

3.0 CALIBRATION STANDARDS

3.1 Preparation, Ranges, and Traceability of Standards

Four standards are used in calibrating the carbon analyzers: 5% nominal CH₄ in He, 5% nominal CO₂ in He, KHP, and sucrose. Only the calibration gases are used on a daily basis as analyzer performance monitors. KHP and sucrose are used in conjunction with the two gases semiannually to establish the calibration curve of each analyzer.

The calibration gases are traceable to NIST standards. The gases are assayed for exact concentrations by the gas supplier to two decimal places. The assay value is obtained from the tag on the cylinders.

The KHP is dried at 110°C for two hours before dispensing. Transfer 0.3826 g of KHP into a glass 100 ml volumetric flask after the KHP has come to room temperature. Dilute to volume with 0.4 ml concentrated hydrochloric acid (HCl) and distilled deionized water (DDW). Mix the KHP thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. This solution is good for 40 days. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. The concentration, nominally 1800 ppm carbon, is calculated by :

$$\left(\frac{\text{Actual g KHP}}{100 \text{ ml}} \right) \left(\frac{96 \text{ Carbon}}{204.23 \text{ g KHP}} \right) \left(\frac{10^{-3} \text{ ml}}{\mu\text{l}} \right) \left(\frac{10^6 \mu\text{g}}{\text{g}} \right) = \frac{\mu\text{g Carbon}}{\mu\text{l solution}}$$

The nominal 1800 ppm sucrose solution is prepared by transferring 0.428 g of sucrose into a glass 100 ml volumetric flask. Dilute to volume with DDW. Mix the sucrose thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. This solution is good for 40 days. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. The concentration is calculated by:

$$\left(\frac{\text{Actual g Sucrose}}{100 \text{ ml}} \right) \left(\frac{144 \text{ Carbon}}{342.31 \text{ g Sucrose}} \right) \left(\frac{10^{-3} \text{ ml}}{\mu\text{l}} \right) \left(\frac{10^6 \mu\text{g}}{\text{g}} \right) = \frac{\mu\text{g Carbon}}{\mu\text{l solution}}$$

To prepare a blank solution, add 0.4 ml of concentrated HCl to a glass 100 ml volumetric flask and dilute to volume with DDW. This acidified DDW is made fresh each time a 1800 ppm KHP stock solution is prepared.

No primary standards (NIST-traceable) currently exist for carbon analysis. Ideally, such standards should include a range of organic compounds from low to high molecular weights and with varying degrees of susceptibility to pyrolysis, as well as elemental carbon and carbonate compounds. Currently, KHP, sucrose, and the two calibration gases are used at DRI for calibration and system audit purposes.

3.2 Use of Standards

The calibration slopes derived from the two gases and the KHP- and sucrose-spiked filter punches are averaged together to yield a single calibration slope for a given analyzer. This slope represents the response of the entire analyzer to generic carbon compounds and includes the efficiencies of the oxidation and methanator zones and the sensitivity of the FID. Note that the current calibration procedure is based only on the total carbon; currently no routine procedure exists to check the accuracy of the OC/EC split.

3.3 Typical Accuracy of Calibration Standards

The accuracy of the calibration standards is primarily limited by the accuracy of the calibration gas assays and by the accuracy of the preparation of the KHP and sucrose solutions. The calibration slopes determined by these four compounds historically differ by less than 5% on a given analyzer if sufficient care is taken during the calibration procedure (Section 5.1). Refer to Figure 3-1 for an example of plotted calibration curves.

4.0 PROCEDURES

4.1 Analyzer Start-Up

The following steps outline analyzer start-up:

- Check all gas cylinders' pressures; cylinders with gas pressures less than 500 psi should be replaced before beginning the day's analysis. The cylinder pressure of new tanks should be recorded in **ALL** analyzer log books.
- Check that all gas delivery pressures are correct:

Hydrogen	--	17 psi
Helium	--	15 psi
Compressed air	--	10 psi
O ₂ /He mix	--	10 psi
CH ₄ /He mix	--	10 psi
CO ₂ /He mix	--	10 psi
- Check that the FID is lit by holding a pair of tweezers over the FID exhaust stack and watching for condensation. If the FID is not lit (as immediately after the hydrogen or compressed air cylinders are changed), relight the flame by turning the H₂ rotameter to "100" and holding a butane lighter or match over the FID stack. A light pop indicates that the flame is lit. Verify that the flame remains lit by the tweezers test. Often the flame will not stay lit the first time, especially after the hydrogen cylinder is changed and air gets into