A143 MS/MS Method to Differentiate Dyes in Diesel Fuel

Lisa A. Karwacki, BS, 809 South Jefferson Street, #8, Allentown, PA 18103*

After attending this presentation, attendees will understand the power of MS/MS.

This presentation will impact the forensic community by explaining the development of this method allowing for the rapid analysis of diesel fuels for the presence and identification of fuel dyes.

In the United States, diesel fuels used in normal vehicle road traffic by automobiles and trucks are subject to taxation at what is termed an on- road rate. Off-road machinery using diesel fuel such as tractors, boats, farm, and logging equipment, are exempt from such taxes and as a result cost less to the consumer who purchases such fuel. Since 1994, federal and state laws have mandated the addition of red dye spectrally equivalent to 11.1 mg/L C.I. Solvent Red 26,[1] (Oil Red EGN). Such dyes are added to fuels in order to prevent their use in applications intended for higher- taxed purposes. With the current cost of fuel rising daily, people are more inclined to illegally use lower-taxed fuel in order to save money. Currently, there are two dyes that are added to off-road diesel in the United States: Solvent Red 26 and Solvent Red 164. The Environmental Protection Agency (EPA) uses the red dyes to identify high-sulfur fuels used in off-road vehicles. [2] The Internal Revenue Service (IRS) also requires the use of these dyes to identify tax-exempt diesel fuels. [3] The IRS requires that Solvent Red 164 be added at a concentration spectrally equivalent to at least 3.9 pounds of the solid dye standard solvent Red 26 per thousand barrels of diesel fuel or kerosene.

The most common method currently utilized for determining the presence of these dyes in fuels is visible spectrophotometry. This technique identifies the presence of a dye based on its absorption of light at a distinct wavelength. If significant absorption is present, a determination is made that the dye is present. This technique offers a quick and easy way to make such a determination. However, as samples become more dilute, perhaps due to the addition of higher tax fuel without the dye, the results using such means become less definitive. In such circumstances, it would be beneficial to utilize a technique to detect any dye that might be present and provides molecular confirmation in order to conclusively identify the dye specifically.

A tandem mass spectrometry method using electrospray ionization was developed to identify Solvent Red 26 and Solvent Red 164 that may be present in a diesel fuel sample submitted to the laboratory for analysis. The precursor and product ion of each compound was identified. The precursor ion for the Solvent Red 26 was m/z = 395 with product ions of m/z = 91 and 238, whereas the precursor ion for the Solvent Red 164 was m/z = 353 with product ions of m/z = 199 and 335. A multiple reaction monitoring method (MRM) was then set up to be able to monitor both dyes simultaneously in a diesel fuel sample.

Many other countries also employ the use of fuel dyes for regulatory purposes. Several other dyes were investigated. For each dye, the precursor, as well as the product ion was determined. A MRM method was set up to monitor all the different dyes tested. Each dye had a different precursor and product ion set, so each dye was successfully individualized by the method. After the completion of the method development, a blind proficiency test was completed, with each of the dyes being successfully identified. The development of this method allows for the rapid analysis of diesel fuels for the presence and identification of fuel dyes.

References:

U.S. code title 26, section 4082. Code of Alabama 1975, section 40-17-22.
http://www.epa.gov/otaq/regs/fuels/diesel/diesel.htm#regs
http://www.irs.gov/businesses/small/industries/article/0,,id=98980,00.html

Forensic Science, Fuel Dyes, Diesel Fuel

 ** Presenting Author*