C8 Quality Assurance in Qualitative Analyses

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The goals of this presentation are to describe quality assurance methods for the qualitative procedures used in the forensic analysis of environmental samples by GC-FID.

Analytical data are used to make a variety of forensic decisions, e.g., whether a chemical or product is present, the concentration of the contaminants, how the contaminants have interacted with the environment, the identity of the contaminant, etc. Much of this work is performed by gas chromatography with flame ionization detection (GCFID). Errors in the interpretation of the data can have costly effects – either fiscal, environmental, or both. It is the role of the laboratory quality assurance program to provide safeguards, minimize errors, and provide a means of detecting errors when they occur.

Characterizations of petroleum products by GC-FID, (sometimes called "fingerprinting"), are specifically mentioned in EPA SW-846 Method 8015, and Washington State Department of Ecology NWTPHHCID. Method 8015 Section 1.3 limits the discussion to: "This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. In addition, if this method is used for the analysis of petroleum hydrocarbons, it is limited to analysts experience in the interpretation of hydrocarbon data. Each analyst must demonstrate the ability to generate acceptable results with this method." The language in NWTPH-HCID is almost identical.

There are no established quality assurance methods for the characterization of petroleum products by GC-FID. Similarly, no performance evaluations or testing is either performed or required by any agency promulgating this method. However, many laboratories perform this analysis and freely offer their interpretations, whether requested or not. An interlaboratory comparison of five labs analyzing soil samples for total petroleum hydrocarbons (TPH) by GC-FID generated interpretations of the contaminants by four of the five laboratories, each of which incorrectly described the contaminant, a weathered diesel fuel.

The GC-FID traces of fresh petroleum products, particularly automotive gasoline and diesel fuel, are easily recognized, even by a neophyte. Moderate evaporation, biodegradation, and dissolution processes generally alter the chromatograms in predictable ways. Consequently, simple products may be characterized reproducibly by different laboratories. However, unfamiliar products, such as aviation gasoline, jet fuels, solvents, and mixtures of products, rapidly increase the uncertainty in product characterizations. Similarly, the combination of several weathering processes will complicate the interpretation of GC-FID data.

The ability to recognize a petroleum product from the GC-FID trace is due to the relationship that exists between the chromatogram and the physical and chemical properties of the material. Gas chromatography separates components based upon their molecular weight, boiling point, and their interaction with the solid phase of the GC column.

Petroleum products, particularly fuels, are designed to boil within a certain range. Thus, automotive gasoline, which has a fuel specification to boil between approximately 50°C and 190°C, will have a GC-FID trace which shows the presence of peaks eluting from approximately hexane to triadecane.

Diesel fuel is a petroleum distillate, i.e., it is distilled from crude oil with relatively little modification; automotive gasoline is a 'manufactured' material generated by the combination of several refinery product streams. The production of these fuels generates distinctive chemical mixes that may be recognized in the chromatograms of the fresh materials. The chromatograms differ in the separation and relative heights of the component hydrocarbon peaks.

Quality assurance in the characterization of petroleum products by GC-FID is not merely a whim of the analyst, but can be dictated by certain reproducible, measurable observations. The boiling range of the material as determined from the chromatogram limits the number of possible product identifications that can be ascribed. The spacing of the peaks is dictated by the chemical composition of the product. The relative peak heights of the components are indicative of the chemical formulation. Consequently, the GC-FID trace immediately yields three points on which the identification or characterization any petroleum product must comply: boiling range; peak spacing; and relative peak height.

Weathering of petroleum products distinctly affects the GC-FID trace. Evaporation removes the earlier eluting peaks, while biodegradation and dissolution tend to selectively remove certain chemicals. While these mechanisms can be recognized and distinguished in the GC-FID trace, they confound the principles of identification that were previously described. An evaporated product does not have the same boiling range as a fresh product; a biodegraded fuel will have different peak heights and peak spacing based upon the removal of certain classes of chemicals.

The principles of characterization of a weathered petroleum product are the same as those for a fresh product. The boiling range is diminished, but the high-boiling point will still match that of the original product. The peak heights of some components will change during biodegradation and dissolution, but other peaks are recalcitrant and will not change significantly during those processes. Thus, while the specific points on which an

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initial characterization had been made might have changed there are other related points on which identifications can be based.

Quality assurance requires setting limitations on the variability of the analysis – this principle is enforced in quantitative procedures but is never applied to qualitative analyses of environmental samples. Petroleum contamination can be characterized by GC-FID analyses using 'points-ofcompliance' such as boiling range, peak spacing, and relative peak height. Those points of compliance may be quantified and applied objectively between samples and between labs to determine the accuracy of product characterizations.

Quality Assurance, Qualitative Analysis, Fingerprinting

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