± 50% of the IAR observed in the mid-point initial calibration standard. If project-specific requirements involve reporting sample concentrations below the LOQ, the IAR must fall within ± 50% of the IAR observed in either the mid-point initial calibration standard or the initial CV (see Section 14.3.5 for applicability).

The total response of all isomers (branched and linear) in the quantitative standards must be used to define the IAR. In samples, the total response should include only the branched isomer peaks that have been identified in either the quantitative or qualitative standard (see Section 7.3 regarding records of traceability of all standards). If standards (either quantitative or qualitative) are not available for purchase, only the linear isomer can be identified and quantitated in samples. The ratio requirement does not apply for PFBA, PFPeA, NMeFOSE, NEtFOSE, PFMPA, and PFMBA because suitable (not detectable or inadequate S/N) secondary transitions (Q2) are not available.

15.1.4 If the field sample result does not all meet the criteria stated in Sections 15.1.1 through 15.1.3, and all sample preparation avenues (e.g., extract cleanup, sample dilution, etc.) have been exhausted, the result may only be reported with a data qualifier alerting the data user that the result could not be confirmed because it did not meet the method-required criteria and therefore should be considered a tentative identification and an estimated value. If the criteria listed above are not met for the standards, the laboratory must stop analysis of samples and correct the issue.

15.2 Quantitative determination

Concentrations of the target analytes are determined with respect to the extracted internal standard (EIS) which is added to the sample prior to extraction. The EIS is quantitated with respect to a non-extracted internal standard (NIS), as shown in Table 9, using the response ratios or response factors from the most recent multi-level initial calibration (Section 10.3). Other equations may be used if the laboratory demonstrates that those equations produce the same numerical result as produced by the equations below.

For the target analytes:

$$Concentration\ (ng/L\ or\ ng/g) = \frac{Area_t\ M_{EIS}}{Area_{EIS}(\overline{RR}\ or\ \overline{RF})} \times DF \times \frac{1}{W_S}$$

where:

$Area_t$ = Measured area of the Q1 m/z for the target analyte

$Area_{EIS}$ = Measured area at the Q1 m/z for the EIS. *See note below.*

M_{EIS} = Mass of the EIS added (ng)

$\overline{RR}$ = Average response ratio used to quantify target analytes by the isotope dilution method

$\overline{RF}$ = Average response factor used to quantify target analytes by the extracted internal standard method

DF = Dilution factor. If no dilution was performed, then DF=1.

W_S = Sample volume (L) or weight (g)

Note: *For better accuracy, EPA recommends that PFTrDA be quantified using the average of the areas of labeled compounds $^{13}C_2$-PFTeDA and $^{13}C_2$-PFDoA.*

And for the EIS compounds:

$$Concentration\ (ng/L\ or\ ng/g) = \frac{Area_{EIS}\ M_{NIS}}{Area_{NIS}\overline{RF_s}} \times DF\ \times \frac{1}{W_S}$$

where:

$Area_{EIS}$ = Measured area at the Q1 m/z for the EIS

$Area_{NIS}$ = Measured area of the Q1 m/z for the NIS

M_{NIS} = Mass of the NIS added (ng)

DF = Dilution factor. If no dilution was performed, then DF=1.

W_S = Sample volume (L) or weight (g)

$\overline{RF_s}$ = Average response factor used to quantify the EIS by the non-extracted internal standard method

Results for target analytes are recovery corrected by the method of quantification. EIS recoveries are determined against the NIS and are used as general indicators of overall analytical quality. The NIS has no impact on the target analyte result.

The instrument measures the target analytes as either their anions or neutral forms. **The default approach for Clean Water Act uses of the method is to report the analytes in their acid or neutral forms,** using the following equation to convert the concentrations:

$$C_{Acid} = C_{Anion} \times \frac{MW_{Acid}}{MW_{Anion}}$$

where:

C_{Anion} = Analyte concentration in anion form

MW_{Acid} = Molecular weight of the acid form

MW_{Anion} = Molecular weight of the anion form

15.3 Sample dilutions

15.3.1 If the Q1 area for any compound exceeds the calibration range of the system, dilute a subsample of the sample extract with the methanolic ammonium hydroxide and acetic acid solution in Section 7.1.9 and analyze the diluted extract for the analyte(s) that exceeded the calibration range. If the responses for any EIS in the diluted extract that is associated with one of those analytes meet the S/N and retention time requirements in Sections 15.1.1 and 15.1.2, and the EIS recoveries from the analysis of the diluted extract are greater than 5%, then the compounds associated with those EIS compounds may be quantified using the EIS response. Adjust the compound concentrations, detection limits, minimum levels, and LOQs to account for the dilution.

If the EIS responses in the diluted extract do not meet those S/N and retention time requirements, then the compound cannot be measured reliably by isotope dilution in the diluted extract. In such cases, the laboratory must take a smaller aliquot of any affected aqueous sample and dilute it to 500 mL with reagent water and prepare and analyze the diluted aqueous sample, or prepare and analyze a smaller aliquot of soil, biosolid, sediment, or tissue sample. Adjust the calibration ranges, detection limits, and LOQs to account for the tested sample mass/volume and any dilution factors.

If a dilution results in an EIS recovery less than 5% for the analyte that required the dilution, then the laboratory must prepare and analyze a diluted aqueous sample or a smaller aliquot of a solid sample.