

Summary

This application note describes a method of measuring hexafluoroisopropanol (HFIP) via gas chromatography/mass spectroscopy.

Background

HFIP is a commonly used solvent for dissolving polymer such as polyethylene terephthalate, a normally difficult-to-dissolve polymer. HFIP is however a very toxic solvent. Consequently, devices fabricated from a solution containing HFIP must be adequately de-gassed to ensure that any residue HFIP concentration is below dangerous limits.

Experimental

Described below is a test method developed at CPG for the analysis of residual HFIP by gas chromatography/mass spectrometry (GC/MS).

A sample is weighed on a precision balance and then extracted in methanol for seven hours. The solvent extract is tested on an Agilent 6890 series gas chromatograph under the following conditions, developed at CPG for HFIP analysis:

Column: Phenomenex ZB-5ms, 30 m x 0.25 mm ID x 0.25 μ m film thickness
Detector: Agilent 5973 mass selective detector (MSD)
Injection parameters: Split injection (5:1 Split Ratio)
Injection volume: 1 μ L
Inlet temperature 250 $^{\circ}$ C
Helium flow: 1 mL/min
Oven temperature program: Hold at 40 $^{\circ}$ C for 2 minutes, ramp 10 $^{\circ}$ C/minute to 50 $^{\circ}$ C, hold for 10 minutes
Solvent delay: 0.25 minutes
EI scan mode: SIM (m/z 99, 129, 149)

To prevent cross-contamination between samples, a methanol blank is injected between sample runs, and the autosampler needle is cleaned with two methanol washes before and after each injection.

A typical chromatogram and mass spectrum of a sample containing HFIP is shown in Figure 1. The measured mass spectrum was compared against the NIST Mass spectral library, and the results of that search are shown in Figure 2. HFIP is the closest spectral match to the sample's mass spectrum (with a probability of 92.8%).

The detection mode of the mass selective detector greatly influences sensitivity and the limit of detection. While operating in a scan mode (i.e. monitoring m/z 50-550), the limit of detection of the instrument is approximately 1ppm.

Instrument sensitivity can be improved by operating the detector in selective ion monitoring (SIM) mode. For HFIP, the detector only monitors the compounds characteristic m/z values of 99, 129, and 149. The ratios of the ion peak intensities are used to identify HFIP in the presence of other compounds with similar ion fragmentation patterns. While operating in SIM mode, the limit of detection is less than 100ppb, and the relative standard deviation of the instrument response is less than 5%.

Quantitation is performed by preparing an HFIP calibration curve from stock solutions and testing it by GC/MS on the same day as the unknown samples. A typical calibration curve ranging from 0.4ppm – 1300ppm HFIP is shown in **Error! Reference source not found.** The precision of the calibration curve may be improved by introducing an internal standard to correct for injection-to-injection variability.

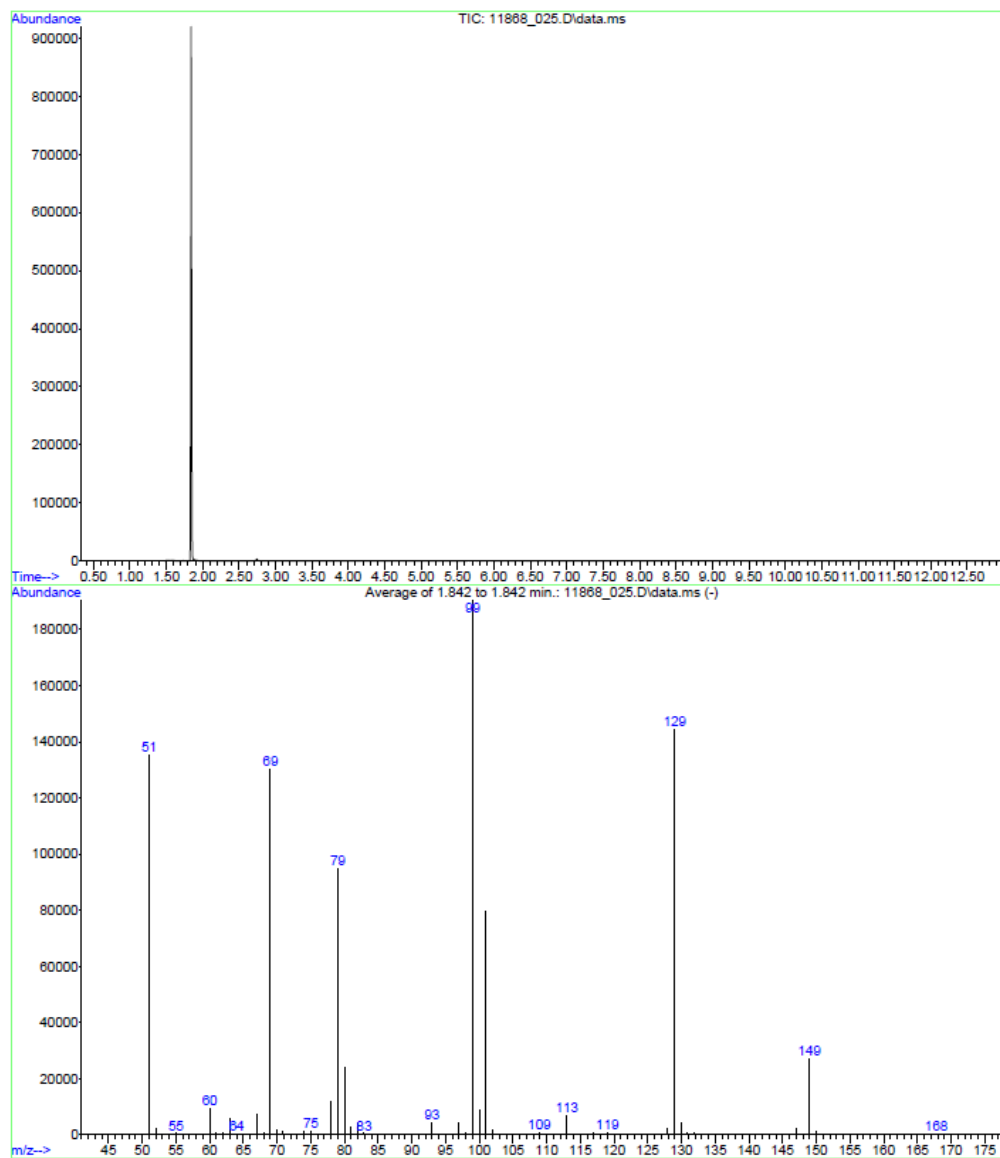
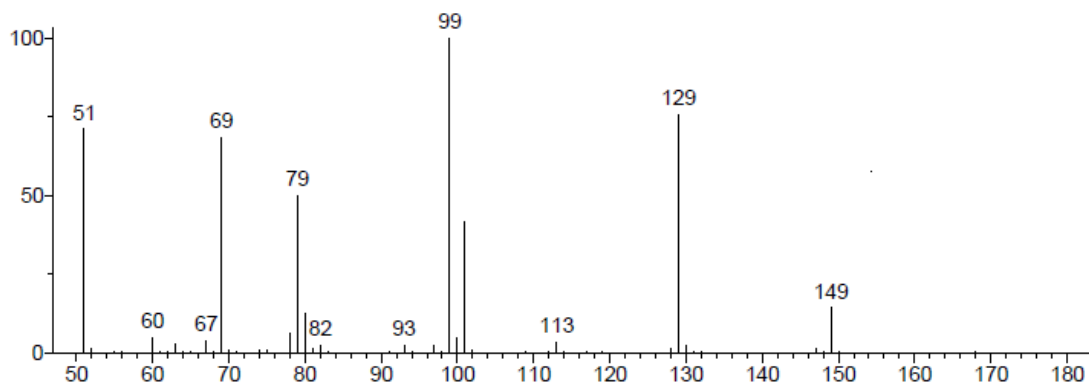


Figure 1: Typical total ion chromatogram (top) and mass spectrum (bottom) for a sample containing HFIP. The mass spectrum was measured at a retention time of 1.842 min.

Unknown: Average of 1.842 to 1.842 min.: 11868_025.D\data.ms
Compound in Library Factor = 1972



Hit 1 : 2-Propanol, 1,1,1,3,3,3-hexafluoro-
C₃H₂F₆O; MF: 948; RMF: 949; Prob 92.8%; CAS: 920-66-1; Lib: replib; ID: 3968.

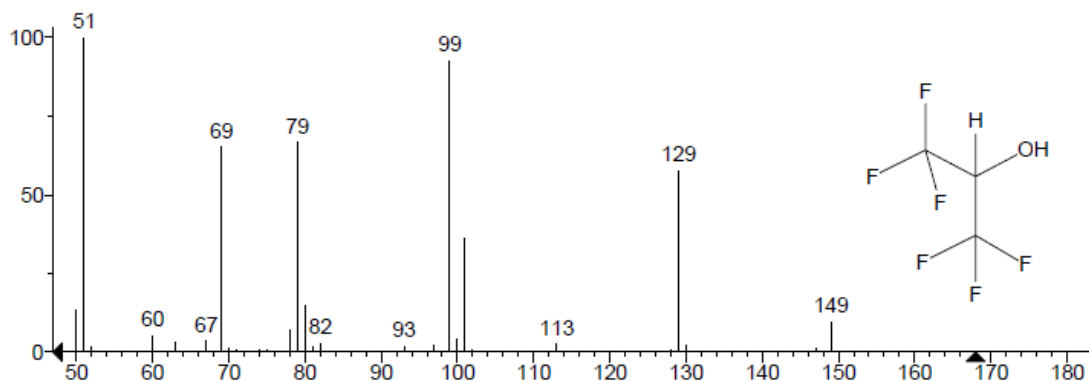


Figure 2: Results of NIST spectral library search. The top spectrum is the measured mass spectrum at 1.842 retention time of sample 11868-3 (Figure 1). The bottom spectrum is the closest spectral match.

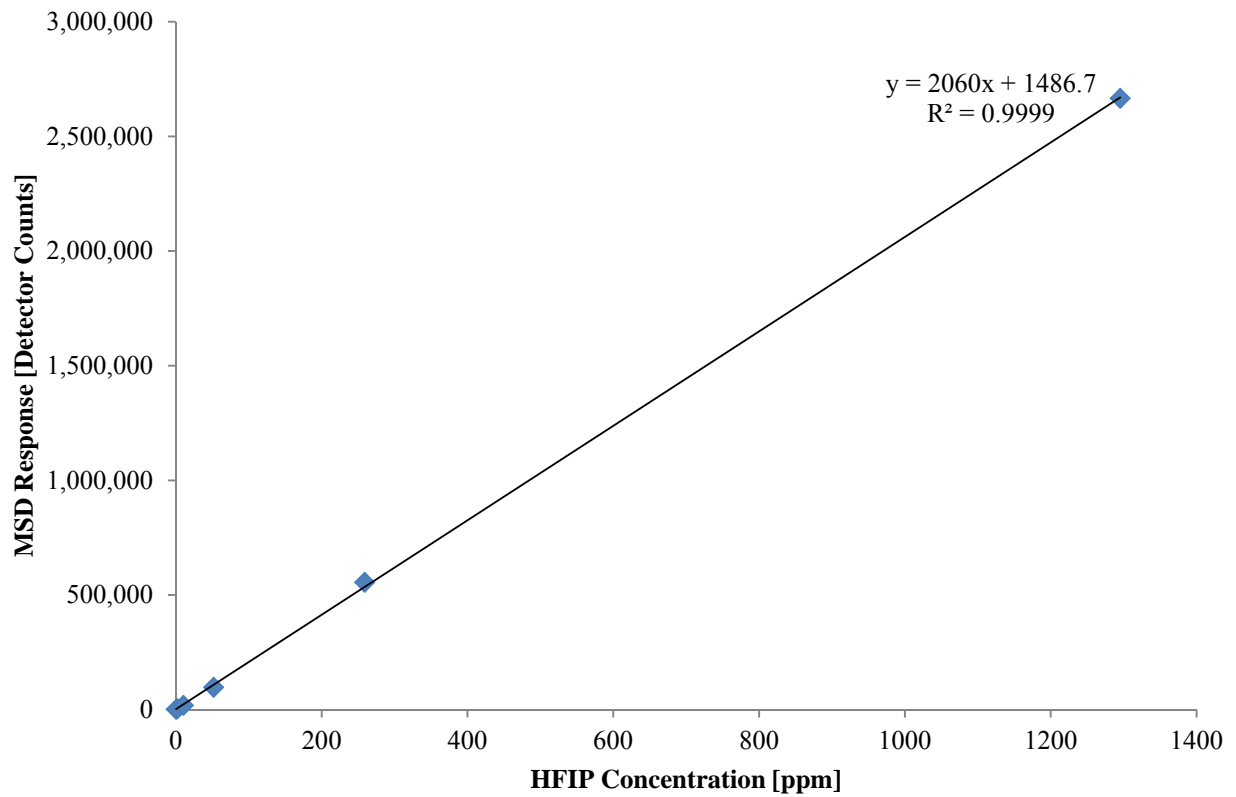


Figure 3: Calibration curve used for quantitation, spanning HFIP concentrations of 0.4ppm-1300ppm.

Table 1: Tabulated calibration data.

HFIP Concentration [ppm]	HFIP Peak Area [MSD Response]
0.41	1,482
2.07	4,212
10.36	18,701
51.82	97,807
259.08	555,812
1,295.40	2,666,297