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Background

Food preservation by humans dates to 20,000 BC, with the first evidence of pickling dating to ancient Greek and Egyptian cultures.[1] Pickling techniques have since been practiced and evolved by cultures around the world, including the early pioneer settlers of 19th century South Dakota.[1] Inspired by the potential to obtain new insights into the food preservation techniques and environmental conditions of early South Dakota, and to address the lack of studies of historical foods, we developed a simple "AtmosBag"-based SPME sampling method for profiling the volatile constituents of homemade preserved foods prepared in Moody County, South Dakota during the period 1950-1953. We also serendipitously detected and then quantified the toxic plasticizer bisphenol-A (BPA) in these preserves.

Methods

- 31 jars of preserves prepared during the period 1950-1953 were obtained from the basement of the Bowen Family home of Moody County, South Dakota (Fig. 1).
- To develop an analytical method, store-bought pickle and cherry preserves were spiked with pure BPA, sealed in an "AtmosBag" with the SPME device, and sampled for 30, 60, 120, 240, and 360 minutes to determine the optimum sampling time for aroma volatiles and spiked BPA (Fig. 1).
- The 1950s preserves were then sampled for 120 minutes in triplicate with SPME, followed by direct gas chromatography-mass spectrometry (GC-MS) analysis of adsorbed volatiles (Fig. 1).
- Volatile compounds were identified by comparison of measured mass spectra to reference spectra in the NIST Mass Spectral Library.
- Volatile compounds were sorted into classes as follows: acids (ACD), alcohols (ALC), aldehydes (ALD), aliphatic hydrocarbons (ALH), aromatic hydrocarbons (ARH), esters (EST), ethers (ETH), halogen-containing (HAL), ketones (KET), nitrogen-containing (NIT), sugar alcohols (SUG), sulfur-containing (SUL), terpenoids (TER).

Figure 1. Representative images of the late 19th century-constructed basement housing the early 1950s preserves, SPME sampling of store-bought preserves and 1950s preserves inside the argon-filled AtmosBag, and direct injection of the SPME device into the GC-MS for analysis of sampled volatiles.

Findings

- Optimum SPME sampling time was determined to be 120 minutes for aroma volatiles and spiked BPA in the store-bought preserves (Fig. 2).
- The SPME method sampled spiked BPA from store-bought preserves with excellent efficiency and reproducibility (Fig. 2)
- Volatile profiles of store-bought cherries were dominated by ACD and ALD compounds, while pickles were predominated by ALH, ETH, and TER compounds (Fig. 2).
- Volatile profiles of the 1950s preserves varied widely in number of compounds detected, intensity, and class composition (Fig. 3).
- BPA was detected in the volatile profiles of all preserves and all sampling replicates at levels ranging from below the quantitation limit (1 µg/kg) to 19.2 µg/kg (Fig. 4).
- BPA was below quantitation levels in samples 20 and 28 (sweet pickle & apricots), likely due to being sealed with lids lacking BPA-treated plastic liners (Fig. 4).
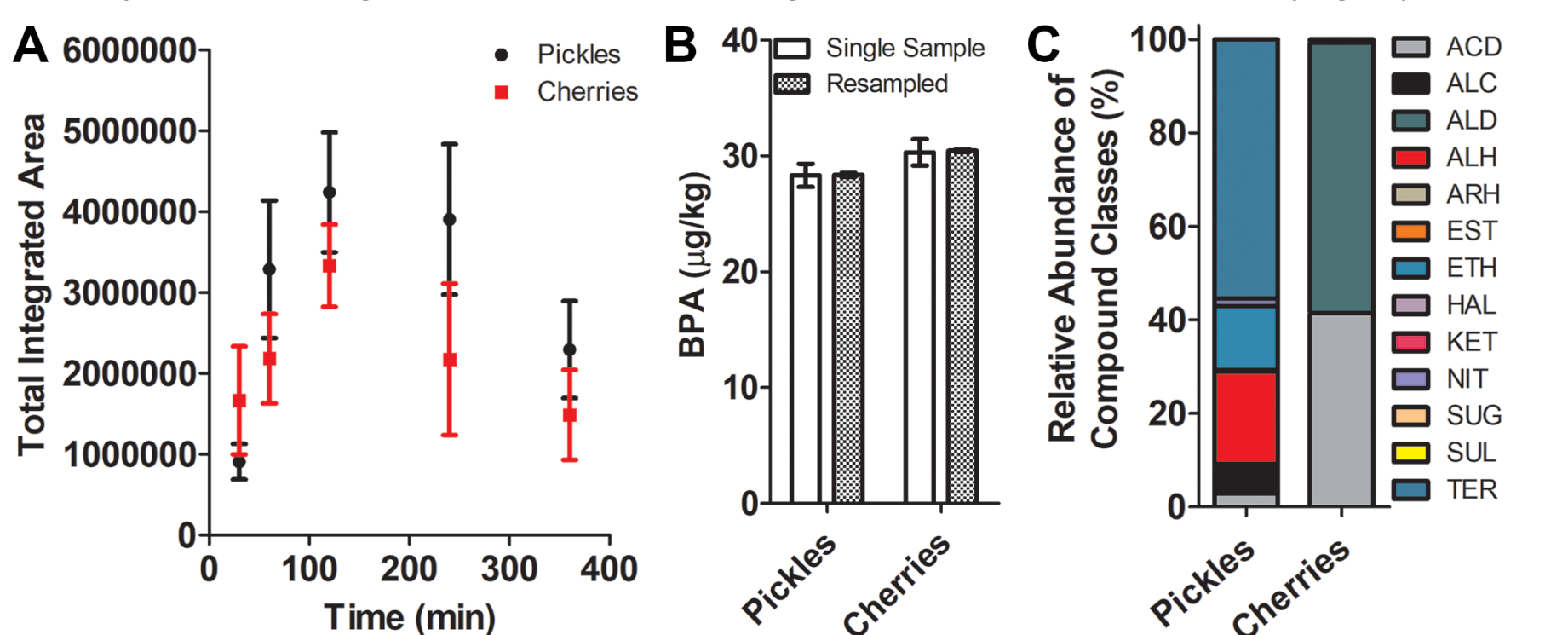

Figure 2. Total integrated chromatographic area for volatiles detected in the store-bought preserves with sampling time (panel A); Concentrations of spiked BPA detected in store-bought preserves after 120 minutes of SPME sampling from single jars (N=5) and triplicate 2-hour samplings of each of those jars (panel B); Relative abundance of compound classes detected (as percent of total) in store-bought preserves (panel C).

Findings Continued

- BPA levels were consistent over all samples and sampling replicates (Fig. 4).
- BPA levels were in the range of those reported to induce endocrine disruption effects in biochemical assays.
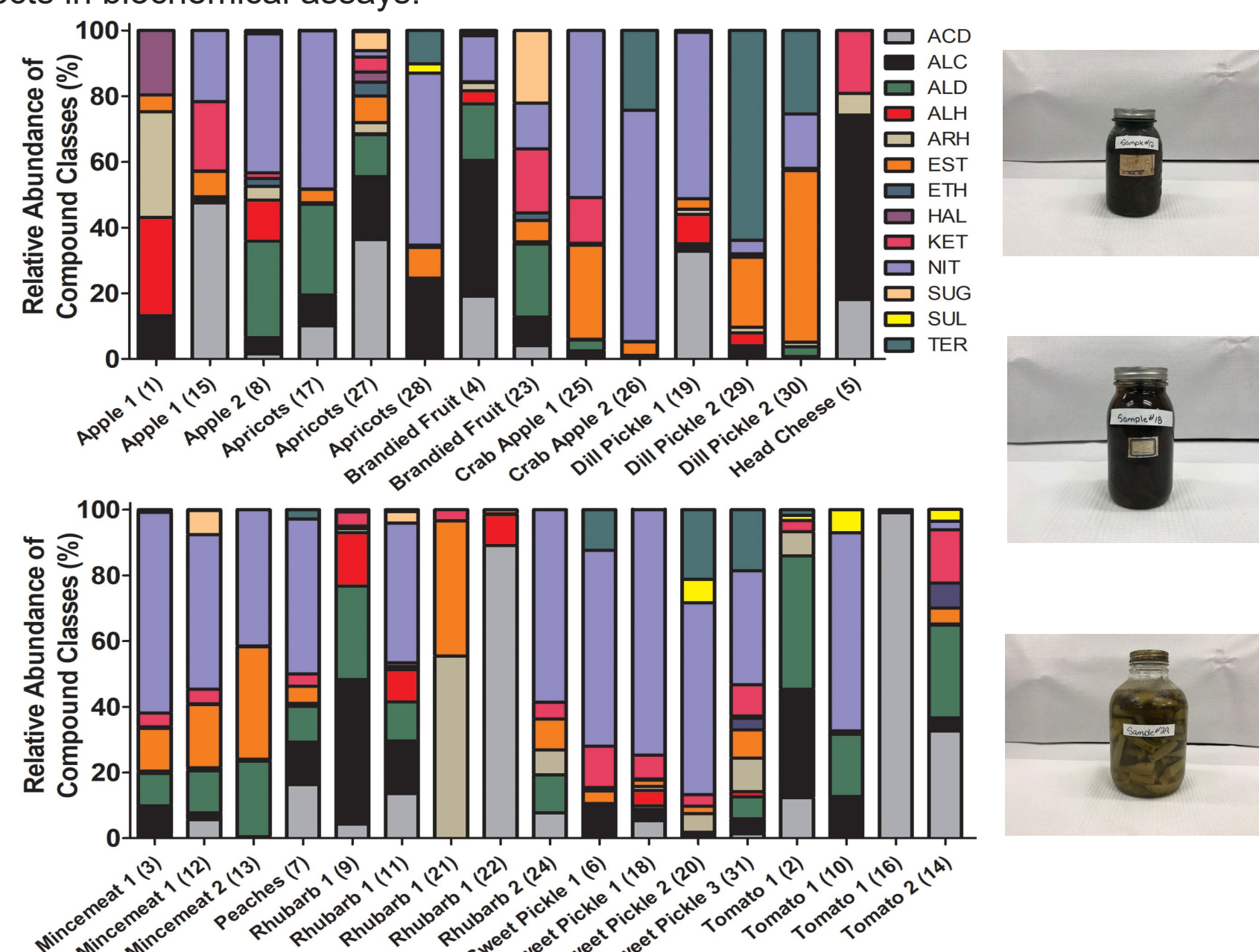

Figure 3. Relative abundance of compound classes (as percent of total) detected with SPME in the 1950s preserves. Samples are ordered alphabetically by type with the sample number in parenthesis. Compound class abbreviations are defined in the Methods section.
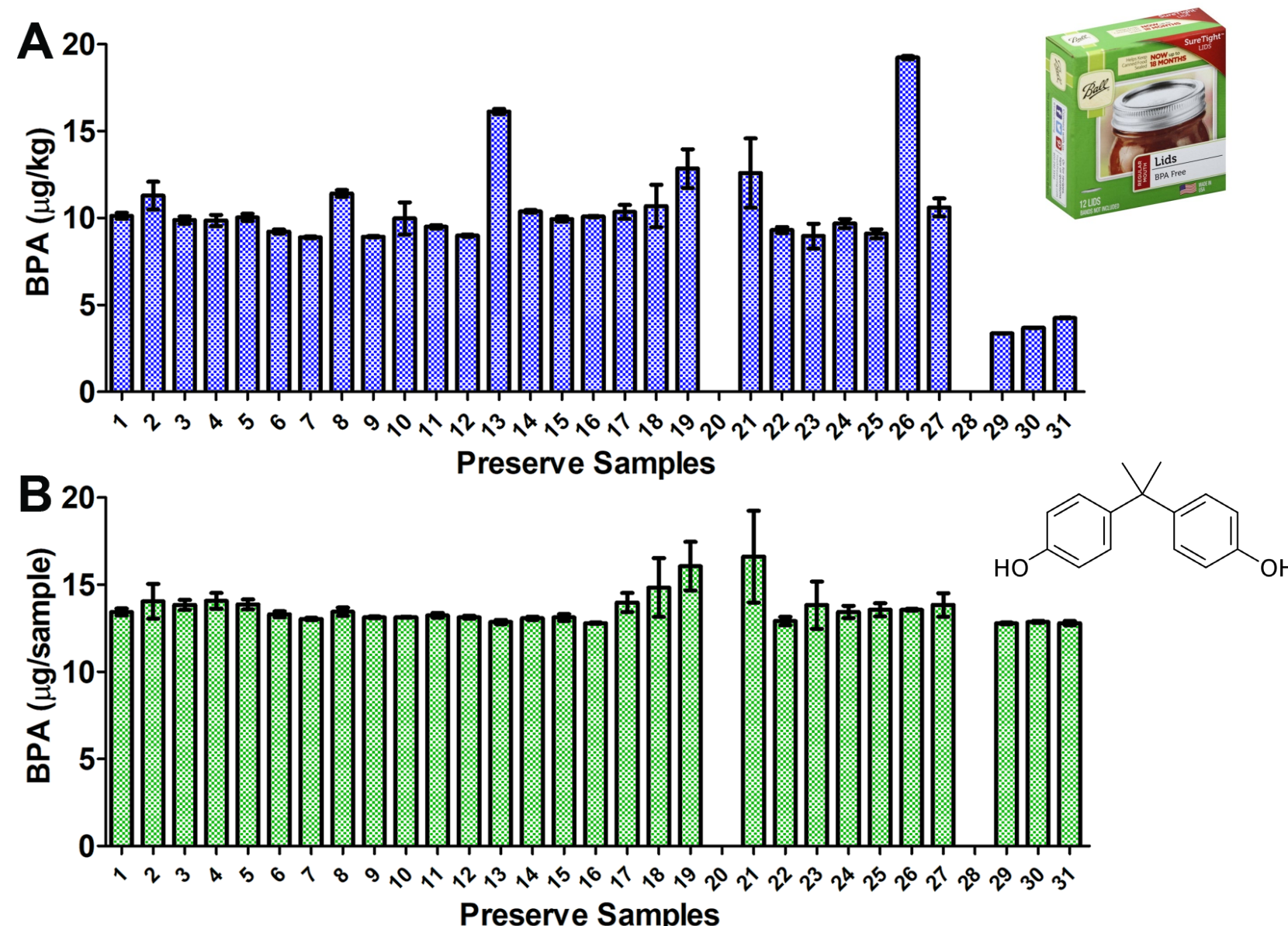

Figure 4. BPA concentration in 1950s preserves. Panel A is BPA amount per sample mass and panel B is BPA amount per sample. Panel B better shows the uniformity of BPA concentrations over the entire sample set. Samples 20 & 28 were sealed with lids lacking BPA-treated liners. Error bars are standard deviations from the mean of successive 2-hour samplings of each preserve.

Conclusions & Future Work

- The developed SPME method is simple and cost-effective and easily adaptable to assessing volatile emissions from any large and/or oddly-shaped container.
- The SPME method showed excellent accuracy and precision for both spiked BPA and aroma volatiles in store-bought and 1950s preserves.
- Volatile profiles of the 1950s preserves varied widely, but were generally consistent with those reported for comparable preserves of present-day.
- BPA levels were quite uniform over the sample set and sampling replicates and are in the range of those shown to induce endocrine disruption effects.
- To the best of our knowledge, this is the first published report of volatile profiles of rare historical preserves, and the earliest reported detection of BPA in consumer products.[1]
- Work is now ongoing to screen these early 1950s preserves for the presence of legacy pollutants (e.g. DDTs, PCBs).

Acknowledgements

References

1. Leinen, L.J.; Swenson, V.A.; Juntunen, H.L.; McKay, S.E.; O'Hanlon, S.M.; Videau, P.; Gaylor, M.O. Profiling Volatile Constituents of Homemade Preserved Foods Prepared in Early 1950s South Dakota (USA) Using Solid-Phase Microextraction (SPME) with Gas Chromatography–Mass Spectrometry (GC-MS) Determination. Molecules 2019, 24, 660.