Evaluation of HATS Calibrations Scales: Is the Microtube Gravimetric Method Reliable?

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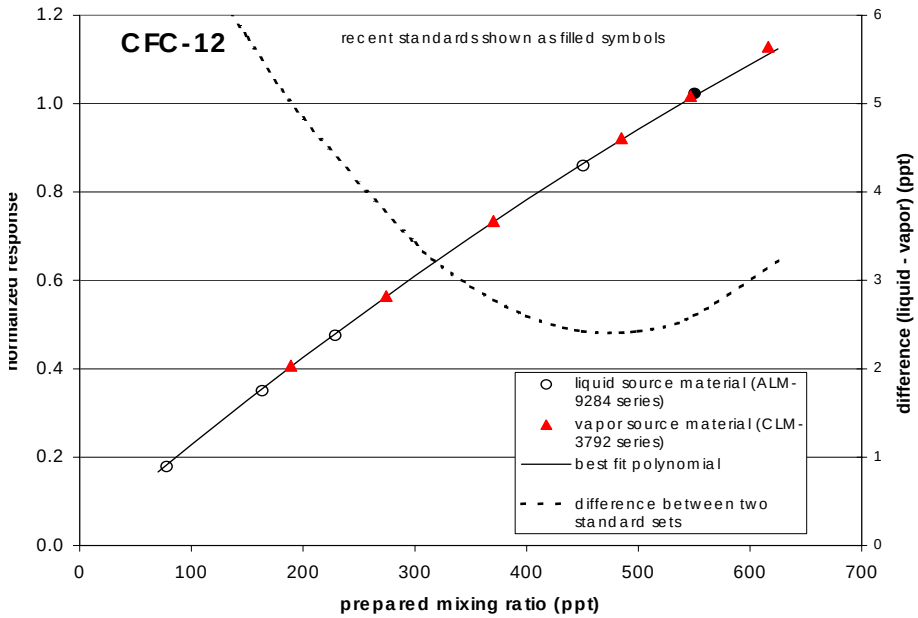
It has been suggested that the liquid-based microtube method might be vulnerable to an artifact when used to prepare standards of compounds with high vapor pressures. This potential artifact may contribute to discrepancies in calibration scales. Comparisons between NOAA and AGAGE calibration scales have shown that the NOAA scales often lead to higher atmospheric concentrations. An experiment to test for H_2O condensation within the microtubes during the sealing step was performed. The mass gained because of condensation was found to be negligible. The existence of an artifact can also be examined by comparing CFC-12 standards prepared by two independent techniques, the liquid-based method and a vapor-based method that does not involve microtubes. Calibrations of ambient air samples performed using these two independent sets of gravimetric standards agree to within 2.5 ppt (at 535 ppt mixing ratio). Larger differences exist at lower mixing ratios. The uncertainties associated with the response curves are about 1.8 and 1.7 ppt for liquid-based and vapor-based standard sets, respectively. While the microtube method results in a slightly higher calibration scale than the vapor-based method, the difference is not significant for ambient CFC-12 mixing ratios. Long-term drift of the low level standards is being investigated.

In an effort to improve the reliability of calibrations performed on GC-ECD instruments and improve detection of long-term drift, five "working standards" were prepared from mixtures of ultrapure air and natural air. These standards have been analyzed monthly on the main GC-ECD instrument used for the calibration of standards for the in situ monitoring program. The long-term record of these new working standards will be used to track minor changes in instrument response. This will increase the life of gravimetric standards because the new working standards can serve as surrogates for gravimetric standards, reducing the need to frequently analyze the gravimetric standards.



ECD response curves of two sets of gravimetric standards prepared from liquid and vapor starting materials. The dashed line is the difference between calibration scales derived from each set.