DEVELOPING ANALYTICAL METHODS THAT STAND THE TEST OF TIME: DETERMINATION OF FLUORINATED ORGANICS IN VARIOUS MATRICES

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Introduction

There is increasing interest in the determination of fluorinated organic compounds, especially in environmentally relevant systems[1-16]. Due to the nature of the extremely strong carbon-fluorine bond, these molecules often have properties, which make them quite different from their hydrocarbon analogues[17]. These unexpected properties make them difficult to handle, especially for trace analysis.

Fluorine is the most electronegative element in the periodic table (401 kcal/g-atom). It is also the most reactive of all the elements. The bond energy of the C-F bond is approximately 116 kcal/mole compared to the C-H bond (99 kcal/mole) and the C-Cl bond (79 kcal/mole). Fluorine content of an organic compound can be determined by neutron activation analysis (not convenient or readily available), x-ray fluorescence (semi-quantitative), ^{19}F nuclear magnetic resonance spectroscopy (not good at low levels), and combustion with an oxy-hydrogen torch followed by ion-selective electrode measurement. Since the C-F bond is so strong, only the oxy-hydrogen torch is hot enough (2700°C) and persistent enough to degrade some fluorocarbons. The ion selective electrode is capable of measuring fluoride ion solution to 20 ppb (μg/L). In order to improve the measurement at low levels, the method of standard addition must be used.

Gas chromatography with mass spectrometry (GC/MS) and gas chromatography with electron-capture detection (GC/ECD) can be used for determining volatile fluorine-containing compounds. GC/MS is preferred since single ion monitoring can be used to improve both the sensitivity and selectivity of the measurement. GC/ECD is usually not significantly better than GC with flame ionization detection since the fluorine atom is so small. Its cross-sectional area is not large enough to effectively capture electrons. The ECD is notoriously non-linear as well. For nonvolatile compounds derivitization may be used, but derivitization adds another (often not easily reproducible) step to the analysis process.

Liquid chromatography tandem mass spectrometry (LC/MS/MS) is preferred for nonvolatile compounds that are also ionizable. LC/MS/MS provides good sensitivity and excellent specificity, but is rather expensive and difficult to maintain.

The most important aspects in the determination of fluorine-containing compounds are the sampling and sample preparation. An isotopically enriched internal standard is ideal, but not always readily available. Blanks are essential to obtaining results that stand the test of time. Good spike recoveries at and around the level of quantitation are required.

A useful document that details the requirements for selective and sensitive analytical methods, especially for environmental and biological systems, is available from the US FDA web

site[18]. Another useful document that addresses issues concerning background and blank measurements is on the EPA web site[19].

Conclusions

Fluorinated organic compounds have unique properties that make them difficult to measure, especially in complex matrices. Since these compounds "look" like hydrocarbons, one might assume they have similar characteristics. In practice they are quite different and require a high level of quality assurance. Method validation studies must include studies of analytical recovery, storage stability, and measures of precision and bias. Blanks are an important component of the analytical method.

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