MATRIX AND SITE SPECIFIC QA/QC SAMPLES – A TOOL FOR ONGOING QUALITY CONTROL

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Introduction

The Dow Chemical Company is using several contract laboratories for the analysis of compliance related environmental and internal process samples. In addition to the requirement that the contract laboratories be accredited and certified, which includes laboratory audits by independent institutions and the analysis of proficiency test (PT) samples, we have established an additional tool for an ongoing quality control of our preferred laboratories in the analysis of our specific samples. This Quality Assurance and Control (QAQC) program for metals, volatile and semi-volatile organic components is based on blended, diluted, and intensively homogenized real internal water and solid stream samples which are submitted camouflaged to the laboratories with a certain frequency. These samples can also be used for the initial quality control of contract laboratories anywhere in the world. The initial and ongoing control of the laboratories covers not only the pure comparison of the analytical data but also a data validation and an evaluation of the overall service.

Materials and methods

The qualification process for contract laboratories has traditionally been based upon the results of the analysis of proficiency tests, reference material, and spiked samples for metals, volatile (VOC) and semi-volatile organic compounds (SVOC). This information allows an evaluation as to what extent the basic principles of the quality assurance and control are being implemented and controlled in the laboratory. It also allows for the assessment of the laboratory deliverables and the entire analytical process from sample receipt to the delivery of the final report and data package. With this procedure, we established a list of preferred laboratories which demonstrated both high quality data and data deliverables.

However, this selection process was based upon samples which were spiked water or solid samples and did not necessarily reflect the matrix of real samples with potential specific interferences and matrix effects. Furthermore, it does not allow the quality to be controlled over time. Ongoing precision and recovery (OPR) samples or Matrix spike samples which are often used for such control, may not address these potential effects as the spiked components and the target components in the matrix may be in different physical states. In addition, certified reference material is most likely not available for the specific type of sample matrices to be investigated. In order to assess and control the data quality in specific matrices, we developed special control samples which included most of the key components of interest at different concentration levels and which encompassed their typical sources. The positive experience of using similar types of matrix inherent QAQC samples in previous studies related to dioxin investigation programs[1,2,3] and in our regular laboratory tests for PCDD/F samples provided a useful template in designing this program.

For the creation of the QAQC samples we used internal waste water streams which were blended and diluted to the extent that the key components in this artificial sample were present at different concentration levels. We did not filter the liquids to remove particles, as they are the carrier for some of contaminants. In addition, the presence of more than one phase in the samples posed a further challenge to the laboratories and reflected more the conditions we experience in our real samples. However, creating heterogeneous samples is labor intensive and requires extraordinary precaution to generate identical subsamples which will be the QAQC samples distributed to the laboratories. Thorough homogenization is the key for the intended inter-laboratory comparison of the data and evaluation of the quality.
The procedure to create the water sample included the provision of the entire sample volume diluted to the final concentration range. While the entire mixture was stirred, a small portion was taken out for each sub-sample and

transferred to the final sample bottle. This process was repeated several times until the desired final sample volume was achieved. The potential loss of components between the different rounds of compositing was acceptable because the target was not the determination of the actual concentration in the sample but the inter-laboratory variation which requires the identical amount in all sub-samples. Similarly, the entire amount of the solid sample was rotated and tumbled intensively. The entire sample was passed through a 1 mm mesh size sieve and the sub-samples were generated by distributing small amounts to each jar and repeating the process to achieve the needed final sample volume.

As we anticipated submitting the samples to the laboratories in approximately quarterly intervals, the aspect of the long term stability and integrity of the samples was important.
The holding times for the various components mandated in the different methods are a convention. It does not mean that beyond this point the analytes start to degrade and/or the samples start to disintegrate immediately. However, the different components might have (significantly) different stability periods which would limit the comparison of the data over a longer time period. But, for the purpose of this study, even with such changes over time, the inter-laboratory comparison is still possible as all samples experience the same degree of degradation for the time when the samples were distributed.
When the samples were prepared we had to generate enough bottles to provide duplicates and enough sample volume to perform all the necessary method quality measurements (such as "Matrix Spikes").

In total we generated and homogenized about 50 L of the blended water sample distributed over ~ 500 bottles and about 5.5 kg of a solid sample distributed over ~ 400 bottles. In addition, we prepared ~ 350 blank water samples which accompanied the shipment of the samples. All laboratories received the samples, duplicates and blanks individually labeled with fictitious project names. The shipment was accompanied by a list of components to be analyzed, the requested Reporting Limits (RL) and the analytical methods which were required. We requested the analysis of 69 volatile components with SW-846 method 8260, 114 semi-volatile components with SW-846 method 8270, and 22 metals with SW-846 method 6020. The data were to be delivered as an electronic level II report as well as a hard copy level IV data package accompanied by an EDD (electronic data deliverables). The turn-around-time and other requirements were already specified in contracts and were to be followed as well. The data evaluation was divided into several categories and was not limited only to the pure comparison of the data but also included an evaluation of the overall laboratory performance.

category	Weighing factor	Maximum points
Method QA/QC	2	20
Turn Around Time	2	20
Data quality		
VOC	3	30
SVOC	3	30
Metals	3	30
Quality Exceptions	3	0
Reporting Limits met	2	20
Hold Time met	2	20
Cost (Charged contract price)	2	20
Project Specifications met	2	20
No Additional Compounds reported	2	20
Responsiveness	1	10
Data Package Quality & Completeness	1	10

Table 1: Categories used for evaluation

For instance, the category "Method QA/QC" evaluated the performance vs. the method quality criteria for Relative Percent Difference (RPD), surrogates, Lab Control Spikes (LCS), and Matrix Spikes (MS). Also the number of compounds analyzed in the LCS and MS were factored in.
Depending on the overall performance in each category, the laboratories received scoring points on a scale from 0 to 10 which were multiplied with the weighing factor for that category. These weighing factors represent the importance of that category for the overall performance.

In the reporting limit category, deviations from the requested limit were evaluated. The number of deviating components was summarized and multiplied by factors based on the degree of deviation. These values were then transferred into scoring points as well.

The category "data quality" was divided into the evaluation of the VOC, SVOC, and metals data. Here, the number of components which were outside 2 and 3 standard deviations, respectively, and those which were not analyzed were counted, multiplied with a severity factor, summarized and the results converted into scoring points. While in all other categories the laboratories could collect points, in the category "quality exceptions" they were penalized with negative points for quality issues which were not covered in one of the categories. The point value was dependent on the severity.
Some examples were that data in the EDD did not match the data in the report or that methods other than requested were used or that the analysis was sub-contracted without permission.

Results and discussion

The intent of the study was to investigate the ability of our preferred contract laboratories to analyze actual matrices with a high degree of quality and performance. Therefore, we used a fairly rigorous process with stringent requirements.
A key issue, which led to devaluation of most of the laboratory data, was that the required reporting limits were not met. Often, most of the analytical data were reported from excessive dilutions of the sample which made the majority of the reported data useless. A common issue with several of the laboratories was that they did not analyze the full list of requested components or reported more analytes than requested.
However, all these points do not necessarily pose permanent quality issues, as they may be easily addressed by the laboratories.

Figure 1: Comparison of only the Data Quality

When evaluating the results for the category "Data Quality", which focused solely on the inter-laboratory variation of the data, most of the laboratories exhibited an acceptable to good performance (see figure 1). The laboratories C and D reported only a fraction of the requested analyte list and most of the reported values were from over-diluted samples which provided no data to evaluate.

The evaluation of all data for the solid and the water sample and the overall laboratory performance as depicted in figure 2 showed a different ranking. Interestingly, laboratories F-H had a very good performance level for the data quality, but several quality exceptions were discovered which led to deductions of the overall points. Some issues - such as analyzing only one of the two samples, not using the required method, or sub-contracting analysis without permission - can be addressed by the laboratory management. In contrast, findings of laboratory blanks at elevated levels, not following all method requirements and misidentification of components as seen in the data from laboratory H present a quality issue of concern. A suspension from the list of preferred laboratories is pending.

In general, the laboratories had lower scores for the solid sample which indicates that this matrix was more challenging than the water sample.

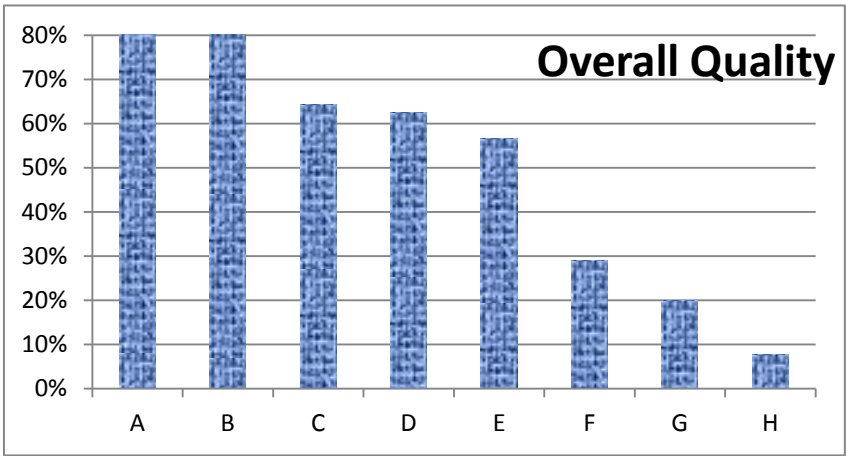

Figure 2: Summary of the overall quality of the participating laboratories

Although all participating laboratories had excellent results in the initial proficiency tests to qualify them as preferred laboratories, with this more challenging matrix some performance issues became apparent.
All issues were communicated to the laboratories and addressed. Most of the laboratories improved their internal process and eliminated most of the deficits.

The study showed that such QA/QC samples in conjunction with a thorough review of the data and deliverables can be an excellent tool to evaluate the quality of laboratories when analyzing real matrices. But there are enormous efforts associated with the generation, storage and distribution of more than 1000 samples, and the evaluation of the associated data and data packages. Therefore, for project specific quality control, we are currently evaluating the concept of site specific QA/QC samples which, similarly, are generated from material from the specific site and are submitted as an additional sample with each shipment. This will allow on-going control of the laboratory with the site specific and realistic matrices.

Acknowledgements

The study would have not been possible without the tremendous efforts and excellent work of all co-workers at Dow's Environmental Laboratory generating around 1250 samples and blanks.

References:

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