

## Gas Chromatography Problem Solving and Troubleshooting

### Question:

The response for my NPD changes on a constant basis, making it difficult to maintain the same response factors. What can I do to eliminate the frequent response changes?

### Answer:

It is not unusual for an NPD's response to change over time. Unfortunately, the response can change over a short period of time. Sometimes the response can change within a single day, but response changes over 1–2 weeks are more typical. NPDs are very sensitive to changes in their conditions or environment. Detector contamination and changes in the bead, gas flows, or purity are some of the more common sources of NPD response changes.

Changes in the hydrogen, air, or auxiliary or makeup gas flow rates can change NPD response. Whenever a sudden change in NPD response is noted, the gas flows should be checked before undertaking more extensive troubleshooting procedures. Changes in gas purity can also be responsible for a response change. Even a very small change in the gas composition may result in a response change. Slight differences between various lots of the same grade of gas, leaks in the gas lines, or expired gas impurity traps are potential causes of gas composition changes. Gas purity tends to decrease when the cylinder pressure drops below 10% of the original pressure. This means that gas purity can change while the same gas cylinder is still in use. It is recommended that you change all gas cylinders when they reach 10% of their original pressure.

The most common source of a change in NPD response is the bead. NPD beads become depleted or contaminated with normal use. Sample or column bleed compounds can contaminate the bead, thus altering its behavior. Changes in the absolute and relative responses, along with an increase in noise, may occur. Sometimes increasing the bead current will compensate for bead contamination. The jet and collector can also become contaminated, potentially changing response. Depletion of the bead is normal and occurs whenever current is applied to the bead. As the bead becomes depleted, higher bead currents are necessary to maintain the same response. Eventually, the bead will need replacing. Because NPD beads are not all the same, each bead becomes depleted at a different rate and requires a different amount of current to maintain a given response.

Using a known test sample may be a very useful technique to measure and set NPD response. A test sample contains compounds of known concentration and is analyzed using a fixed set of conditions. Because of previous injections done while the GC system was satisfactory, the appearance of the resulting chromatogram and detector responses should be well known. Whenever the NPD needs evaluation, the test sample is injected, and the bead current is adjusted until the response is within 10% of the target value. Usually peak-area or signal-to-noise ratio is used to compare responses. After a little practice, only a few injections and current adjustments are needed to obtain the target response value. Using a test sample standardizes the NPD response and provides a consistent reference point.

Obviously, nitrogen- or phosphorous-containing compounds are suitable as test compounds, but some are better than others. Alcohols, carboxylic acids, and primary and secondary amines are less desirable because of their activity. Active compounds may exhibit peak tailing or response losses due to adsorption by the column or injector liner. Thus, a change in response (i.e., loss) may not be caused solely by the NPD, but by compound adsorption. Tertiary amines containing a large amount of hydrocarbon character such as a trialkyl amine (e.g., tributylamine) are often ideal because they are less susceptible to adsorption. An alkyl phosphate (e.g., trimethylphosphate) can be used to measure phosphorous response. One commercially available test sample contains malathion (2 pg/ $\mu$ L), azobenzene (10 pg/ $\mu$ L), and octadecane (2 ng/ $\mu$ L) in iso-octane. The malathion is used to measure phosphorous response, the azobenzene is used to measure the nitrogen response, and the octadecane is used to measure the relative nitrogen and phosphorous response to a hydrocarbon.

Even with a standardized or referenced NPD, multiple-point calibration curves should be run with each set of samples, especially if the samples are run more than one day apart. Relying on response factors or calibration curves generated more than one day prior to the analysis of the samples will lead to quantitation errors. Even if a detector maintains a fairly stable response over time, changes in other parts of the GC may affect the absolute response, thus calibration curves need to be generated with each set of samples.

The purpose of *Chromatography Problem Solving and Troubleshooting* is to have selected experts answer chromatographic questions in any of the various separation fields (GC, GC-MS, HPLC, TLC, SFC, HPTLC, open column, etc.). If you have questions or problems that you would like answered, please forward these to the *Journal* editorial office with all pertinent details: instrument operating conditions, temperatures, pressures, columns, support materials, liquid phases, carrier gas, mobile phases, detectors, example chromatograms, etc. In addition, if you would like to share your expertise or experience in the form of a particular question accompanied by the answer, please forward to JCS Associate Editor, *Chromatography Problem Solving and Troubleshooting*, P.O. Box 48312, Niles, IL 60714. All questions/answers are reviewed to ensure completeness. The *Journal* reserves the right not to publish submitted questions/answers.

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