Quality Control Algorithm for Determining Data Acceptability

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Introduction

Many analytical operations associated with the determination of persistent organic pollutants (POPs) have realized increased efficiencies during the last several years. Most of these achievements have come from improved instrumentation and analytical determination steps[1]. However, some improvements have been associated with increased extraction efficiencies[2] and to a lesser extent, data processing. There has been increased interest in data evaluation, such as evaluating patterns of large data sets[3]. Some efforts have been made to improve the techniques for data evaluation at the laboratory level. One such technique is to use the ratio between the Lower Bound (LB) and Upper Bound (UB) Toxic Equivalence (TEQ) of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans (D/Fs) and polychlorinated biphenyls (PCBs) to assist in determining data acceptability[4]. The focus of our work includes the use of LB/UB comparison to calculate a relative number, identified as a Usability Factor (UF), while incorporating defined Data Quality Objective (DQO) for assessing the data quality of analytical sample results.

Materials and methods

All determinations of D/F and non-ortho PCBs were completed using either a Waters Autospec Premier or a Waters Xevo with MassLynx software and TargetLynx data processing package (Waters, Milford, MA). Results were manually copied into an Excel Workbook (Microsoft) to calculate a UF. Results from this procedure, established in April of 2015, were used for data evaluation in a production setting beginning October of 2015. The procedure involves data suitability determination to verify acceptable responses, including; (1) internal standard recovery, (2) detection limits, (3) absolute response, (4) chromatography, (5) lack of interferences, and (6) associated quality control concerns such as no elevated levels found in method blanks. The associated UF is then used to determine if (1) data are deemed acceptable and meet the data quality objectives (DQOs) for a given assignment, or (2) the DQOs are not met leaving results in question, thus samples may need re-extraction or extracts re-analyzed.

We simplified the decision-making process, as illustrated in Figure 1, by incorporating a DQO-TEQ for given production assignments. If the Total UB-TEQ is less than the DQO-TEQ, the results are acceptable - otherwise, the UF is the next decision point, which is calculated by using the Total TEQ Blank Level (BL_{TEQ}), defined as the average of the Estimated Maximum Possible Concentrations (EMPC) based upon 275 blank results, and is used as follows:

- $UF = D_{abs}/(2xBL_{TEQ} + TEQ_{AmtFnd})$
  - D_{abs} is the absolute difference between the "Amount Found" TEQ_{AmtFnd} (LB) and the $TEQ_{AmtFnd+LOD}$ (UB),
  - $2xBL_{TEQ}$ is 2 times the the calculated blank level based upon 275 blanks.
- If UF < 50%, data are deemed acceptable.
- If UF > 50% data are subjected for further evaluation – Congener Contribution (CC) – because the TEQ contribution from the LOD is significantly higher than the expected LOD contribution based upon historical results.

The Limit of Detection (LOD) values for 5898 samples were determined with an average result slightly higher than the BL, thus the factor of 2xBL resulted in an approximate 95% data acceptablity, which approximates the manual determination of samples subjected to further evaluation.

If the UF exceeds the predetermined setting (50% in this case) the final step for data acceptability, the CC, will be implemented. This is calculated as a ratio from the TEQ sum of elevated LODs compared to the UB-TEQ. If

this ratio exceeds a given percentage (a pre-determined value based upon the assignment), the results will be re-evaluated, the extracts re-analyzed or the sample re-extracted and analyzed. If, on the other hand, the UB TEQ does not reach the DQO value, there are no questionable congener results, or the CC does not surpass the pre-determined percentage and the data are deemed acceptable, results are reportable.

Results and discussion

Upon completion of samples in a production (servicing) laboratory, relatively quick determinations for data usability are needed. Decision points for this process are illustrated in the Figure 1 flowchart. Using UB values makes it relatively simple to identify the low area response, low recovery, elevated levels detected in blanks or other issues that may lead to elevated detection limits.

Table 1. Batch Summary showing data usability.

Sample Number	Matrix	Usability Factor	QC % R	QC Blank	Summary
63-S4	Method Blank	49.98%			Acceptable
63-S1	Whole Milk	0.63%			Acceptable
63-S2	Milk, 2% Low Fat	5.41%			Acceptable
63-S5	Milk, Skim	49.98%			Acceptable

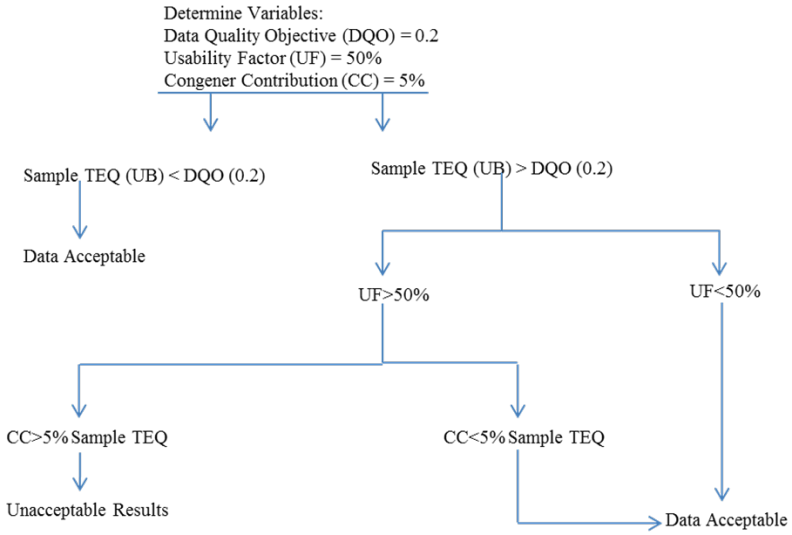
The results shown in Table 1 were acquired from a batch of dairy sample extracts. The Method Blank was fully successful meeting acceptable recoveries, absolute responses and had no detectable quantities above the determined blank levels. Sample 63-S5, Skim Milk, demonstrated the same results as the Method Blank and a UF of 49.98, which indicates no abnormal results. As the fat content increased from skim, to low fat (63-S2) to Whole (63-S1) the UF values decreased indicating an increase in detectable levels, as expected and data were acceptable.

Table 2. Batch Summary showing associated samples should be considered for re-extraction.

Sample Number	Matrix	Usability Factor	QC % R	QC Blank	Summary
693-S3	Method Blank	69.90%	Review	Review	Review
693-S1	Beef Steak- Sirloin	60.38%	Review	Review	Review
693-S2	Luncheon Meat	97.77%	Review	Review	Re-Extract
693-S4	Chicken Breast, Fried	63.83%	Review	Review	Review
693-S5	Chicken Thigh, Oven Roasted	93.29%	Review	Review	Re-Extract
693-S6	Chicken Leg, Fried	48.29%		Review	Review

Results shown in Table 2 illustrate a batch of samples that were identified as needing to be critically reviewed and likely re-extracted. In this case the Method Blank results were questionable due to elevated LODs thus the UF was greater than 49.98. All samples indicate the QC for the Blank has a potential fail, thus indicating the batch, collectively, needs additional review. The UF for samples 693-S1, S2, S4 and S5 were all greater than 49.98; however, the lower UF limit was set at 65% for acceptable and greater than 75% for re-extraction, others require only a review. Consequently, S1 and S4 were determined to be "Re-Extract" due to further manual evaluation of chromatography, recoveries and batch QC. Chromatographic results and reportable values appear to be acceptable for sample S6, but with the issues associated with the batch blank, the results were reviewed and determined to be "Re-Extract" due to consensus batch results. At this point, data were manually evaluated in the next step to determine if DQOs were met.

Figure 1. Flowchart showing process for determining data usability using DQO = 0.2, UF = 50% and CC = 5%.



Using the decision chart shown in Figure 1, the data acceptance step has become automated. With a pre-determined DQO–TEQ the data acceptability can be automatically determined while still incorporating minimum areas, recoveries and batch QC evaluations. Pre-processed data can be moved as .txt files directly into the evaluation stage. For example, if a DQO of 0.4 pg/g TEQ is desired and the sample TEQ is greater than 0.4 pg/g, any UB TEQ conger contributions are summed together to determine if it is greater than 5%. If the sum is less than 5%, the contribution is determined to be negligible, or has an amount found and therefore irrelevant. Table 3 is populated from data used in Table 2. The calculated results show, by including the calculation for DQO, UF and CC that 4 of the five samples need re-extraction. The single sample that does not need re-extraction resulted in an UB TEQ of 0.306, below the DQO of 0.4 pg/g TEQ.

Table 3. Algorithm process to determine data usability.

Sample Number	Matrix	DQO = 0.4	UF = 50	CC =5	Summary
693-S1	Beef Steak Sirloin	0.674	60.38	65.7	Re-Extract
693-S2	Luncheon Meat	0.704	97.77	84.6	Re-Extract
693-S4	Chicken Breast, Fried	0.404	63.83	64.2	Re-Extract
693-S5	Chicken Thigh, Oven Roasted	0.61	93.29	88.8	Re-Extract
693-S6	Chicken Leg, Fried	0.306	*	*	Acceptable Results

*Not calculated due to DQO "Acceptable Results".

There are additional factors to be addressed in data decision making and especially if re-extraction(s) is warranted. These include the history of the matrices, the firms and geographical data. The goal of this work is to minimize the tedious manual searching of questionable data by automatically flagging data for further evaluations. The advantages of the inclusion of these automated data checks, discussed in this work, reduces analyst evaluation time and allows data acceptability to easily be determined with structured criteria.
The risk of using this process is that data evaluations are weighted upon higher TEFs. Thus OCDD, OCDF, PCB77, etc. will have to contribute at a significant concentration level to impact the result.

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