Lab Highlights
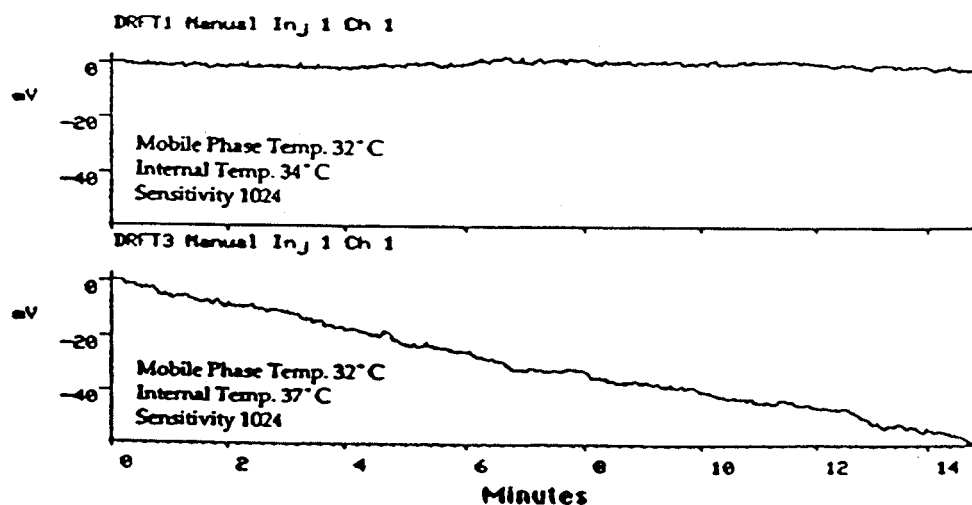
Minimizing Baseline Drift for High Sensitivity Refractive Index Detection

Differential refractive index detectors respond to the difference in refractive index between the sample and reference cells. Baselined drift results when this refractive index difference gradually changes over time and can be observed even when no sample has been injected. At the high sensitivity settings required for low detection limits, even minute changes in the refractive index of the mobile phase relative to the reference will cause significant drift. It is necessary to recognize the possible sources of drift and the best means of control in each case.

Dissolved Gases:

The most common and often overlooked source of drift is the presence of dissolved atmospheric gases in the mobile phase. The solubility of gases is affected by temperature, and as the quantity of dissolved gases varies, so does the refractive index of the solution. The gas content is best stabilized by maintaining the mobile phase at a constant temperature while allowing the solution to be saturated with gases at this temperature. This violates the conventional wisdom that mobile phases must always be degassed. However, a degassed solvent will immediately begin to dissolve gases once the degassing procedure is complete, thus resulting in a continuous change in refractive index until the solution is once again saturated.

Figure 1

DRFT1 Manual Inj 1 Ch 1

mV

Mobile Phase Temp. 32°C
Internal Temp. 34°C
Sensitivity 1024

DRFT3 Manual Inj 1 Ch 1

mV

Mobile Phase Temp. 32°C
Internal Temp. 37°C
Sensitivity 1024

Minutes

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A simple method for stabilizing water for use with the Waters™ 410 Differential Refractometer has been successfully employed in our laboratory. The day before it is to be used the water is drawn, filtered and placed in a loosely covered Erlenmeyer flask. The flask is stirred on a magnetic stirrer overnight. The heat generated by this stirrer is sufficient to maintain the water at a constant temperature of approximately 32°C (other stirrers may give different temperatures) and establish a steady state concentration of dissolved gases. The detector internal temperature is then set at a temperature near that of the water. (Some trial and error may be required to find the optimum internal temperature for minimum drift.) Because there is little or no temperature difference between the detector cells and the solvent reservoir, the solubilities of the gasses will be the same in both locations and there will be no problems with outgassing. Heated columns should not affect the results since the heat exchanger built into the 410 will assure that the temperature of the effluent is the same as that of the cell. Figure 1 shows a stable high sensitivity baseline achieved by this method and the drift caused by too high an internal temperature.

Because the internal temperature of the 410 is adjustable in 1 degree increments, a degree of control over drift can be achieved which is not possible with competitors' units, where 5 degree increments are typical.

Column Bleed:
A second source of drift is bleeding of sample contaminants from the column. This problem can be eliminated by appropriate sample clean-up, use and timely replacement of guard columns, and regeneration or replacement of a contaminated analytical column. When the mobile phase has been changed to regenerate a column, or for any other reason, drift may be visible for some time. It may be necessary to operate the column for a day or more with a new solvent in order to eliminate all traces of the previous solvent.

Solvent Aging:
Another source of drift is "aging" of the solvent. This is most often seen with unstabilized THF, where peroxides form on exposure to oxygen. The solution in this case is to use stabilized THF if possible (note: not suitable for UV detection at low wavelengths), or to blanket the solvent with inert gas.

If mixed mobile phases are used, selective evaporation of the more volatile component of the mixture from the mobile phase reservoir will cause baseline drift and alter the retention volumes of the sample components. The solvent reservoir should be covered to minimize evaporation. When starting up a column, selective sorption of one mobile phase component by the column will cause drift until equilibration of the column is achieved.

With due care, baseline drift may be reduced to insignificant levels, permitting remarkably low limits (eg. nanograms) of refractive index detection.

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