APPLICATIONS OF CARBON DIOXIDE-INDUCED ATMOSPHERIC SAMPLE DESORPTION AND IONIZATION

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OVERVIEW

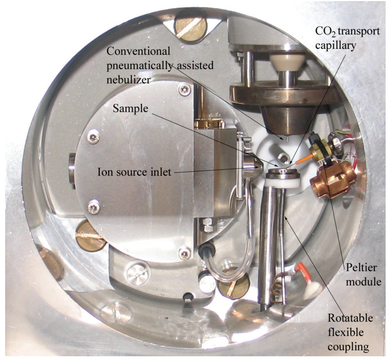
An expanding jet of liquid CO_2 may be used to desorb and ionize solid samples on a surface.

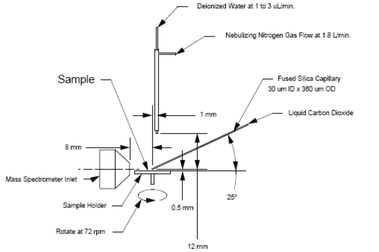
INTRODUCTION

There is much current interest in devising new ways of producing ions from solid samples in atmospheric environments[1-9]. Previously[10], we demonstrated that it was possible to desorb and ionize small molecules such as diphenhydramine from a surface in an atmospheric environment, by directing a jet, formed by rapidly expanding liquid carbon dioxide through a small orifice, at that surface. This abstract reports further applications and refinements of this new technique.

METHODS

A cylinder of supercritical chromatography grade carbon dioxide is used as a source of liquid carbon dioxide. The carbon dioxide expands as it exits the end of a small (25 – 40 um i.d.) capillary placed near the sample surface. In previous work, we demonstrated that the water vapor present in ambient lab air, was both necessary and sufficient to produce ionization. To reduce signal variability, however, it has been found useful to carefully control the humidity of the local environment around the sample. This has been accomplished by mounting the sample within a standard API source enclosure of an orthogonal TOF of conventional design (Waters LCT Classic). 1-3 uL/min of liquid water is introduced as vapor into the source enclosure by nebulizing it with a gas flow of about 1.8 L/min of gas from a nitrogen generator. Temperature control of the capillary provides greater signal stability. The use of a small Peltier module to pre-cool the capillary allows the process of desorption and ionization to commence within a few seconds. As with MALDI, there can be significant spatial variation in signal intensity. Thus it has proven useful to provide an automated means for sampling many different locations. To this end, the disposable disc upon which the sample is mounted is rotated at a 72 rpm via a motor-driven flexible link.





RESULTS

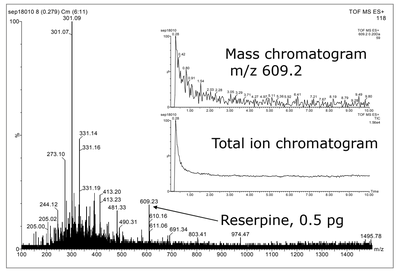


Figure 1. Positive ion spectrum summed over 12 seconds from 0.5 pg Reserpine. Sample was deposited from a 1 µL volume spotted and dried on a stainless steel substrate.

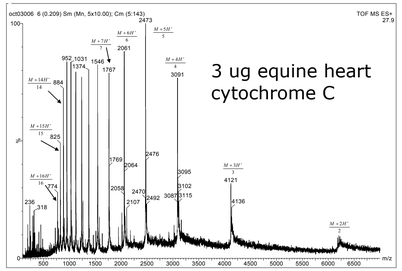


Figure 2. Positive ion spectrum acquired over 5 minutes from 3 ug deposited from 1 µL solution and dried on a stainless steel substrate.

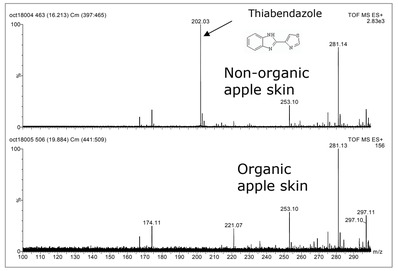


Figure 3. 3/8" discs were cut from apples' skins, mounted and rotated on sample stage. Positive ion spectra summed over 2 minutes.

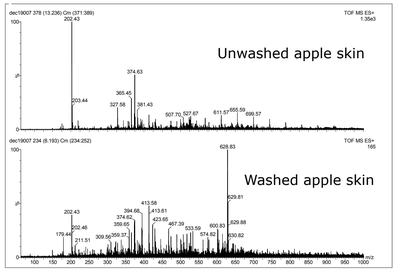


Figure 4. Positive ion spectra of apple skin washed with scrub brush and hand soap still has thiabendazole present.

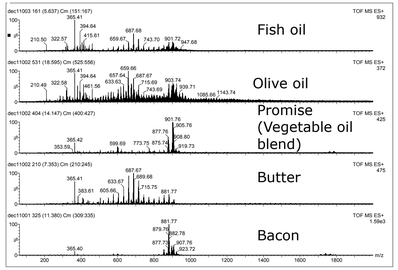


Figure 5. Positive ion spectra from oils and fats. Samples were typically a drop or two or a smear of material on a stainless steel substrate.

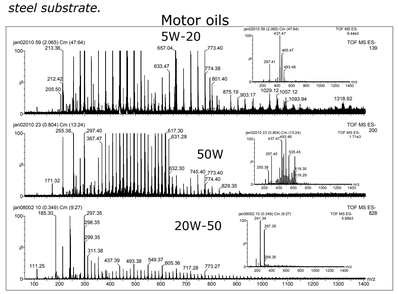


Figure 6. Negative ion spectra from motor oils. Approximately 10 µL of each deposited on a stainless steel substrate.

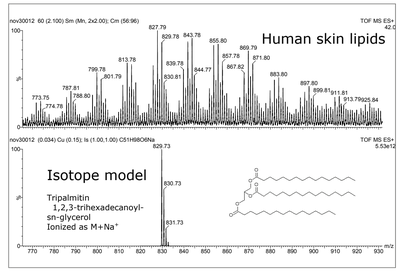


Figure 7. Human skin lipids. Sample collected by rubbing finger tip in cleft between nose and cheek and applying finger to stainless steel substrate. Positive ion spectra. Note that these ions appear as sodium adducts

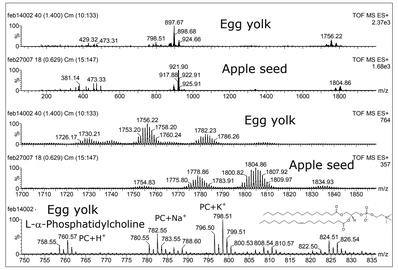


Figure 8. Positive ion spectra from egg yolk smear on a stainless steel substrate and sliced open apple seed.

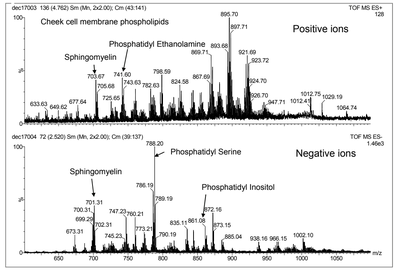


Figure 9. Positive and negative ion spectra from cheek cells on a stainless steel substrate.

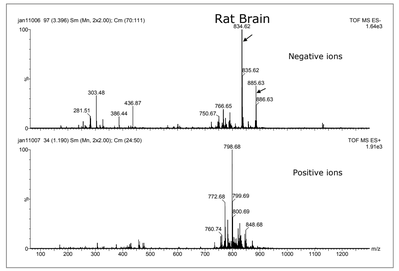


Figure 10. Positive and negative ion spectra from slices of rat brain. Sample obtained from Rockland Immunochemicals (RT-T077), sliced with razor blade and mounted on sample stage. Some ions present appear similar to those recently reported[11] using DESI by Manicke et al.

DISCUSSION

In general, sensitivity is higher for smaller molecules. Limits of detection for reserpine spotted onto a stainless steel substrate have now been improved by at least an order of magnitude and can be as low as 0.5 pg. While far less sensitive, it is possible to observe multiply charged ions of cytochrome C with charge states as high as $(M+16H)^{16+}$.

Residues of the common fungicide, thiabendazole, are easily detectable on the skin of non-organic apples. Both positive and negative ions are readily obtained from a wide range of organic molecules ranging from different grades of motor oils, olive oils, butter and bacon fat. Human skin samples produced spectra from molecules containing fatty acids with both even and odd numbers of carbons, consistent with this unique structural property of human skin lipids. Additionally ions tentatively identified as phospholipids have been obtained from human cheek cells and small slices of frozen rat brain.

CONCLUSIONS

- **Carbon dioxide-induced sample desorption and ionization may be a useful complement to other existing and emerging techniques for the analysis of samples on surfaces**
- **In some environments, e.g. food safety analysis, carbon dioxide may be perceived as a benign sample probe**
- **Small cylinders of compressed carbon dioxide, having a very long shelf life, may represent a convenient alternative for portable sampling devices.**
- **More experiments are needed to understand the underlying mechanisms.**

References

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