The DOW Laboratory Qualification Program

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1.) Introduction

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 PT 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.

2.) Initial Qualification Process

In order to implement an ongoing PT sample program we initially selected 16 full service laboratories we were using and sent commercial (spiked water) PT samples for VOA's only. Due to the vendor's false declaration of the concentration, the information from this commercial PT sample was useless. Therefore we created our own PT samples by blending and diluting internal waste water and solid samples ("real world" samples) which we used for further evaluation of the laboratories. The key components in these matrices were present at varying levels from ppb to ppm range. We did not filter the liquids to remove particles, as they are the carrier for some of the contaminants. In addition, the presence of more than one phase in the samples posed a further challenge to the laboratories and more closely reflected the conditions we experience in our real samples.
Based on the results, 8 specific laboratories exceeding the 75% overall performance margin, which includes not only the data quality but also aspects of service and deliverables, became Dow preferred laboratories. Contracts which specify not only the pricing but also turn-around time and additional quality requirements were established with these laboratories.

3.) Ongoing Laboratory Evaluation

The successful generation of the "real world" PT samples enabled us to implement an ongoing quality assessment tool by submitting and evaluating such samples on a regular basis. We established a Control Plan which outlines the criteria to achieve and maintain the status of a Dow preferred contract laboratory (see figure 1).

The successful analysis of the commercial PT and DMRQA samples is the prerequisite to analyze the Dow PT samples. A score of at least 75 % of the data quality and performance criteria is required to achieve and maintain the status of a Dow preferred laboratory.

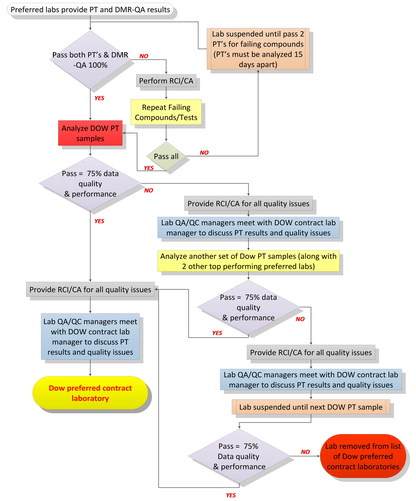

Figure 1: Control Plan

4.) Creation of the PT Samples

The important step is the creation of a series of identical subsamples which will be the DOW PT samples distributed to the laboratories, especially when several phases are present. Thorough homogenization is the key for the intended inter-laboratory comparison of the data and evaluation of the quality. This can be achieved by intensively stirring the stock solution and transferring the sample in several small sub-portions to the final bottles.

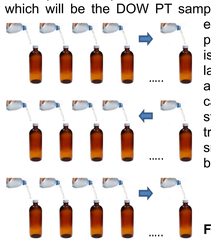

Figure 2: Creation of PT-samples

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. A detailed description can be found in Wilken M, Richardson J (2012)[4].
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 adjusted the list of components to be analyzed to those which are regulated in any of the permits:

- 69 volatile components with method 8260
-114 semi-volatile components with method 8270,
- 22 metals with SW-846 method 6020

We focused the analysis to these methods as they represent ~ 80% of our environmental workload. 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.

5.) Data Evaluation Process

The data quality was determined by compiling the analytical data from all participating laboratories to calculate the average and standard deviation for each compound. Laboratory data for each component that was outside of 2 or 3 standard deviations was computed and multiplied with a weight factor. A similar approach was used for components which were not analyzed. The sum of these points corresponded to a scoring point or percentage, respectively, for data quality for the respective method.

	weight factor	# of hits	points
no data (NA)	2	4	8
> 3 SD	30	1	30
> 2 SD	15	2	30
total points			68

SCORING POINTS	10	9	8	7	6	5	4	3	2	1	0
Data Quality	0	<10	<20	<30	<40	<50	<60	<70	<80	<90	>=90

Table 1: Example of Scoring System

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 2: 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.

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.

Examples for quality issues which fall into the "Quality Exception" category are (**all laboratories are NELAC accredited!**)

- changing the analyte name
- reporting wrong components
- reporting outside calibration range w/o notifying in case narrative
- using other methods than requested
- not following method requirements
- sample hold time exceedances
- analysis of only 1 of the 2 samples
- turn-around-time significantly exceeded (15-98 d)
- not reporting from most appropriate sample dilution
- according to company policy: no matrix spike
- exceeding requested reporting limits
- not following contract specifications
- not charging contract price
- un-authorized sub-contracting

6.) Results of Ongoing Evaluation

In total, we submitted the PT samples three times. After each round we presented the compiled data and the evaluation to the laboratory QA-QC management. We also addressed the discovered issues and requested the laboratories to perform a root cause investigation and provide a corrective action report. The data quality increased from an initial range of 43-78% to 83-96% after the third round.

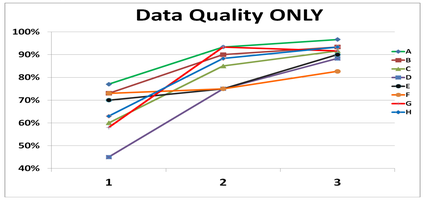

Figure 3: Improvement of Data Quality

In contrast, a steady and overall improvement could not be observed for the performance. While some laboratories showed some improvement, others did not. One laboratory even had a permanent low performance and consequently the status of a preferred contract laboratory was revoked.

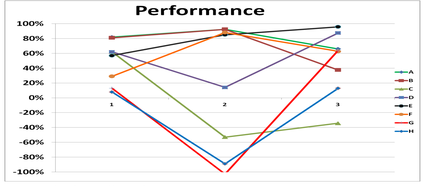

Figure 4: Overall Performance Trend

7.) Annual PT Samples

For the recertification of the Dow preferred contract laboratory status we submit samples to the laboratories on an annual basis. We limit the analysis to blended internal waste water samples but send them neat and diluted. In addition, one of the samples will be submitted as a duplicate

The advantages of this approach are:
- water samples are easier to homogenize
- by changing the origin of the water samples, different matrices can be tested over the years
- quality can be evaluated over a range of concentrations
- the duplicate samples allow the determination of the RPD

Due to the closure of two of our preferred laboratories and the elimination of another we expanded the investigation to a total of 12 laboratories in 2013. The results are shown in figures 5 and 6

Figure 5: Data Quality for 2013 PT-samples

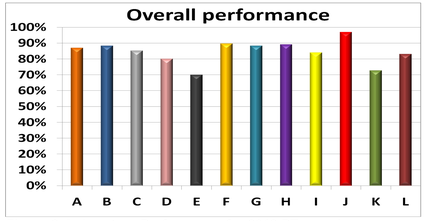

Figure 6: Laboratory Performance for 2013 PT-samples

According to the Control Plan, 3 laboratories which failed to achieve the necessary margin for acceptance as a preferred laboratory in the first place, had to analyze an additional PT sample. For this evaluation two preferred laboratories were included as reference

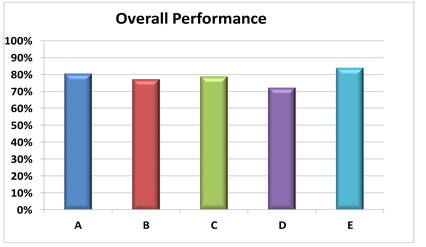

Figure 7: Performance Results for "Second Chance" PT-samples

Based on these data, all 12 laboratories are now in the Dow preferred contract laboratory network.

8.) Site Specific QA/QC

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. Therefore, for project specific quality control, we are using the concept of the annual PT samples in a slightly modified way as "site specific QA/QC-samples". Ahead of a site investigation water samples from that site will be blended and submitted, camouflaged as a regular sample, together with the project samples to the laboratory. In addition, this QA/QC-sample is provided as a duplicate and diluted. These samples are also sent to at least one preferred laboratory as a reference laboratory.

The advantages are:
- the samples have the site specific "backbone" of the local contaminants
- can be submitted as replicates and diluted
- can be used to determine RPD
- are true double blind samples

9.) Summary

The study showed that such PT 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.
Despite the intensive discussions with the laboratories and the significant overall improvements, a persistent issue is that the required reporting limits are frequently 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. However, this does not necessarily pose permanent quality issues, as it may be addressed through effective communication with the laboratories and implementation of a dilution policy in our contracts.

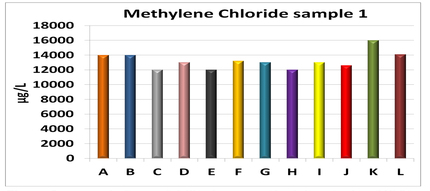

Figure 8: example for variability between the laboratories (VOC)

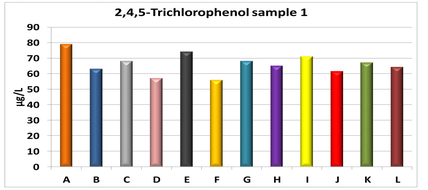

Figure 9: example for variability between the laboratories (SVOC)

10.) 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 over 2000 samples and blanks.

References:
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4. Wilken M, Richardson J (2012) *Organohalogen Compounds* 74, 169-172