Petroleum Research

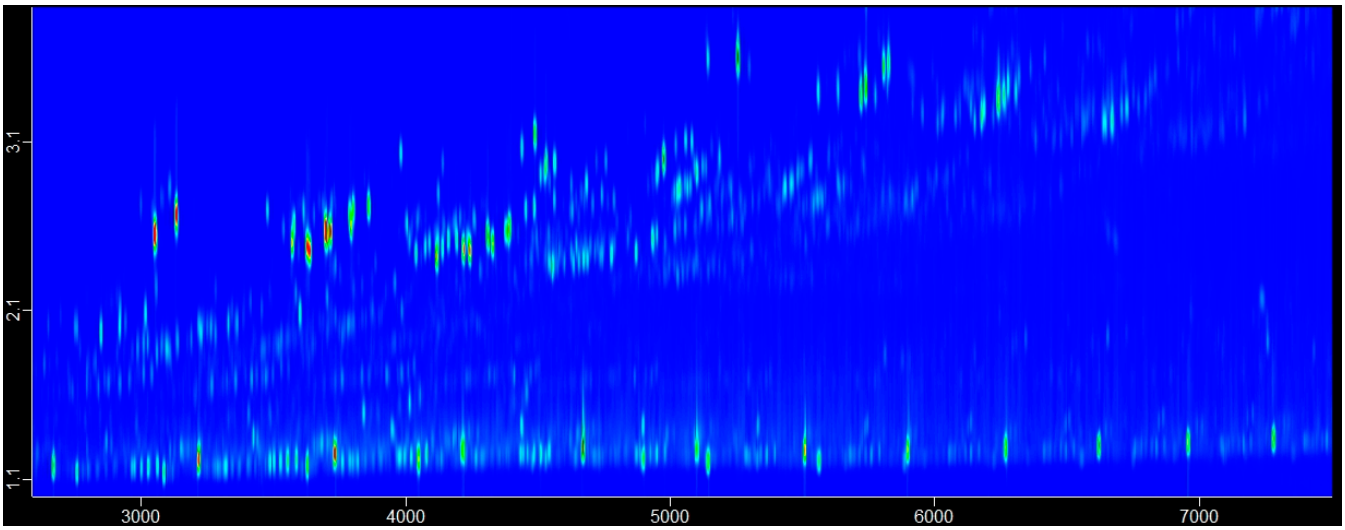
Curated Compilation of Articles Employing GCxGC and TOFMS Technology

LECO

EMPOWERING RESULTS

Comprehensive two-dimensional gas chromatography (GCxGC) provides powerful information for solving real-life problems in the petroleum field, both in routine analysis and for research. Coupled to the LECO Pegasus® series of mass spectrometers that provide the requisite fast acquisition speeds to properly quantitate and deconvolute narrow GCxGC peaks, GCxGC-TOFMS data from laboratories around the world are helping to make decisions that solve global problems that impact modern energy supplies and environmental safety. With the *Pegasus* supporting them, these labs can do so much more than run their samples: **They can fly.**

Table of Contents



Intermediate fuel oil contour plot

Summary: *Every Chromatogram Tells a Story*

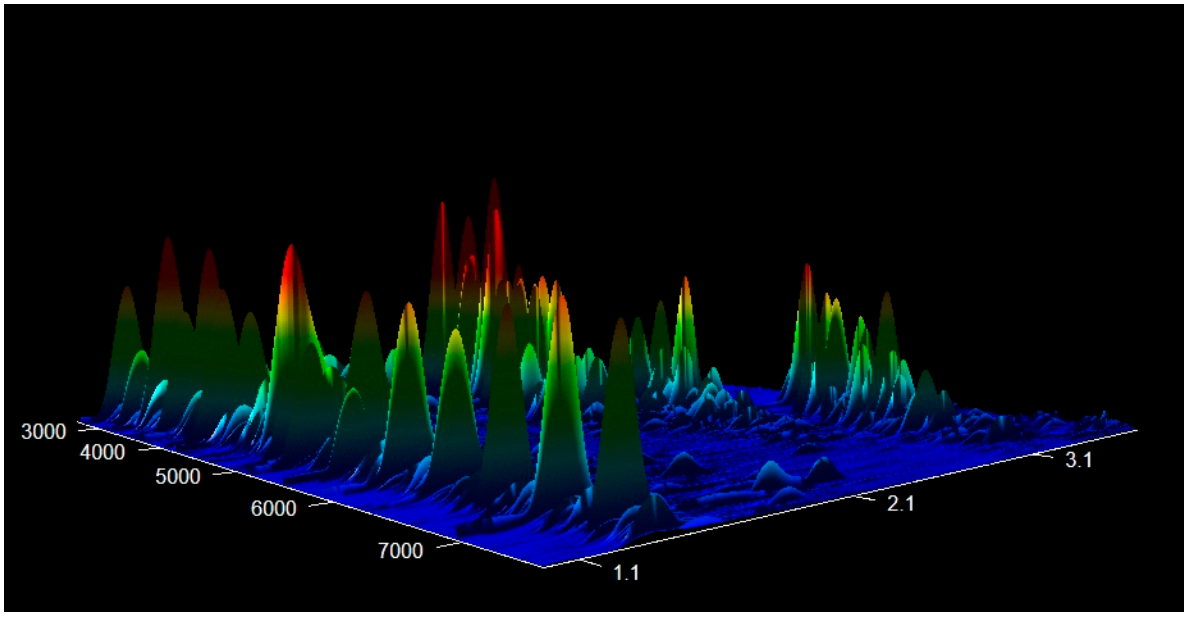
Source: https://www.whoi.edu/oceanus/feature/every-chromatogram-tells-a-story/
Oceanus, 2011

In this article, Bob Nelson and Chris Reddy at the Woods Hole Oceanographic Institution (WHOI) share their favorite analogy about GCxGC chromatograms and topographical maps. A quick history into the legacy of oil spill research at WHOI and use of gas chromatography is presented along with a simple explanation on how GCxGC works, what the value of the structured nature of GCxGC chromatograms for finding analytes of interest in "a haystack of chemical needles" can be, and how using "molecular fossils" unearthed by GCxGC can determine geographic source and develop further insights into Earth's tectonic movements.

Bob Nelson

Access the Article

Chris Reddy



Rotated 3D-surface plot of heavy fuel oils

Summary: Predictive Modeling of Aerospace Fuel Properties Using GCxGC with TOFMS and PLS Analysis

Source: https://pubs.acs.org/doi/10.1021/acs.energyfuels.9b04108
Energy & Fuels, March 2020

Researchers at the University of Washington used a LECO *Pegasus* GCxGC system to analyze 74 distillate and multicomponent aerospace fuels, using statistical modeling and a chemometric approach to prove the correlation between chemical compositions of samples to measure bulk physical properties like viscosity, heat of combustion, measured hydrogen content, and density. These bulk physical properties for aerospace fuels are especially important because requirements are increasingly strict for engines with very narrow margins of error to meet performance needs in high-risk situations.

The authors credit GCxGC-TOFMS as a tool that "significantly improves upon the separation power of one-dimensional (1D) GC and provides additional insight into complex mixtures of volatile compounds including kerosene-based fuels."

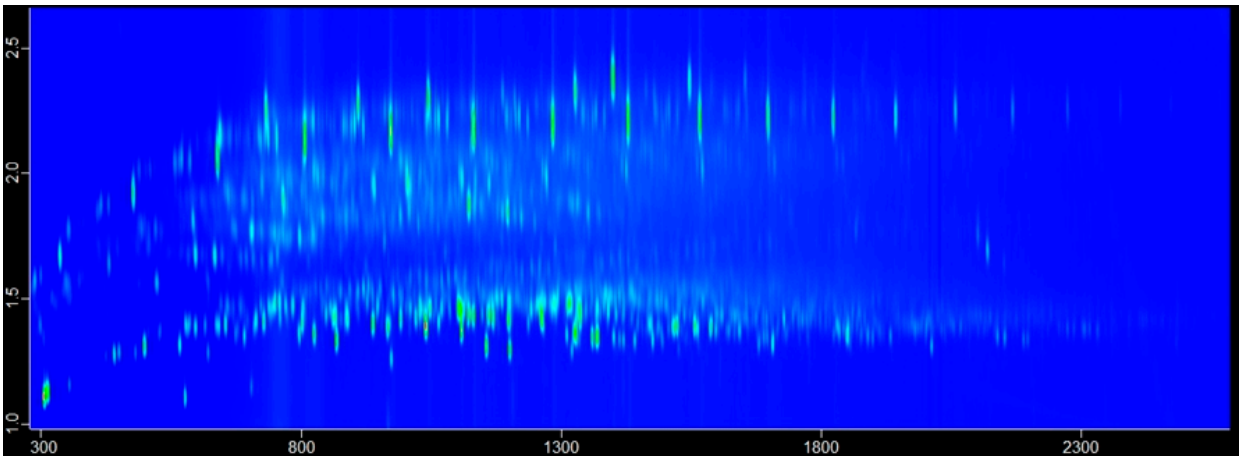
Choosing to use a "reversed-column configuration" with a higher polarity column as primary and a lower polarity column as secondary, the authors claim this setup "enables a much more detailed examination of the physical properties in relation to chemical composition than previously demonstrated." The improvement in chromatography is not their only advantage, however.

Because a TOFMS detector was used, "informative utilization of m/z that are representative of chemical compounds classes present in the fuel is possible," so that the additional mass dimension can be leveraged. Several extracted ion chromatograms with representative masses that correspond to compound classes and subclasses such as alkanes, mono- and di-cycloalkanes, alkyl benzenes, naphthalenes, and sulfur-containing compounds clearly showed how mass selectivity for each class allows for additional criteria that assist in resolving individual compounds.

This separation of individual compounds is especially important, as the authors assert that "GCxGC-TOFMS analysis provides a means to investigate the chemical composition of fuels at a deeper level, while partial least squares (PLS) modeling leverages these chemical composition differences in the samples at the specific compound level instead of the bulk compound level."

The authors conclude that "the underlying goal of this research is to gain a fundamental comprehension of the chemical basis for fuel performance through chemometric modeling by relating measured fuel property data to chemical composition data acquired by GCxGC-TOFMS" and were able to show correlations between the presence and concentration of specific chemical classes to be consistent with expected bulk properties behaviors.

Access the Article



Reverse-phase separation

Summary: *GCxGC Analysis of Novel 2α-Methyl Biomarker Compounds from a Large Middle East Oilfield*

Source: https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c00949
Energy & Fuels, June 2022

Petroleum biomarkers are important tools for determining how to best extract oil from reservoirs and what refinery procedures are necessary for treating the raw material downstream, as well as for use in fingerprinting sources of petroleum products in environmental applications.

In this paper, a new subclass of 2α-methyl biomarker compounds in Middle Eastern crude oil samples is revealed with high confidence in identification using pieces of information from multiple technologies, without the use of pure chemical standards. As the authors state, "GCxGC-FID, GCxGC-ToF, and GCxGC-HRT accurate mass capabilities were utilized to elucidate the chemical formulas of 2α-methyl transformation products derived from 2α-methyl hopanoids that have not been previously described in the chemical literature."

The use of GCxGC technology was a clear choice in this analysis, as "GCxGC analytical instrumentation is uniquely well adapted for the analysis of GC-amenable compounds in the C8 to C40 carbon range, which constitutes a large portion of the liquid fraction of crude oil." Because of the structured nature of GCxGC chromatograms, "physical characteristics of a given compound, such as boiling point and polarizability, can be visualized and modeled by its elution position on the 2D chromatographic plane." In addition, GCxGC provides necessary additional chromatographic resolution and sensitivity because these 2α-methyl compounds often coelute with other compounds in a densely populated chromatographic region that cannot be resolved with a single dimension separation alone. The authors acknowledge that the combination of this enhanced chromatographic information with accurate mass spectral data provided by the HR-TOFMS "lends a high degree of confidence to the discovery and identification of the 2α-methyl compounds presented here."

The mass spectra for sesquiterpanoids and tetracyclic terpanoids along with the novel 2α-methyl sesquiterpanoid analogs and 2α-methyl tetracyclic terpanoids are shown with calculated mass accuracies of the molecular ion and expected major fragments within 1ppm. The excellent mass accuracies and GCxGC position combine for confident identification of these newly-discovered compounds, which are "valuable biomarkers for ancient cyanobacterial inputs to petroleum producing sedimentary organic systems/reservoirs.

Access the Article

LECO Pegasus GC-HRT⁺ 4D

Summary: *MV Wakashio grounding incident in Mauritius 2020: The world's first major spillage of Very Low Sulfur Fuel Oil*

Source: https://www.sciencedirect.com/science/article/pii/S0025326X21009516
Marine Pollution Bulletin, October 2021

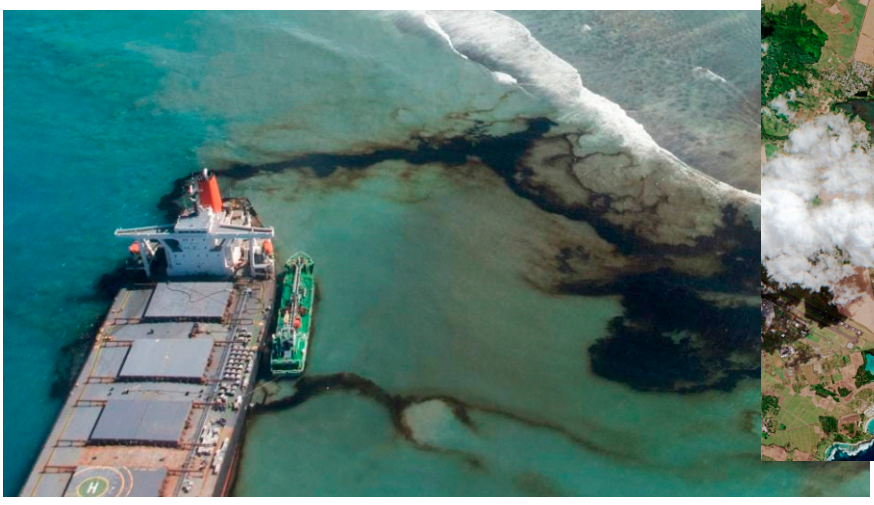
Very Low Sulfur Fuel Oils (VLSFO) have been required for use in ships since the Global Sulfur Cap regulation was implemented by the International Maritime Organization in January 2020, reducing total sulfur in ship fuels from 3.5% to 0.5% by weight. Since then, the first documented case of an accidental release in the environment occurred in July 2020 from the MV Wakashio, a ship that was reported to have released 1000 tons of VLSFO when it ran aground on a reef in Mauritius.

In this paper, a variety of techniques including GCxGC-FID and GCxGC-HRTOFMS "shown to be highly capable of resolving complex mixtures such as weathered crude oils" were used to provide characterization of fuel oil from the MV Wakashio and an oily sheen collected from the environment in order to confirm the source of the oil spill and to provide detailed information on composition of the spilled fuel so that proper post-spill management strategies could be implemented off the Mauritius coast.

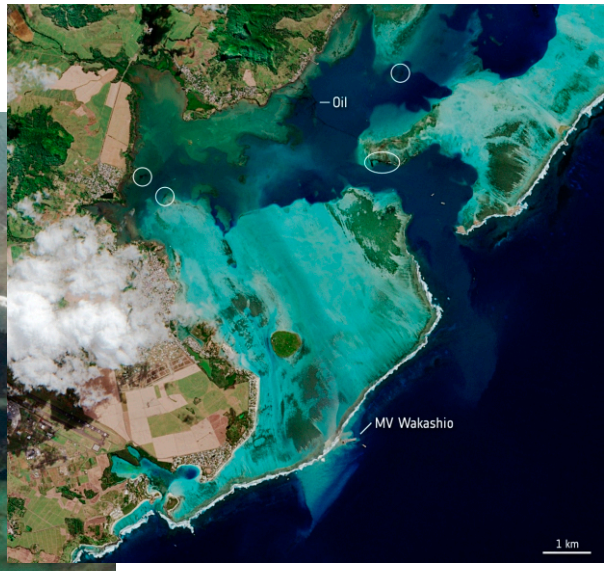
The study confirmed that the oily sheen collected was indeed from the grounded ship, using elemental analysis as well as detailed petroleum biomarker information from the *Pegasus* GCxGC-HRTOFMS, which provided "unambiguous identification of biomarkers (mass accuracies typically under 1ppm) even in highly weathered oils." In addition to the typical suite of hopanoid and terpanoid molecules used as biomarkers, even though sulfur compounds were in very low abundance, the sensitivity of the *Pegasus* HRT+4D revealed that sulfur thermal maturity markers of "dibenzothiophene and its alkylated homologs showed the same profile in both oils".

In the same GCxGC-HRTOFMS analysis, information beyond just biomarker identification was extracted, looking at the total PAH content as well as individual species in order to assess the toxicity of a sample. The authors were able to conclude that compared to other oil spills in the past, "the potential impact of the spilled oil due to the release of toxic PAHs appears to be relatively low compared to traditional marine fuels or many crude oils although it is possible that localized concentrations… could have been sufficient to cause acute toxic effects."

Access the Article



MV Wakashio



Mauritius coast where ship was grounded

Featured Collaborator: Woods Hole Oceanographic Institution

The Organic Geochemistry Analysis Lab-GCxGC Facility at Woods Hole Oceanographic Institution (WHOI) has been a world leader in using multidimensional gas chromatography coupled to multiple types of detectors to routinely identify environmental pollutants and fingerprint fuels from oil spills in oceans all around the globe. Since 2005, when they first featured a comprehensive two-dimensional gas chromatogram on the cover of the ACS journal of Analytical Chemistry, Robert K. Nelson and Dr. Christopher M. Reddy, the main GCxGC users in this lab, have published over 100 scientific papers and several book chapters that provide guidance on how to analyze hydrocarbon samples using multidimensional gas chromatography.

Dr. Christopher M. Reddy received his Ph.D in Chemical Oceanography in 1997 from the University of Rhode Island and has continued to research marine pollution, marine natural products, and "focus on communicating science and how science works." Most recently, he has provided a voice for scientific understanding of the world in many news events including interviews with U.S. News & World Report on nanoparticles in takeout coffee cups, NPR on washed-up rubber bales on the coast of Texas, and WIRED on extinguishing ocean fire in the Gulf of Mexico.

Robert "Bob" K. Nelson specializes in using GCxGC, which he considers a "very high resolution chromatographic technique" coupled with time-of-flight mass spectrometry or flame ionization detection to study the source, transport, and ultimate fate of petroleum hydrocarbons and other man-made contaminants in the environment. The additional resolution of the second dimension of separation offered by GCxGC has allowed him to more accurately quantify and even continually discover new petroleum biomarkers which act as oil spill fingerprinting tools and indicators of ancient sedimentary depositional environments.

In 2007, Nelson and Reddy won the John B. Phillips award for their manuscript (Arey et al. 2005), chosen by an international committee and judged to have the highest potential impact on the future of GCxGC science. A few years later in 2010, they established the first U.S. patent using GCxGC for detailed petroleum analysis: "High accuracy contamination estimation in hydrocarbon samples using GCxGC."

Vision & Mission

The ocean is a defining feature of our planet and crucial to life on Earth, yet it remains one of the planet's last unexplored frontiers. For this reason, WHOI scientists and engineers are committed to understanding all facets of the ocean as well as its complex connections with Earth's atmosphere, land, ice, seafloor, and life—including humanity. This is essential not only to advance knowledge about our planet, but also to ensure society's long-term welfare and to help guide human stewardship of the environment. WHOI researchers are also dedicated to training future generations of ocean science leaders, to providing unbiased information that informs public policy and decision-making, and to expanding public awareness about the importance of the global ocean and its resources.

Mission Statement

The Woods Hole Oceanographic Institution is dedicated to advancing knowledge of the ocean and its connection with the Earth system through a sustained commitment to excellence in science, engineering, and education, and to the application of this knowledge to problems facing society.

In recent years, the addition of the high-resolution Pegasus HRT+ 4D system has enabled the team at WHOI to take an even deeper dive into the already rich petroleum data from oil spills and identify petroleum biomarkers with even greater confidence as well as add further environmental compounds to their list of interests using new accurate-mass information. From analyses of DDT-tainted barrels on the seafloor in California to the safety of new marine ship fuels, plastics contamination in washed-up nurdles to biofuels for home heating oil, LECO instrumentation leads the way for detailed studies that lead to results that help solve real-life energy and environmental problems on a global scale.

WOODS HOLE OCEANOGRAPHIC INSTITUTION®

LECO Corporation
3000 Lakeview Avenue | St. Joseph, MI 49085 | 800-292-6141 | Phone: 269-985-5496
info@leco.com | www.leco.com | ISO-9001:2015 Q-994 | LECO is a registered trademark of LECO Corporation.

EMPOWERING RESULTS

6/22-REV0