



Schlieren Effect in Flow Injection Analysis: Friend or Foe?

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When working with certain samples, such as seawater or estuarine water, the analysis often face the annoying problem of the so-called ‘schlieren effect’. Schlieren effect is normally found in spectrophotometric flow analysis, including flow injection analysis (FIA) and sequential injection analysis (SIA). Schlieren effect is the result of the deflection of light in a medium with gradient refractive index. In FIA, schlieren effect is often observed when injecting a sample with a high refractive index into a flowing stream having a lower refractive index. The boundary region at the head and tail of the injected plug has a gradient of refractive index which results in the schlieren effect. Even with no absorption of light from the sample, there is still a notable signal profile.

A good friend and a well-known FIA researcher, Prof. Ian D. McKelvie, has devised many ways to reduce the schlieren effect since his work deals mostly with analysis of estuarine waters. The simplest approach is matrix matching technique [1]. The sample is injected into a carrier that has closely matched matrix as the sample, e.g., injecting seawater into a stream of a saline water that has equivalent concentration of sodium chloride to the sample. Prof. Ian D. McKelvie and his colleagues have also presented other approaches to diminish the schlieren effect, including use of a multi-reflective flow-cell [2] or the ‘total internal reflection photometric detection’ [3]. Instead of allowing the light to pass through cuvette-flow cell in the usual axial direction, these flow cells are designed to generate more than one directions of light path inside the flow cell. The ideas of these detectors are very clever and they are very effective.

Outside flow injection technique, schlieren effect can be useful in liquid chromatography (LC) and high performance liquid chromatography (HPLC). As undergraduates, we all learn in analytical chemistry laboratory that we can find the position of the void peak in the chromatogram by injecting a plug of a non-retained solvent into the LC or HPLC systems. The signal of the void peak is the result of the schlieren effect. After injection, the solvent plug travels through the column with negligible interaction with the packing materials and comes out more or less as a plug of diluted solvent at the column exit. Inside the Z-flow cell of LC or HPLC, the boundary of the solvent and the mobile phase form a gradient of refractive index causing a signal at spectrophotometric detector. The signal of void peak is not a result of spectrophotometric absorption of the solvent but it is the result of the phenomenon of schlieren effect.

Since we can detect the passage of a non-light absorbing liquid through the schlieren effect, we should be able to utilize this phenomenon to measure its refractive index [4] and density [5]. Applications of the schlieren effect for measuring concentration [6,7] have been carried out based on laser source.

We have also used the schlieren effect to determine sucrose in carbonated soft drinks [8]. In our SIA module, a plug of a degassed sample is inserted into a water carrier before flowing into a cuvette-flow cell with a near-IR detector. Sucrose gradient at two boundaries (head and tail) between soft drink sample and water causes the deflection of light away from the photodiode resulting in two signals. In our arrangement, the light deflection gave two positive peaks for the head and the tail of sample plug. For a better sensitivity, the first peak was used for calibration. Near-IR detector was chosen so that the detector can be used with colored samples. The same SIA module was used to measure color and dissolved CO₂ in the soft drink sequentially.

The schlieren effect is not always a foe to FIA. We can manipulate it for quantitative chemical analysis by forming a sharp boundary of two liquids. If there is a significant difference in the refractive indices, the light passing from one liquid to another liquid will be refracted. The schlieren effect can either deflect the light away from detector or focus the light onto the detector. This can enhance a signal of the spectrophotometer and correlates to the concentration of a solute (analyte) in the liquid medium. However, schlieren effect is not always a friend to FIA. We frequently find this effect as an interference in analysis of samples containing salt or in reversed-FIA, in which a plug of reagent is injected into a flowing stream of sample. In SIA, we may see positive and negative responses in one profile, as there are more than two boundaries of liquids that are formed. Well, this is like the two sides of a coin, a positive and a negative side.

References

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