
E102 Preparation of Molecularly Imprinted Polymers for the Extraction of Azo and Anthraquinone Dyes From Diesel Fuel

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Learning Overview: The goal of this presentation is to demonstrate preparation, characterization, and efficiency of Molecularly Imprinted Polymers (MIPs) designed to extract azo and anthraquinone dyes from complex matrices such as diesel fuel. MIPs are prepared for the Solid Phase Extraction (SPE) to be a faster, simpler, and more accurate way for the determination of the presence of these dyes in "laundered" fuel, even when they are present at very low concentrations.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by providing insight into how novel polymeric materials, prepared in a laboratory in an economical and fast way, and used as a sample pretreatment can improve detection of the desired analytes and thus provide valuable forensic evidence.

Fuel consumption is steadily rising, which generates substantial profits for the oil industry, but also causes fuel prices to rise. Except, the economic factors, local laws, and regulations also determine the level of fuel tax, which differs from country to country and depends on its use. In Croatia, fuels are distinguished by use for transport vehicles, heating fuel, and fuel for propulsion of agricultural machines. Blue diesel, intended for use in agriculture, fishing, and aquaculture, has a taxable amount of 0.0 and is classified as a tax-reduced energy source, unlike tax-fueled diesel, for which the price is higher for even 0.4 €L. In order to distinguish fuels depending on use and to prevent misuse, fuels are marked with a dye and a marker. The most commonly used marker in the European Union is Solvent Yellow 124 (SY124), the application of which is legally prescribed in Croatia. This marker is not visible to the naked eye, but only by extraction with hydrochloric or sulfuric acid, and the fuel is also labeled with visible colorants. Colorant used for labeling blue diesel in Croatia is Solvent Blue 35 (SB35), and Solvent Red 19 (SR19) is used for labeling heating oil. The fuel quantity is not legally prescribed, as opposed to the SY124 marker, which is added to the fuel in the amount of 6.0mg/L to 9.0mg/L. A big difference in the tax on such fuels, unlike fuel for transportation and its ever-increasing cost, leads to misuse. The illegal practice of removing fuel differentiation components and reselling it at a higher price is called fuel "laundering." Fuel "laundering" occurs by adsorption of markers and colorants from fuel with widely available materials and chemicals. Losses for the state are measured in the millions. Except for the state, users of such fuel are also damaged, and the substantial damage is made to the environment because of the waste, which is disposed without proper care.

As marker SY124 is not noticeable in fuel to the naked eye, intense work is conducted on the development of analytical procedures for its detection, especially in "laundered" fuel where its concentrations are extremely low. In addition to the SY124 marker, it is also important to prove the presence of blue and red dyes such as SB35 and SR19. For this purpose, MIP syntheses were performed using 4-vinylpyridine, methacrylic acid, or hydroxyethyl methacrylate as functional monomers, ethylene glycol dimethacrylate as a crosslinker, 2,2'-Azobis(2-methylpropionitrile) (AIBN) as an initiator, and acetonitrile as a porogen. Template molecules were dyes SY124, SR19, and SB35 or combinations thereof. Various methods such as Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), the Brunauer-Emmett-Teller surface analysis method, and Evolved Gas Analysis-Mass Spectrometry (EGA-MS) have been used to characterize the MIPs. The efficiency of the prepared printing polymers was monitored by Liquid Chromatography/Tandem Mass Spectrometry (LC-MS/MS) and compared to commercially available SPE columns. The obtained results indicate that MIPs have a possible application in the daily problem of fuel "laundering."

Solvent Yellow 124, Fuel Laundering, Molecularly Imprinted Polymers