Quality Control and Assurance for CSIA of VOCs in Water Samples

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1. Sample custody and traceability

1.1. Newly arrived samples are inspected and cross-checked against the Chain of Custody provided by the client.

1.2. Information from Chain of Custody is entered into the OU laboratory database. In reporting, both the OU reference number and the client's reference numbers are included.

1.3. Prior to analysis, samples are stored refrigerated. If the samples are preserved by acid, pH of the samples is confirmed prior to analysis (results from samples with pH out of specification are flagged in the report).

1.4. After analysis, unused samples are held until potential follow up questions are resolved. After that, the samples are disposed following the University of Oklahoma hazardous waste protocols. Unused samples can be shipped back to the client or archived, if requested.

2. Determination of isotope ratios

2.1. Identification of target compounds. In C and H CSIA, target compounds are identified by: 1) comparing the time of elution of an unknown compound (GC retention time) to a benchmark time obtained from analysis of a control sample spiked with the target analyte; and 2) comparing the signal obtained for the compound with that predicted by known concentration of that compound in specific sample. In certain situations, peak identification based on retention time and signal intensity alone is equivocal. If necessary, target compound identification is confirmed by CSIA of authentic sample spiked with excess of the target analyte or by reanalysis of the sample using GC/qMS in full scan mode. In Cl CSIA, in addition to the retention time, partial mass spectrum (molecular ions only) is obtained during the analysis, permitting unequivocal identification of the target.

2.2. Initial normalization of the isotope ratios. In C and H CSIA, target compounds are first converted to a surrogate gas (H_2 or CO_2). The isotope ratios are determined by analysis of that surrogate gas. Identical standard gas is pulsed into the IRMS instrument during analysis, to provide reference peaks with known isotope composition. Multiple pulses of the reference gas are introduced to bracket the peaks of the target analytes. CSIA software uses the known isotope ratios of those bracketing pulses to convert raw detector outputs to isotope ratios. These isotope ratios require additional correction for analytical bias (2.8). In Cl CSIA, the approach is similar, but instead of bracketing by gas pulses introduced during an analysis, unknown samples are bracketed by LCS samples analyzed at frequent intervals (see 2.3). No more than three samples are analyzed within each LCS bracket.

2.3. Laboratory Control Samples. LCS samples are prepared using the target analytes of interest, for a specific batch of unknown samples. The target compounds are dissolved in water. LCS are analyzed using the full analytical protocol, identical to that applied to analyze unknown samples (combining extraction, GC separation, thermal conversion and mass spectrometry). LCS samples are analyzed daily, at the minimum at the start of given sample sequence and then repeated after not more than 10 unknowns (carbon) or after 3 unknowns (hydrogen and chlorine). LCS results outside of the expected range (in terms of signal strength and the isotope ratios) trigger appropriate corrective actions to restore the performance. Afterwards, the performance is verified by reanalysis of the LCS. Depending on the nature of the problem, samples analyzed prior to the failed LCS may have to be reanalyzed. The LCS data define the method precision and, if the isotope ratios of the standards used in LCS are known independently (see 3.1), they can be used to correct for the analytical bias of isotope ratio determination (see 2.8).

2.4. Laboratory Duplicates. LDs are run as a routine quality control measure. At least 10 % of reported C isotope ratios are duplicated. At least 20 % of reported Cl and H isotope ratios are duplicated. The results from the duplicates provide an additional line of evidence on CSIA precision. The offset between the results of lab duplicates should not exceed a double of the analytical precision (see 2.6).

2.5. Field Duplicates. FDs are analyzed if requested by a client. FDs are treated as separate samples.

2.6. Precision. Precision for a given analyte is confirmed using the LCS data. The precision is defined by the offset of individual measurements from the mean of the LCS data set, for the specific analyte. For C CSIA, the precision of $\delta^{13}C$ at ±0.5 ‰ or better is typical. In addition, the results from the LDs should be within the same precision margin.

2.7. Detection limits. The error of CSIA increases for analytes below certain concentration threshold. That threshold has to be determined for new analytes or new method configurations, by analysis of control samples at a range of concentrations. Any results reported for analytes present below the threshold concentration are flagged in the report.

2.8. Analytical bias. Bias is defined by comparing the LCS results with the known isotope ratios of a specific target analyte. The difference between the known value and the average of all LCS samples analyzed with a specific batch of samples constitute the analytical bias for a specific analyte. The main source of the bias in C CSIA is extraction and preconcentration of environmental VOCs. In H CSIA, analytical bias also results commonly from the thermal conversion to H_2. Unless clearly indicated, data are reported after bias correction. See 3.2 for additional information.

2.9. Chromatographic separation. Chromatograms and isotope mass ratio plots are examined visually for evidence of anomalous chromatographic peak geometry. Such anomalies may indicate that the analyte peaks overlap with a non-target compound or compounds, and that the isotope ratios obtained are “diluted” by the interfering compounds. As a second line of evidence, peak areas obtained in CSIA are compared to the those predicted from independently known concentrations of the target analytes. If the signal obtained from CSIA is unreasonably high, it is possible that the GC peak of the target compound is completely hidden by another, much larger GC peak.

Problem results are flagged in the report. Samples with certain or suspected GC resolution problems may require confirmation by 2D-GC-CSIA (2D-GC resolves the target and non-target compounds). If the separation problem is suspected but not positively proven, the question of result validity may be answered by compositional analysis (GC/qMS), using identical GC configuration to that in CSIA.

3. Reference standards

3.1. Ideally, LCS should be made using target analyte(s) with their isotope composition(s) calibrated to the appropriate international isotope scale (VPDB, VSMOW or SMOC). Calibrated standards permit accurate calibration of the results from the unknown samples to the international isotope scales. Calibrated standards can be obtained commercially or developed using high purity (e.g., ACS-grade) specimens, by off-line isotope ratio analysis. E.g., $\delta^{13}C$ is determined by combustion to CO_2 in a sealed glass tube with copper oxide, followed by analysis of the CO_2 product on a dual inlet-IRMS. Calibrated standards can be obtained commercially or developed using high purity (e.g., ACS-grade) specimens, by off-line isotope ratio analysis; $\delta^{13}C$ is determined by combustion to CO_2 in a sealed glass tube with copper oxide, followed by analysis of the CO_2 product on a dual inlet-IRMS; $\delta^{37}Cl$ is determined by combustion to CO_2 in a sealed glass tube with copper oxide, followed by conversion of the product to Methyl Chloride and analysis on a dual inlet-IRMS; $\delta^{2}H$ is determined by reduction to hydrogen, followed by analysis of the H_2 product on a dual inlet-IRMS. Unless indicated to the contrary, the analyses of the standard materials were performed as follows: C isotope analyses were performed by the lab of Dr. Engel at Univ. Oklahoma; Cl isotope analyses were performed by the lab of Dr. Sturchio at Chicago Univ.; H isotope analyses were performed by the lab of Dr. Schimmelmann at Indiana Univ.

3.2. Certain compounds of interest cannot be obtained at sufficient purity to permit off-line isotope analysis. Alternatively, the cost of independent verification of the isotope ratios of a standard may be prohibitive. If no calibrated standards are available, results from the unknowns are reported without bias correction (the latter is indicated in the report). Result without bias correction are typically within 1 ‰ from the true value for C CSIA and within several ‰ for H CSIA. In Cl CSIA, results obtained without SMOC-calibrated standards are reported relative to an arbitrary value of 0 ‰ of the laboratory standard for the compounds of interest.