solvent extraction of different parts of the aromatic plants including the buds, flowers, leaves, seeds, roots, stems, bark, wood, and rhizomes etc. Chemical constituents of volatile oils can be divided into two broad classes: 1.) terpene derivatives formed via acetate mevalonic acid pathway and 2.) aromatic compounds formed via shikimic acid phenyl propanoid route.¹

Essential oils are used in perfumery, aromatherapy, cosmetics, medicine, incense, household cleaning products, and for flavoring food and drinks etc. Variations in climatic conditions, type of soil in which the plant was grown etc. will produce natural variations in the relative distribution of components in essential oils. For example, the same oil extracted from plants grown at different locations can manifest quantitative change in the oil composition.^{1,2} However, certain basic profile pertaining to relative composition or presence of certain key components can help the analyzer to determine the purity of the particular essential oil. Because of high price, many of these premium essential oils are adulterated, diluted, or substituted with poorer quality natural oil or synthetic oils, alcohol, cedar oil, cheap terpenes and low density petroleum fractions. Determining such adulteration is of importance to the users and manufacturers of essential oils. For such reasons, the characterization of the oils through chemical analysis is necessary for production, as well as quality control laboratories. Essential oils are very complex; hundreds of components can be present, and most of the components which confer aroma or flavor may be present only at ppm levels.^{1,2}

Capillary Gas chromatography-Mass spectrometry (GC-MS) proves to be an efficient and precise method for qualitative, as well as quantitative estimation, for almost all combinations of components in such mixtures down to minute traces. The most commonly used capillary column for the analysis of essential oils is Polyethylene Glycol (PEG). Most of the components of essential oils are identified using capillary GC with Mass Detector. The data can be compared to an established profile or fingerprint for that particular essential oil to finally determine the purity of that oil. Certain key components which are valuable to the particular essential oil are often quantified using suitable standards to determine the quality or grade and the value of the essential oil.

Complex essential oils such as peppermint oil, turpentine oil, eucalyptus oil, cinnamon oil, citronella oil, lemon grass oil, thymol, camphor, menthol, and methyl salicylate, etc. are well analyzed using GC-MS. Conventional analytical methods based on GC and GC/MS operate with 30-60 m long columns. High chromatographic efficiencies are required to achieve baseline separation and quantitative determination of the important groups of components. Such methods generally require 30-60 minutes to perform an overall analytical cycle.

This research paper reports an alternative method based on the GC-MS technology implemented on the Thermo Scientific CERES 800 Plus with a Thermo Scientific mass spectrometer which operates with long capillary columns. The results demonstrate high performance in repeatability and accuracy as usually requested in this field.

The real-world examples shown and the comparison with respective conventional analyses prove that reliability and unambiguous characterization of these types of complex samples can be achieved by said GC-MS method.

All of the important components of the essential oils analyzed were identified through the use of a GC-MS technique. The injections were performed using a manual injection technique. "Fingerprinting" of plant or food extracts can be valuable in quality control of products, as well as in identification of adulterated commercial products. GC-FID can be a good starting point in this typical application field, however, sometimes unambiguous qualitative identification of some key components becomes extremely important. GC-MS with electron impact ionization (EI) offers a powerful tool for separation and identification with EI-MS library facility, which is a much more efficient technique than GC-FID for such critical requirements. Analytical challenge is high in the case of essential oils, particularly for the identification of various isomers, hence EI-MS library searches need to be complemented by retention time information in TIC chromatograms. Additional characterization can be also achieved by using a chiral column using the same GC-EI-MS technique³ if the analyzer wants to determine certain optical isomers of essential oil components.

Methods

GC Configuration

For this application, the Thermo Scientific CERES 800 Plus gas chromatograph with a Thermo Scientific mass spectrometer GC-MS is configured with a SSL injector. The assembly allows the instrument to achieve heating rates up to 50 °C/min, and fast cooling times occur rapidly, as well, taking about five minutes to return to 50 °C from 450 °C at 22 °C compared to about 4 minutes in conventional mode.

Thermo Scientific Chrom-Card software was used to acquire consecutive runs in EI modes for different essential oils. Retention times in TIC were also used for the characterization. To avoid overloading the GC column and the MS detector, the essential oils were diluted 50:1 in ethanol and then split 80:1 in the injector.

GC and MS Conditions

Column: Poly Ethylene Glycol (PEG), 60m x 0.32 mm ID x 1.0µm film, GC: Inject 0.2 µL, Split 80:1, He flow 0.5 mL / min, Column 45°C, 8 min hold, ramp to 230°C @ 8°C/min- hold 10 min. MS: 220 °C Interface temperature: 200 °C Scan Range EI: 30 - 300

Results

TIC chromatograms and EI spectra were acquired for peppermint oil, turpentine oil, eucalyptus oil, cinnamon oil, citronella oil, and lemon grass oil.

Figures 1 to 6 illustrate the TIC Chromatograms and EI/MS spectrum for cinnamon oil, eucalyptus oil, lemongrass oil, peppermint oil, citronella oil, turpentine oil and standard components such as camphor, menthol, thymol, methyl salicylate.

Cinnamon oil: Cinnamon oil is a volatile oil derived from the leaves and twig of Cinnamomum cassia Nees. The main constituent of the oil is cinnamic aldehyde. The other constituents are, citral, pinene, limonene, terpenes benzyl alcohol and eugenol etc. Cinnamon oil is used as a flavoring agent and also used as antiseptic and carminative.¹

Citronella oil: Citronella oil is a volatile oil derived from the herb of Cytopogon winterianus Jowitt. The main constituent of the oil is Citronellal. The other constituents are, geraniol, citronellol, citronellol acetate, limonene, terpineol etc. The oil is used in perfumery and soap industry. It is also used as a mosquito repellent.¹

Eucalyptus oil: Eucalyptus oil is a volatile oil derived from the fresh leaves of Eucalyptus globulus Labillardiere. The main constituent of the oil is Cineol (Eucalyptol). The other constituents are, cinnamaldehyde, pinene, limonene, terpinen, cymene etc. It is extensively used as a flavoring agent and in pharmaceutical preparations and also used as antiseptic, diaphoretic and expectorant.

Lemon grass oil: Lemon grass oil is a volatile oil derived from the herb of Cytopogon citratus DC. The main constituent of the oil is Citral. The other constituents are, pinene, limonene, terpenes benzyl alcohol, menthadiene and camphene etc. The oil is used in perfumery and soap industry.

Peppermint oil: Peppermint oil is obtained from the fresh over-ground parts of the flowering plant of Mentha piperita Linne. The main constituents of the oil are menthol and menthone. The other constituents are, menthyl acetate, pinene, limonene, terpenes etc. The peppermint oil is used as flavoring agent, carminative, stimulant, counterirritant, and gastric stimulant. It is extensively used as a flavoring agent in pharmaceutical and other consumer products such as tooth paste, mouth washes, chewing gums, gargles, cough drops, candy, confectionary and perfume

Turpentine oil: Turpentine oil is obtained from the Pinus polustris Miller. The main constituent of the oil is Terpinene. The other constituents are, limonene, carene (or methadiene) and camphor etc. It is used as antiseptic, insecticide and solvent for shoe polish, furniture polish, paints and waxes.

Figure 1. GC-MS: TIC Profile CINNAMON OIL and EI Spectrum of Cinnamaldehyde

