KUDER ENVIRO-ISOTOPES

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Quality Control and Assurance for CSIA of VOCs Water Samples

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1 Sample custody and traceability

1.1 Chain-of-Custody. Newly arrived samples are inspected and cross-checked against the Chain of Custody provided by the client. Information from Chain of Custody is entered into the KEI database. In reporting, both the KEI reference number and the client's reference numbers are included.

1.2 Preservation. Prior to analysis, samples are stored refrigerated and pH of the samples is confirmed prior to analysis (results from samples pH exceedance are flagged in the report).

1.3 Sample disposal. After analysis, leftover samples (intact VOAs) are retained for at least 4 weeks to permit reanalysis in case of potential follow up questions (clients can request extended retention period). After the retention period, leftover samples are disposed of under contract with a licensed Hazmat waste company.

2 Determination of isotope ratios

2.1 Identification of target compounds. Chromatograms of VOC samples commonly contain peaks associated with the target analytes and with non-target compounds present in the same samples. Target compounds are identified by comparing the GC retention time of a specific peak to the benchmark time obtained from analysis of a control sample spiked with the target analyte. 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 CI 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 The quality of chromatographic separation. Chromatograms and isotope mass ratio plots are examined visually for evidence of anomalous chromatographic peak geometry. Some of the apparent peak deformations do not affect the isotope analysis (for example, peaks can appear "smeared" if the column is overloaded by organic phase of the sample). However, peak geometry anomalies commonly indicate co-eluting peaks (the analyte peak overlapping with a non-target peak or peaks). As a second layer of evidence, peak areas obtained in CSIA are

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compared to 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.

Co-elution means that the obtained isotope ratios are biased. KEI duplicates marginal results at increased dilution as necessary to confirm the absence of true GC coelution(s). Verified problem results are flagged in the report.

Problem results may require additional analytical work after discussion with the client. GC resolution can be verified by 2D-GC-CSIA but needs to be confirmed by clients. 2D-GC is reliable to produce well-resolved VOCs in the presence of a complex organic matrix. 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.

2.3 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 then determined by analysis of surrogate gas. Pulses of matching standard gas are introduced into the IRMS instrument during analysis, providing reference peaks with pre-determined isotope composition. Multiple pulses of the reference gas are introduced to bracket the peaks of the target analytes. Data processing converts detector outputs for chromatographic peaks into isotope ratios, using the reference isotope ratio values programmed for the standard gas pulses. The initial processing also removes peak amplitude linearity effects. These isotope ratios require additional correction for analytical bias (2.9). In Cl CSIA, the approach is similar, but instead of bracketing by gas pulses introduced during an analysis, unknown samples are bracketed by lab control samples (LCS) analyzed at frequent intervals (see 2.4). No more than three Cl CSIA samples are analyzed within each LCS bracket.

2.4 Laboratory Control Samples. LCS samples are prepared using the target analytes of interest, for a specific batch of unknown samples. LCS are prepared to match the characteristics of the real samples. For purge-and-trap analysis, 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, optionally combustion of pyrolysis to produce surrogate gases, 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 3-5 unknowns (hydrogen) and 3 unknowns (chlorine). LCS results outside of the expected range (in terms of signal

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strength and the isotope ratios) trigger appropriate corrective actions to restore 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. LCS data obtained alongside the samples for given sample set document the analytical precision and, if the isotope ratios of the standards used in LCS are known independently (see Section 3), they can be used to correct for the analytical bias of isotope ratio determination (see 2.9).

2.5 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 H isotope ratios are duplicated. The default approach for Cl CSIA is to duplicate 100% of the results. 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 that defined by the LCS data (see 2.8).

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

2.7 Reporting limits. The error of CSIA increases for analytes below certain concentration threshold. That threshold is determined for new analytes or new method configurations, by analysis of control samples at a range of concentrations. Typically, samples for CSIA are selected based on existing concentration data, so that only the samples fitting client's needs of analytical precision are analyzed. Depending on the application, KEI can report data exclusively above the minimum threshold for best achievable analytical precision, or for concentrations below the optimum high-precision threshold if increased analytical uncertainty is acceptable for the project's objectives.

Results reported for analytes present below the high-precision concentration threshold are flagged in the report.

2.8 Precision. Precision for a given analyte is confirmed using the LCS data. Precision is best defined by the offset of individual measurements from the mean of the LCS data set, for the specific analyte. KEI defines the precision as the maximum offset of a single measurement from the mean of a large n of replicates of the sample. For the number of replicates n = 10 or higher, the above is well-approximated by two standard deviations of the data set. For C CSIA, the precision of δ13C at ±0.5 ‰ or better is typical (all replicates of a sample should fall within ±0.5 ‰). The results from the LDs should be within the same precision margin.

2.9 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

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all LCS samples analyzed with a specific batch of samples constitutes the analytical bias for a specific analyte. Bias is the composite of small contributions of isotope fractionation during sample extraction, chromatography and thermal conversion, and mathematical propagation of uncertainty from the reference gas isotope ratio used to calculate the isotope ratios of the samples. Unless clearly indicated, data are reported after bias correction. See Section 3 for additional information.

3. Reference standards

3.1 For VOCs analysis, KEI uses working standards (in the form of LCS) which have been anchored to international isotope scales (VPDB, VSMOW or SMOC), if such standards can be purchased or manufactured. Using such standards assures the results can be compared with similar results produced by different laboratories or at different time periods. Standards chemically identical to the analytes is strongly preferred.

3.2 There is a limited number of CSIA reference materials for common VOCs which can be obtained commercially from academic or government providers. In addition, KEI uses several reference materials developed using high purity (e.g., ACS-grade) specimens by off-line isotope ratio analysis. 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.

3.3. 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. In such situations, the options are (i) bias assessment using nonidentical reference materials (e.g., using chlorinated ethene reference materials in analysis of other chlorinated hydrocarbon); or (ii) determination of isotope ratios of chemically identical working standard material by injection in solvent for GC/IRMS or GC/qMS (chlorine) analysis (direct injection decreases the number of factors contributing to the net bias vs the full PT/GC/MS methodology). If no chemically identical calibrated standards are available, results from the unknowns are reported without full bias correction (the latter is indicated in the report). Results 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.