HIGH PRECISION ISOTOPE RATIO FINGERPRINTING OF ETHANOL AND OTHER COMMERCIAL MOLECULES AND MATERIALS

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The potential of the isotope ratios of C, H, O, N to provide definitive characterization of natural products has long been recognized. While stable isotope ratio mass spectrometry (IRMS) is the most accurate and precise way of measuring these ratios, the utility of IRMS for characterization of chromatographically separated molecules has until recently been limited to $^{13}C/^{12}C$ and $^{15}N/^{14}N$. Recent technological developments now allow the direct measurement of $^{18}O/^{16}O$ and D/H in molecules that have been resolved by capillary GC. Isotope ratios can be used to define isotopically distinctive end members and have been used to characterize high energy explosives (TNT), drugs of abuse (cocaine, heroin), and performance enhancing drugs (testosterone). The more isotopes that can be brought to bear on a problem, the better the chances of unambiguous identification are. The ability to measure multiple isotope ratios in a single molecule allows "stable isotope fingerprinting" of a wide variety of molecules. Three isotope ratios from a single compound can be measured in a variety of commercially important molecules, including ethanol and flavor compounds (e.g. benzaldehyde, vanillin, linalool) with the application being to determine their origin in an effort to detect adulteration or substitution. The measurement of 13C, 18O, and D in the ethanol molecule is under intensive investigation, because IRMS provides an attractive alternative to existing NMR techniques. The ethanol-bearing sample is sampled by a GC autosampler using headspace sampling techniques, and the capillary GC resolves ethanol from water and congeners. The purified ethanol is either combusted on-line for analysis for ^{13}C (with the water of combustion removed to prior to analysis):

$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$$

or quantitatively decomposed by pyrolysis at elevated temperatures (T>1400oC) on-line for analysis of 18O and D:

$$C_2H_6O = CO + 3H_2 + C$$

We will present a case study on the use of GC-IRMS to quantify the ^{13}C, ^{18}O and D contents of ethanol in a suite of tequila samples. Multi-dimensional IRMS is a uniquely powerful tool for defining "appellation controllæes", and for quantitating industrial practices involving mixing of isotopically distinctive different end members.