Overview of Concept
Chemical fingerprinting of hydrocarbon contamination, which is commonly used in forensic investigations involving the nature and source(s) of contamination, is generally conducted using conventional gas chromatography (GC) using fused-silica, capillary columns with a non-polar stationary phase, often with a flame ionization detector (FID) or mass spectrometry (MS) detection. Conventional GC can provide “fingerprints” of hydrocarbons boiling between about C5-C45, with the upper boiling limit constrained by the stability of the GC column’s stationary phase (e.g., EPA Methods 8015 or 8270 and ASTM D2887).

High temperature gas chromatography (HTGC) is an adaptation of conventional GC/FID that utilizes a non-polar, low bleed stationary phase column, which safely can withstand temperatures up to 430°C. The high phase ratio of the column permits the elution of hydrocarbons 260 to 316°C below their true boiling points, and thereby permits elution and quantification of the percent mass of hydrocarbons with boiling points up to 750°C – i.e., up to C120. When combined with cryogenic initial GC conditions, HTGC can expand the carbon range “fingerprint” from C5-C120, and allows the forensic expert to evaluate hydrocarbon distributions that conventional GC cannot (Figure 1).

Figure 1: Example of conventional and HTGC fingerprints for an asphalt material. The conventional GC shows the distribution of compounds containing eight carbons (C8) through 45 carbons (C45). The HTGC shows the presence and boiling distribution of compounds beyond C45, in this case up to 110 carbons (C110) – albeit at lower resolution than conventional GC. HTGC is particularly important in the chemical fingerprinting of asphaltic materials as they contain a significant mass that boils above C45.

HTGC Methodology
The HTGC method used in this study is based on the recently adopted ASTM Method D7169-05, which was based upon the International Petroleum standard IP PM-CF and Deutsches Institut für Normung E.V. standard DIN 51435-2. The development of the HTGC methodology was thoroughly described in Villalanti et al. (2000) and its forensic application was initially discussed by Raia et al. (2004).

Briefly, the method required a dilution of 0.1-0.2 g of each sample - soil, sediments, products, including liquids, semi-solids, and solids - into carbon disulfide to achieve a 1 to 2 percent mass in the solvent. The solution is injected into a programmed temperature vaporization (PTV) injector of a GC equipped with a special high temperature GC column (5 m x 0.53 mm ID, and 0.85-0.15 mm non-polar stationary phase). The GC is programmed from -20°C to 430°C, although the resulting phase ratios permitted elution of mass boiling up to 732°C (C120).

The retention time versus carbon number is calibrated using a hydrogenated polyolefin wax (Polywax 665; Figure 2) and a reference crude oil with a known mass distribution (based upon physical distillation) is used as an external standard. The quality control (QC) protocols used are described in Villalanti et al. (2000).

Figure 2: HTGC fingerprint of a Polywax (n-alkane) standard.

Conclusion
Chemical fingerprinting of high-boiling petroleum products and wastes can benefit from the use of high temperature gas chromatography (HTGC). This technique, in combination with conventional GC methods, reveals potentially diagnostic information in the C45 to C120 range – well beyond the capability of conventional GC.

References