Food Sample Identification via Coated Blade Spray High Resolution Mass Spectrometry

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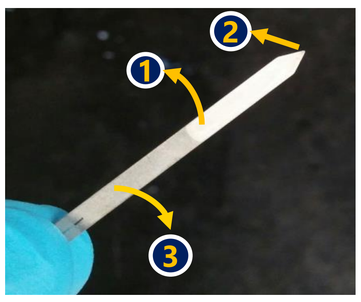
Introduction

Coated Blade Spray (CBS) is an SPME-based analytical technology that facilitates collection of analytes of interest from a sample and the direct interface to mass spectrometry systems via a substrate spray ionization. The device comprises a thin-flat sheet with a pointed tip and it is manufactured of a conductive substrate such as stainless steel (see **Figure 1**). As a SPME device, the substrate is partially coated with an extraction phase comprised of polymeric particles and a binder. The function of the polymeric particles is to enrich the analytes of interest from the sample matrix, while collecting the least amount of interferences. As a direct to MS device, the device requires a pre-wetting of the extraction material so to elute the analytes collected on it. Subsequently, a differential potential is applied between the non-coated area of the substrate and the inlet of the MS system generating an electrospray at the tip of the CBS device. Herein, we demonstrate as a proof-of-concept how CBS coupled to High Resolution Mass Spectrometry (HRMS) enables rapid profiling of aqueous (i.e. beer) and solid food matrices (i.e. animal tissue). Unlike other ambient-ionization technologies, CBS allows you performing sampling remotely, cleaning-up the sample and retaining relevant chemical information that facilitates its classification via chemometric tools.

Figure 1 Anatomy of a CBS device: (1) Extraction phase (binder+particles); (2) Pointed tip for direct injection onto the mass spectrometer via ESI mechanism; (3) conductive and robust support that allows for versatile applications such extraction from liquids or stabbing into tissue. Width: 2.5 mm, coating length: 10 mm.



Methods

Coated Blade Spray devices were manufactured by Restek Corporation (Bellefonte, PA, USA). Hydrophobic-Lipophilic Balance (HLB) particles were selected as the extraction phase. CBS devices have a coating length of 10 mm and coating thickness of 10 µm. Data collection was conducted on an AccuTOF™ Time-of-Flight MS (JEOL, Peabody, MA) within the range of 50-1000 m/z. CBS devices were adapted to fit into the JEOL PaperSpray™ interface and electrospray was generated by adding 1.5 µL of the elution solvent on the coated area and applying a positive voltage of 3.75 kV (see **Figure 2**). Spray time was approximately 10 seconds per blade and the data was processed using msAxel LP. Chemometric analyses were performed with Mass Mountaineer™ software for mass spectra collected over the m/z range 80-1000.

Figure 2 Coated Blade Spray installed on an AccuTOF Time-of-Flight MS via commercially available JEOL PaperSpray interface; hence, facilitating rapid transition between diverse ambient ionization technologies (A-C). Insert D presents an example of an ion chronogram collected with CBS in urine sample, while insert B displays Taylor cone generated from CBS device with a voltage of 3.75 kV and a distance of approximately 4 mm from the MS inlet.

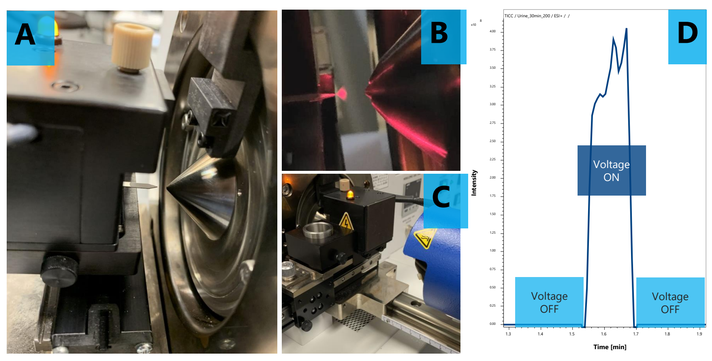
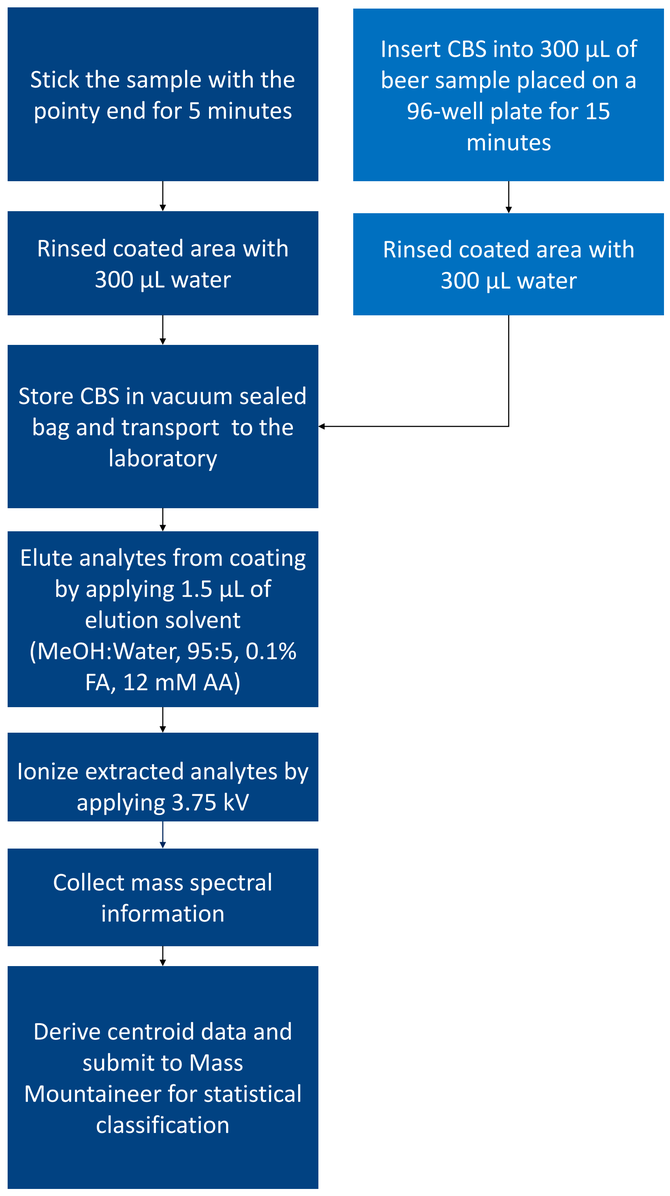


Diagram 1 Experimental workflow followed for analysis of solid samples (left, meat and fish tissue) and liquid samples (right, beer). In the case of liquid samples, the devices were preconditioned, prior to the sampling, following conditions described elsewhere [4].

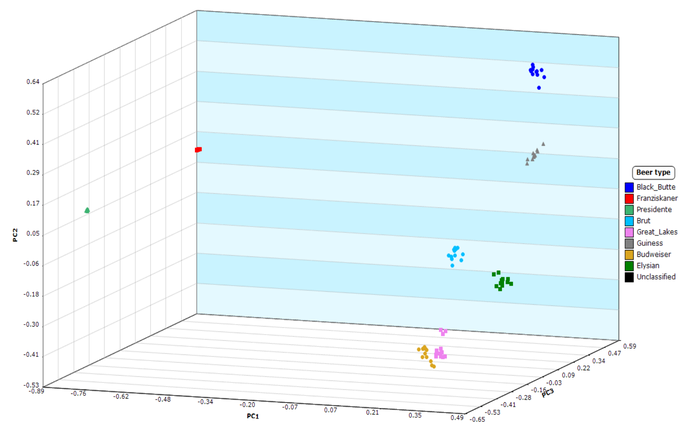


Results

Sample profiling via mass spectrometry requires taking either the sample to the lab or the MS to the sample [8, 9]. Herein, we show how CBS can be used to collect and store chemical information from liquid and solid samples. In combination with a HRMS and appropriate statistical tools, chemicals stored on the coating can be used for sample discrimination. As can be seen in **Figure 3**, the discriminant analysis of principal components (DAPC) in combination with Kernel Principal Component Analysis (KPCA) allowed for adequate classification of each of the beer brands under evaluation. Further, when using 60 principal components (PC), the leave-one-out cross validation (LOOCV) and the Support Vector Machine (SVM) unequivocally identified each of the samples.

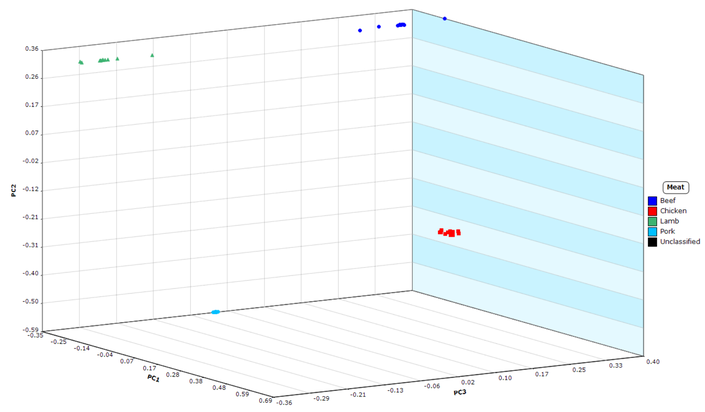
Figure 3 DAPC-KPCA plot classification of diverse beer brands (bottom). Photo of the 96-well plate with 12-samples of each beer kind. Sampling was performed using a 96-CBS arrangement (top).

96-well plate collection



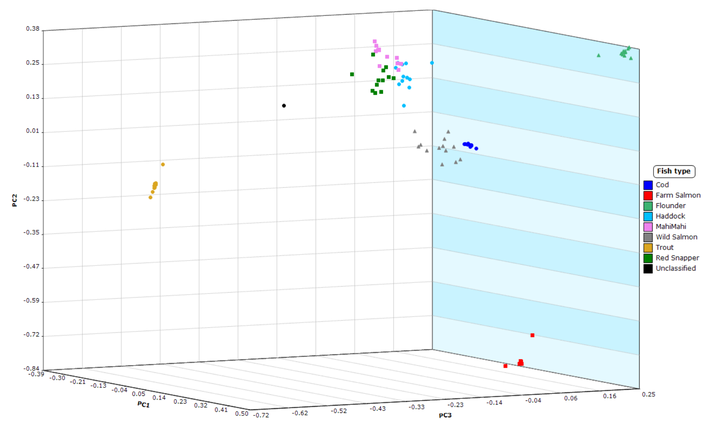
Likewise, CBS was capable of differentiating different types of meat samples. As can be seen in **Figure 4**, the DAPC-KPCA plot showed clear distinction of each meat. By using 60 PC, the LOOCV and SVM lead to a predictability of 94 and 96%, respectively.

Figure 4 DAPC-KPCA plot classification of miscellaneous meat types (i.e. beef, chicken, pork, lamb).



In a third experiment, CBS was used to differentiate diverse fish samples. As can be seen in **Figure 5**, the DAPC-KPCA plot showed clear distinction of each species. Similar to the meat samples, by using 60 PC, the LOOCV and SVM lead to a predictability of 94 and 96%, respectively. Certainly, further improvements are expected by controlling the spatial location where the blade is inserted onto the fish for analyte collection. Besides, our work is also focused on studying a much larger cohort for each of the samples and the exploration of other elution/ionization solvents, so to increase the coverage of analytes under scrutiny (i.e. balance coverage).

Figure 5 DAPC-KPCA plot classification of miscellaneous fish types (i.e. cod, farm salmon, wild salmon, flounder, haddock, mahi mahi, trout and red snapper).



Summary

1. CBS was used, as a proof-of-concept for profiling of beer, meat and fish samples. In the case of aqueous matrices, 96 samples can be scrutinized at the same time, allowing for total analysis time under 1 minute per sample.
2. Unlike other methods, were the mass spectrometer must be transported to the place of sampling, sample collection with CBS was performed in one location (Bellefonte, PA) and analyzed at a different location (Peabody, MA) without major hassle as the "sample" (sample information) was safely transported on a airplane.
3. Since the chemical information of the sample is stored in the coated material, it is invisible to the bare eye and encrypted to the trained eye; thus, making CBS an ideal tool, not only for profiling, but also from a chain of custody perspective.

References

1. Gómez-Ríos, G.A., et al., *Angewandte Chemie*, **2014**, 52, 1403-1407; **2.** Gómez-Ríos, G.A., et al., *Bioanalysis,* **2018***, 10(4), 257–271;* **3.** Gómez-Ríos, G.A., et al., *Trends in Analytical Chemistry*., **2019**, 112, 201-211; **4.** Kasperkiewicz, et al., *Analytical Chemistry*., **2019**, DOI: 10.1021/acs.analchem.9b03225; **5.** Cody, R., et al., Anal. Chim. Acta., 2017, 989, 38-44.