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Technical Report

Analysis of the Yerba Mate Volatile Composition Using Solid Phase Microextraction Comprehensive 2D GC–quadMS

HS-SPME GC×GC–quadMS method for the analysis of yerba mate volatile fraction

Flavio A. Franchina[1], Peter Q. Tranchida[1], Paola Dugo[1, 2], Luigi Mondello[1, 2]

Abstract:

The present research is focused on the use of a head-space solid-phase microextraction-comprehensive 2D GC methodology, in the analysis of the volatile fraction of yerba mate. A rapid-scanning quadrupole mass spectrometer (quadMS), employed as a detection system and operated at a 25 Hz scanning frequency, supplied high-quality mass spectra. The effectiveness of the 3D comprehensive 2D GC-quadMS experiment is highlighted.

Keywords: comprehensive 2D GC, quadrupole mass spectrometry, solid-phase microextraction, yerba mate

1. Introduction

Yerba mate (mate) is a tea-like beverage widely consumed in South American countries as a tonic and as a stimulant to reduce fatigue. The drink is obtained through the infusion of the leaves and stems of the perennial tree *Ilex paraguariensis*.

Mate is also used in popular medicine and is included in commercial herbal preparations. Indeed, several health benefits are known in the literature, such as hepatoprotective, central nervous system stimulant, hypocholesterolemic, antirheumatic, anti-thrombotic, antiinflammatory, and antioxidant effects. Despite such proven health benefits, epidemiological studies have reported negative effects related to mate consumption, correlated to the presence of several contaminants, in particular polycyclic aromatic hydrocarbons (PAH) [1].

The full elucidation of the volatile composition of a natural food matrix can be a cumbersome task, using single-column GC–MS; although MS detection can be very useful in the reliable identification of overlapping peaks (single ion monitoring, extracted ions, deconvolution processes, *etc.*), it is certainly desirable to achieve a high-resolution GC separation step. Unfortunately, 1D GC often fails to provide a satisfactory analytical result, even on moderately complex samples.

In the present article, GC×GC in combination with a rapid-scanning quadrupole MS was exploited to investigate the volatile fraction of yerba mate (Fig. 1a–c). Automated SPME was employed to extract and concentrate volatile compounds from the head-space of a Brazilian commercial sample.

2. Experimental

The C_7–C_{30} alkane mixture was kindly provided by Sigma-Aldrich (Milan, Italy).

The mate sample was purchased from a local market in Rio Grande do Sul (Brazil).

The SPME triple phase 50/30 µm fiber (divinylbenzene/carboxen/polydimethylsiloxane) was purchased from Supelco (Milan, Italy), and was appropriately conditioned before use. A Shimadzu AOC-5000 autosampler (Kyoto, Japan) was used for the HS-SPME operations. Briefly, 150 mg of dry mate sample were introduced in a 5 mL vial. The sample was heated at 80°C for 15 min (pre-incubation) and agitated (using clock-wise–anticlockwise alternate rotation) at 500 rpm.

The fiber, previously cleaned by thermal desorption, was then exposed in the HS for 60 min at the same temperature and agitation speed. After this process, the fiber was thermally desorbed in the GC injection port for 1.0 min at 250°C in the splitless mode (after 1 min, a 100:1 split ratio was applied).

The Shimadzu GC×GC system consisted of:

- two GC-2010 gas chromatographs
- a GCMS-QP2010 Ultra quadrupole mass spectrometer
- an AOC-5000 autosampler
- a loop-type cryogenic modulator

Softwares used:

- GCMSsolution version 2.71
- ChromSquare version 2.0

1 University of Messina, Italy
2 Chromaleont S.r.l.

D1 column	: SLB-5ms 30 m × 0.25 mm ID × 0.25 µm d_f [silphenylene polymer virtually equivalent in polarity to poly (5% diphenyl/95% methylsiloxane], + 2 m × 0.25 mm ID uncoated column to create a double-loop necessary for cryogenic modulation.
D2 column	: Equity-1701 [poly (14% cyanopropylphenyl/86% dimethyl) siloxane] 1.5 m × 0.1 mm ID × 0.1 µm d_f,. Inj. temp.: 280°C; Inj. press.: 165.9 kPa.
GC1 oven temp	: 50°C (hold 2 min) to 270°C (hold 15 min) at 3°C/min.
GC2 oven temp	: +5°C respect to GC1.
Modulation time	: 6 sec.
MS parameters	: full-scan mode (sampling frequency 25 Hz) with a scan speed of 10,000 amu/s (*m/z* 40–360); interface and ion source temperatures were 250 and 200°C, respectively.
MS ionization mode	: electron ionization (70 eV). The MS library used for spectral matching was the FFSNC 2.0.

3. Results and discussion

The GC×GC–quadMS method was developed with the aim of unravelling, in a satisfactory manner, the mate volatile profile. The experiments were carried out setting the a +5°C temperature offset in the second GC oven, resolving the slight degree of wrap-around observed. The rapid-scanning quadMS instrument was operated at a 40–360 *m/z* mass range and generated 25 spectra/s, which was more than sufficient for qualitative aims and was in most cases nearly sufficient for proper peak re-construction (on average, 7–8 data points per peak were attained). Moreover, mass spectral variation was measured across several single 2D peaks (peak skewing) and was found to be negligible.

The optimized SPME-GC×GC–quadMS method enabled the separation of a greatly increased number of peaks: over 1000 were counted on the 2D space plane (Fig. 1a–c). As it can be seen, a considerable amount of the available 2D space was exploited for analyte separation. A dual-filter process (similarity and LRI) was applied during the GC×GC–quadMS data processing; two hundred and fortyone compounds were tentatively identified, with satisfactory library matches and through the application of a rather wide ±20 LRI range; a less restrictive LRI range was applied to compensate the effects of the second polar column. The tentatively identified compounds can be found in ref. 2.

It is noteworthy, that several contaminants were found in the mate sample; in particular, a significant presence of hydrocarbon isomers, with high similarity matches (95%), was determined (many alkanes were not assigned due to the lack of related standards): a classical petrochemical-like hydrocarbon GC×GC band is present in Fig. 1b. The contemporary presence of several PAHs (*see* ref. 2) supported the hypothesis that the sample had been contaminated by some form of mineral oil. However, the drying process can be another important source of PAHs (in particular, parent PAHs), if combustion smoke enters directly in contact with the matrix.

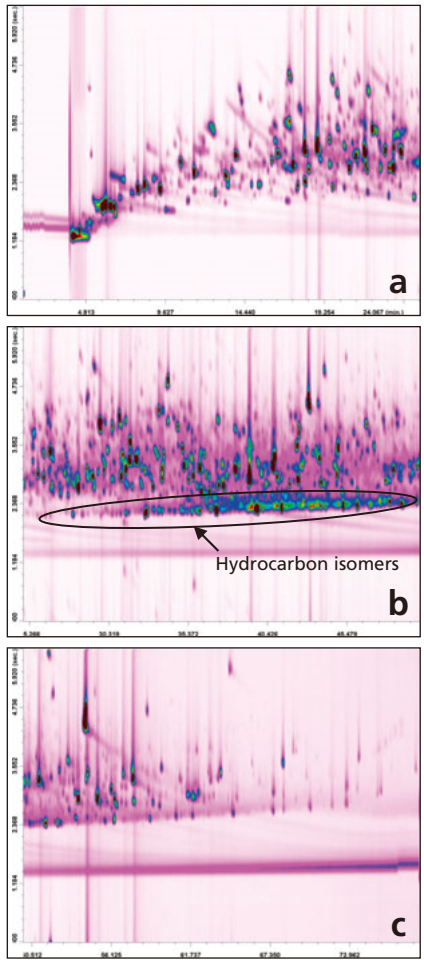

Fig. 1 (a–c). Three TIC HS SPME-GC×GC–quadMS expansion, highlighting the complexity of mate.

4. Conclusions

The HS SPME-GC×GC–quadMS method, developed in the present study, showed a great improvement in terms of separation and number of identified peaks (compared to a GC–quadMS approach). More extensive research should be directed to risk assessment studies related to mate production, considering all steps from harvesting to commercialization. As was seen, several harmful contaminants were found in the sample. The presence of high quantities of aliphatic hydrocarbons and several light PAHs would lead to a strong hypothesis of mineral oil contamination.

References

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