Comparison of Vac-HS-SPME fiber and HS-SPME followed by GC-MS for ripening induced changes in tomato puree analysis

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ABSTRACT

This application note presents the use of vacuum-assisted headspace solid phase microextraction (Vac-HS-SPME) for the analysis of volatile organic compounds in tomato fruits. A comparative study between Vac-HS-SPME and regular HS-SPME was conducted, investigating the effects of temperature and extraction time on 29 target analytes. Compared to the standard methodology, Vac-HS-SPME enabled the detection of additional analytes and demonstrated higher extraction efficiencies.

INTRODUCTION

Tomato (*Solanum lycopersicum* L.) is one of the most widely consumed vegetables worldwide. Its characteristic flavor results from a complex balance of sugars, acids, and volatile organic compounds (VOCs), many of which are formed during ripening. Monitoring these volatiles is crucial for understanding flavor development and optimizing harvest timing. Headspace solid phase microextraction (HS-SPME) coupled to gas chromatography–mass spectrometry (GC-MS) is a preferred solventless method for this purpose. Vacuum-assisted headspace SPME (Vac-HS-SPME) offers enhanced extraction efficiency for semi-volatile analytes at reduced temperatures and shorter times. This application demonstrates the potential of Vac-HS-SPME for sampling tomato volatile profiles.

EXPERIMENTAL

Table 1 describes the final optimized Vac-HS-SPME and standard HS-SPME methods, respectively. Table 2 gives details on the GC-MS method.

Table 1. Optimized Vac-HS-SPME and regular HS-SPME method.

Sample:	4 g fresh tomato puree in 20 mL vial, ExtraTECH Vac-closure (PN: 20-101)
Air- evacuation	30 sec before sample introduction, pumping unit with 7 mbar ultimate vacuum
SPME Fiber:	DVB/CAR/PDMS, 50/30 µm/ 2 cm
Incubation:	15 min, 40 °C (Vac) or 60 °C (HS), 250 rpm agitation
Extraction:	45 min, 40 °C (Vac) or 60 °C (HS), 250 rpm agitation

Table 2. GC-MS method.

Column:	DB-5MS (30 m×0.25 mm i.d.×0.5 µm df)
Oven:	40 °C (3 min), 5 °C/min to 185 °C, 30°C/min to 290°C (8 min)
Inj. Temp.:	250 °C
Carrier Gas:	Helium, 1 mL / min constant flow
Detector:	MS, EI 70 eV, scan 35-450 m/z range
Injection:	splitless
Desorption:	5 min at 250 °C

RESULTS

Initially, the volatile fraction of fresh red ripe puree from Ailsa Craig tomato fruits was evaluated. The extraction proceeded for 60 minutes at 60 °C using Vac- and regular HS-SPME. Table 3 summarizes the 29 identified compounds based on their chemical class (aldehydes, alcohols, ketones, phenols, esters and others).

The performance of Vac-HS-SPME and HS-SPME was then evaluated at two different temperatures (40 and 60 °C) and for varying extraction times (15, 30, 45 and 60 min). The sampling temperature 40 °C represented the temperature during tomato chewing when volatiles are released, while 60 °C is a sampling temperature commonly reported during regular HS-SPME. Figure 1, shows the extraction time profiles for the target compounds at each sampling temperature. As seen, Vac-HS-SPME showed improved extraction efficiency compared to regular HS-SPME, detecting nine additional analytes at 40 °C and three more at 60 °C.

During method optimization, increasing the sampling temperature and extending the extraction time improved performance under both pressure conditions, although this improvement was more pronounced at atmospheric pressure.

Table 3. List of identified compounds in tomato puree using Vac-HS-SPME method.

Coding	Compounds	Coding	Compounds
1	Hexanal	16	(E)-2-Decenal
2	(E)-2-Hexenal	17	Citral
3	1-Hexanol	18	(E,Z)-2,4-Decadienal
4	(E)-2-Heptenal	19	(E,E)-2,4-Decadienal
5	Benzaldehyde	20	Eugenol
6	6-Methyl-5-hepten-2-one	21	(E)-Geranylacetone
7	2-Pentyl-furan	22	(E)-β-Ionone
8	Octanal	23	Pseudoionone
9	2-Isobutylthiazole	24	Farnesyl acetone
10	(E)-2-Octenal	25	Methyl palmitate
11	(E)-2-Octenol	26	Ethyl 9-hexadecenoate
12	Guaiacol	27	Ethyl Palmitate
13	(E)-2-Nonenal	28	Ethyl Linoleate
14	1-Nonanol	29	Ethyl Oleate
15	(E,E)-2,4-Nonadienal		

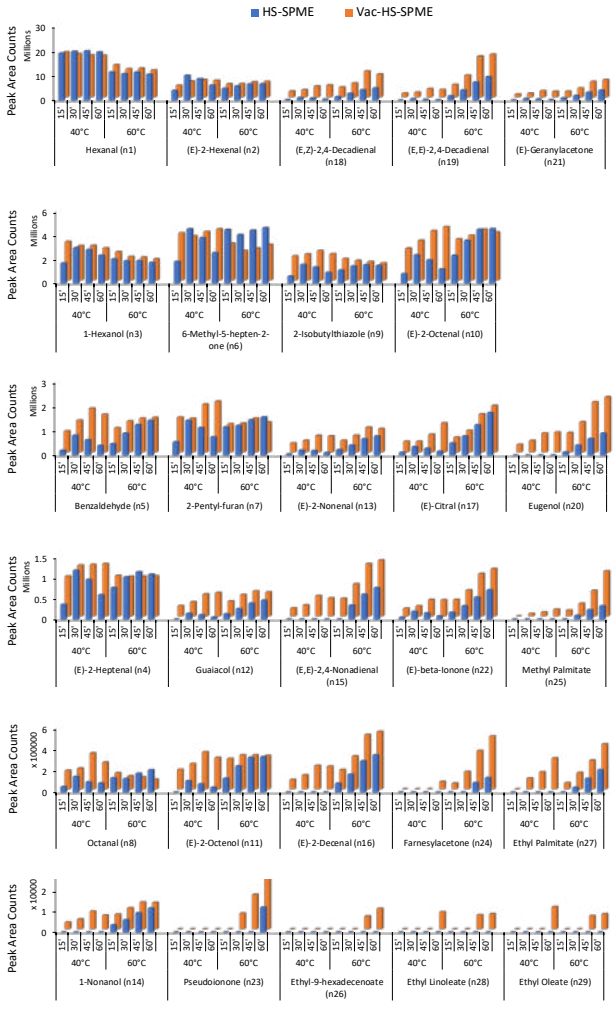

Figure 1. Extraction time profiles (15-60 min sampling) for target compounds in red ripe tomato puree. The data is obtained under regular (HS-SPME; blue bars) and reduced total pressure (Vac-HS-SPME; orange bars) at 40 and 60 °C. Analytes are categorized based on analytical signals rather than presented in ascending coding numbers.

Under vacuum, extraction was markedly enhanced, and compared to the regular methodology, Vac-HS-SPME resulted in the detection of nine additional analytes at 40 °C (#14-#16, #20, #24, #25, #27-#29) and three at 60 °C (#26, #28, #29).

Figure 2 compares chromatograms obtained under (i) vacuum and (ii) atmospheric pressure after 45 min of extraction at 40 °C. These conditions were identified as optimal for Vac-HS-SPME, providing efficient extraction without requiring higher temperatures. In contrast, HS-SPME required an increase in sampling temperature to 60 °C to reach a similar level of extraction performance.

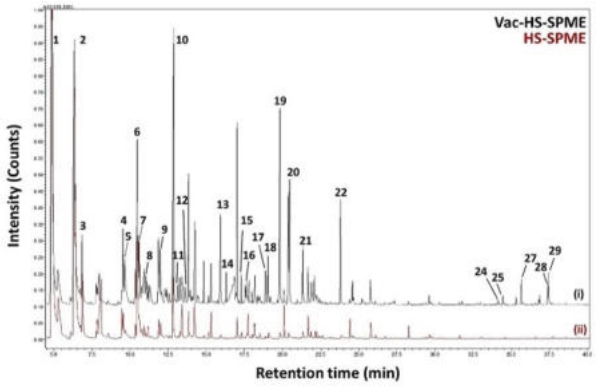

Figure 2. Comparison of chromatograms obtained using (i) Vac-HS-SPME (black, upper chromatogram) and (ii) HS-SPME (fuchia,bottom chromatogram) for sampling the volatile profile of fresh tomato puree. Extraction parameters: 60 min of sampling at 40 °C. Compound coding as in Table 3. Compounds 23 and 26 were detected with Vac-HS-SPME when a higher temperature (60 °C) was applied.

CONCLUSIONS

Vac-HS-SPME sampling increased both the quantity and diversity of analytes detected, revealing nine additional compounds at 40 °C and three more at 60 °C compared with atmospheric pressure. Optimization showed that 45 minutes at 40 °C under vacuum yielded extraction efficiencies equal to or better than those of HS-SPME at 60 °C, allowing more sensitive and comprehensive profiling of aroma-related volatiles during ripening.

REFERENCE:

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