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Short communication

Vapor-phase analysis of isobutyl acetate, isopropyl acetate, *n*-propyl acetate and their respective alcohols using solid-phase microextraction–gas chromatography with a mass selective detector

Corey W. Radtke[a,b,*], Catherine L. Polydore[b], Stephen B. Cox[b], George P. Cobb[b]

[a] *Biotechnology Department, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415, USA*
[b] *The Institute of Environmental and Human Health, Texas Tech University, Lubbock, TX 79416, USA*

Abstract

A solid-phase microextraction (SPME)–GC–MS method for three esters and the corresponding alcohols was tested for responses in accuracy, within-run precision (repeatability), and between-run precision (reproducibility) due to individual operators, individual analysis days, and differing analyte concentrations. At 5 ppm (v/v) [ppmv], three of the six analytes showed significant ($p < 0.05$) operator effects, while five of six analytes gave a significant effect due to the days of analysis. At 20 ppmv, five of the six analytes gave significant operator and daily effects. At 100 ppmv, all the analytes showed significant daily effects but no operator effects were observed. The repeatability was concentration dependent, with all six analytes combining for an average RSD of $12.1 \pm 6.1\%$ at 1 ppmv, becoming most precise at 50 ppmv at $1.01 \pm 0.45\%$, then increasing at 100 ppmv to $4.12 \pm 1.88\%$. The contributors to error trended as: concentration > daily effects > operator.
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1. Introduction

Solid-phase microextraction (SPME) for the analysis of volatile analytes has many advantages and is well established. SPME coupled with GC–MS provides a powerful investigative and quantitative tool which has been employed for many diverse disciplines including the analysis of volatile constituents in air [1,2], flavors [3–5] and volatiles from pharmaceuticals [6], plants [7], fungi [8–10], and bacteria [11,12]. By screening volatiles from these sources, a wide range of compounds may be found and quantified.

The between-run precision (reproducibility) and within-run precision (repeatability) [13] of SMPE–GC–MS has been questioned for reasons including fiber to fiber variation [14,15], matrix effects [3,5,14], fiber aging [14], temperature variations [16], and general changes in experimental conditions [3]. For example, one group reported that "poor reproducibility typically plagues SPME," in a headspace study quantifying derivatized tributyltin [17]. In response, they then developed an isotope dilution method which improved the reproducibility. Because individual analytes have different partitioning properties, using isotope dilution for each analyte should provide the best quality data possible, but this practice would need to be weighed against the increased costs.

Day to day effects on SPME precision have been quantified and reported. Using an ion trap MS and a polydimethyl siloxane (PDMS) fiber, with seven replicate injections, the mean relative standard deviation (RSD) for eight compounds was 2.3% for a given day, and increased to 3.1% for the pooled data by one analyst on the same instrument over three consecutive days [6]. In this system there was little difference between repeatability and reproducibility, in contrast to other reports. Consistent stirring was reported to be one of the most important factors for better precision.

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* Corresponding author. Tel.: +1 208 526 5186; fax: +1 208 526 0828.
E-mail address: radtcw@inel.gov (C.W. Radtke).

A study on flavor analysis using PDMS with GC–MS reports the RSD ranged from 0.5% for phenylethyl alcohol to 18.3% for triacetin and 17.8% for ethyl acetate [3]. The authors of this study observed an average RSD of 7% is generally acceptable in trace organic analysis, revealing that of the 22 compounds reported, 7 exhibited an unacceptably high variation. This is similar to the repeatability reported using a polyacrylate fiber, where the average RSD was 11% for acetone, ethanol, and 13 fatty acids [4].

The repeatability using SPME is reportedly better than charcoal tubes. It was found that charcoal tubes (National Institute for Occupational Safety and Health [NIOSH]-1550) RSDs ranged from 16 to 41% for C_5–C_{15} alkanes, compared to 2–6% for $100\,\mu m$ PDMS coating SPME sampling [1]. In comparisons using benzene, toluene, ethylbenzene and xylene (BTEX) compounds, the accuracy was not significantly different in charcoal versus SPME, while SPME was more precise, resulting in RSDs of 1.6, 3.8, 3.9, and 4.8%; much tighter than the corresponding charcoal tube 5.0; 6.3; 7.1; and 19% RSDs, respectively, for benzene, toluene, ethylbenzene, and p-xylene standards. There was a minimum 10-fold reduction in sampling time for air monitoring of SPME versus NIOSH charcoal tubes.

Further, a manual headspace SPME method has been compared with an automated static headspace method for alcohols and esters in beer, using 1-pentanol as an internal standard [19]. Manually using polyacrylate SPME with GC-flame ionization detection (FID), the RSD in prepared standards ($n = 7$) ranged from 1.80 to 10.80%, with a mean of 5.5%. Similarly, the automated static headspace method ranged from 1.3 to 10.0% RSD, with a mean of 3.1%. In a beer matrix, the manual SPME method again compared closely, with a range of 0.31–6.8% and a mean of 3.0% ($n = 3$), compared to the automated static headspace method, which produced a RSD range of 0.32–10.2%, with a mean of 2.5%. The repeatability of the manual SPME method in this report therefore compares closely with the automated headspace method.

Rocha et al. [5] found similar precision in an investigation on the effect of matrix volatile composition on relative response factors (RRFs) of flavor components in a wine model using polyacrylate SPME fibers. The RSD ranged from 1.5% for 3-methyl-1-butanol to 12% for ethyl octanoate. Interestingly, a temporal replacement effect was found, with ethyl decanoate displacing both ethyl octanoate and ethyl hexanoate.

Namiesnik et al. [16] reported that accuracy is effected by the temperature and humidity of the SPME binding matrix. This is important in that the precision may not be affected, but the accuracy might. The group reports that compared to dry SPME sampling, at 92% humidity ($20\,^\circ C$) there were quantification losses about 70% for chlorobenzene, 60% for toluene and p-xylene, and 30% for CCl_4 and n-decane. This factor may not plague precision but might become a problem with accuracy in gas samples from the field, as gas calibration standards are typically made dry, while the environmental samples may have large differences in humidity.

From these studies, it becomes apparent that finding the unique variation for each specific application and possibly for each run would be a good practice. The analytical reproducibility and repeatability of three small esters and their associated alcohols is the focus of this paper. We developed a method for monitoring soil gases in a subsurface remediation application. Specifically our goal was to develop a method to quantify three small esters and their corresponding alcohols routinely, yet leave room for qualification and further quantification of TICs in the soil gas samples. As such, a SPME preconcentration was performed before analysis by scanning GC–MS. In our field remediation system, we predicted a need to analyze higher concentrations of esters than the corresponding alcohols, and therefore chose polyacrylate (PA) fibers for the increased sorption of alcohols compared to PDMS fibers [20], while still being acceptable for esters, lessening potential abundance problems in the analysis. The PA fiber sorbed for 15 min is reportedly optimal for precision over a range of volatiles [21]. Carboxen SPME fibers were used occasionally for qualitative screens, but were not used for quantification due to the inherent uncertainty of matrix effects in our field samples, the competition for sites on this style of fiber, and the high expected concentrations of all analytes expected in our application. We statistically tested our data to determine if individual operators and daily intra-operator variances effected quantification of several volatile compounds over a 4-day interval. Concentration dependent effects on repeatability were assessed, and the reproducibility of the method over six months is also presented.

2. Experimental

2.1. SPME

The $85\,\mu m$ polyacrylate fibers (Supelco no. 57318) with a manual SPME fiber holder (Supelco 57330-U) were used with a 15 min sorption time at room temperature and a 2.0 min desorption time at $280\,^\circ C$. The high inlet temperature was chosen to ensure the recovery of heavier volatile and semivolatile compounds, to complement the scanning MS detection system for the detection of a wide range of analytes [22–24]. Initially, we determined that target analytes were stable under these conditions.

2.2. GC–MS

We used an Agilent 6890 Series GC System with an Agilent 5973 Network Mass Selective Detector, and an HP-624 Special Analysis Column (HP19091V-402 capillary $25.0\,m \times 200\,\mu m$ ID $\times 1.12\,\mu m$ nominal). Helium was the