Comparison of Headspace Techniques for Sampling Volatile Natural Products in a Dynamic System

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Commonly used dynamic sorption techniques for collecting biologically active volatile compounds have been compared. Solid phase microextraction (SPME) using two types of fibers (polydimethylsiloxane, PDMS, 100 μm, and carbowax/divinylbenzene, CW/DVB, 65 μm) was compared to purge and trap methods (Porapak Q, Tenax TA and charcoal) and a technique based on absorption in methanol in a cooling bath. Sampling was done in a stream of purified air (20 ml/min) in a closed and temperature-regulated (27 °C) glass tube, passing over a capillary tube containing a hexane solution of tridecane, heptadecane, 1-octen-3-ol, 1-hexadecanol, ethyl tetradecanoate, α-pinene, linalool, terpinen-4-ol, *cis*-verbenol, verbenone, β-caryophyllene, *E,E*-farnesol, and geranylgeraniol. With all of the methods, the sampling was performed for a period of 30 min before extraction and analysis was done on a GC-FID system. In general, SPME gave a higher response for all compounds except for α-pinene, which was only extracted by the CW/DVB fiber. Purge and trap methods and methanol absorption gave the same response for all substances extracted. None of the methods extracted hexadecanol and geranylgeraniol under the conditions used. However, the SPME equipped with the PDMS coating extracted heptadecane, *E,E*-farnesol and ethyl tetradecanoate. Our results show that SPME, when selecting the fibers to fit the polarity and volatility of the compounds, is an outstanding extraction method compared to purge and trap and methanol absorption, especially for a qualitative analysis. The best conditions for storing fibers exposed to compounds of high volatility were at low temperatures (6 °C) in sealed vials, while the worst way was to leave the exposed fiber unprotected at room temperature (22 °C). The dynamic sampling system was effectively tested on a fruiting body of a polypore fungus (*Ganoderma applanatum*) emitting 1-octen-3-ol, and again SPME showed to be the most sensitive technique.