

Laboratory Demonstration of Capability Procedure

Effective Date: July 18, 2011

An environmental testing laboratory wishing to submit wastewater compliance and/or Kentucky Pollutant Discharge Elimination System (KPDES) permit effluent sample data to Kentucky Division of Water must use an Environmental Protection Agency (EPA) approved wastewater method specified in 40 CFR Part 136.3. The laboratory must also demonstrate the capability to report the results of wastewater analyses at or below the required reporting limit (RRL) as established by either the Commonwealth of Kentucky or the EPA.

In order to effectively demonstrate method capability the laboratory must: 1) perform an initial demonstration of capability (IDC); 2) perform an on-going demonstration of capability (ODC) annually; 3) perform a minimum detection limit study (MDL) annually using 40 CFR Part 136 Appendix B guideline; and 4) utilize a known standard at or below the RRL as part of their daily calibration/verification procedure.

Initial Demonstration of Capability / On-going Demonstration of Capability - IDC / ODC

An IDC and ODC are used to demonstrate that the laboratory and analyst are capable of performing analysis with acceptable precision, accuracy, sensitivity and specificity pertaining to that particular method. This is done by analyzing four (4) mid-range concentration laboratory fortified blanks (LFB) on the same or different day, and then calculating the percent recovery for each. The percent recovery is used to verify that:

- each of the four IDCs (or ODCs) are within 80 to 120% of the mean value; and
- the calculated percent relative standard deviation (%RSD) is at or below 15% (State Reference).

An IDC must be performed initially by each analyst on each instrument used to analyze compliance/permit samples.

An ODC must be performed annually by each analyst on each instrument used to analyze compliance/permit samples.

Calculate the Percent Relative Standard Deviation (%RSD) as follows:

$$\%RSD = [s / x] \times 100\%$$

where s = standard deviation (n-1)
 x = mean of 4 replicates

Minimum Detection Limit - MDL

The minimum detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the target analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the target analyte and is established using the EPA technique specified in 40 CFR Part 136 Appendix B. A summary of the procedure is as follows:

- Analyze seven (7) laboratory fortified blanks (LFB) over two (2) to three (3) non-consecutive days. The LFBs must be spiked at 3 to 5 times the expected minimum reporting limit. If the spike level exceeds ten (10) times the calculated MDL, then the MDL determination must be performed again using an appropriate calculated spike concentration;
- Calculate the variance (S^2) and standard deviation (S) of the replicate measurements;
- Compute the MDL using the following equation: $MDL = 3.143 * S$;
- The calculated MDL must be less than the required reporting limit.
- Your laboratory's minimum reporting limit must be greater than the calculated MDL and less than or equal to the required reporting limit.

Calculate the MDL using the instructions provided below:

Calculate S^2 and S:	$S^2 = \frac{1}{n-1} \left[\sum_{i=1}^n X_i^2 - \frac{\left(\sum_{i=1}^n X_i \right)^2}{n} \right] \quad S = (S^2)^{\frac{1}{2}}$
Calculate MDL:	$MDL = (S) \times (3.143)$ for 7 replicates

Required Reporting Limit Standard - RLS

In order to demonstrate the laboratory's capability to report down to the required reporting limit on any day that compliance samples are analyzed, the laboratory must analyze a known standard at or below the required reporting limit. The reporting limit standard (RLS) must be analyzed as either the lowest concentration calibration standard or as a stand alone verification standard.

If the RLS is used as the lowest concentration calibration standard it must also be used to determine the acceptance of the calibration curve. The RLS must meet the acceptance criteria of $\pm 30\%$ of the expected value. The lowest value of the calibration standard cannot be ignored or not considered during any future verification of the calibration curve.

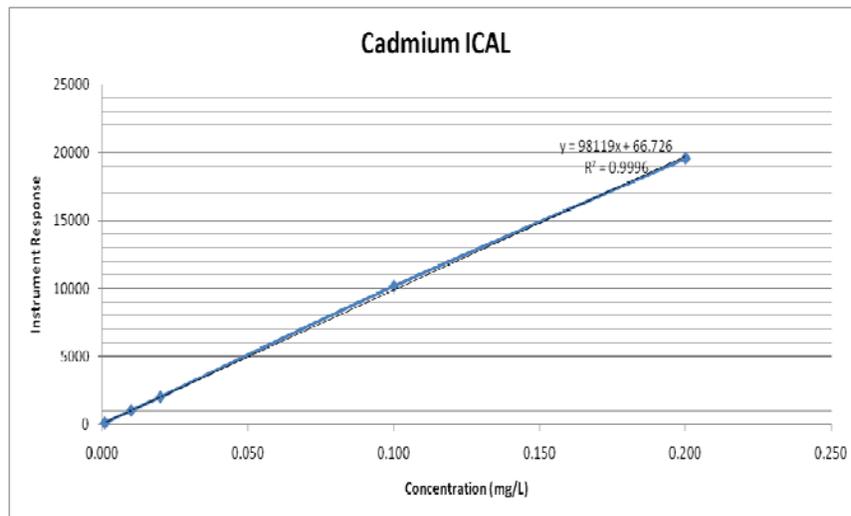
If the RLS is used as a stand alone standard it must meet the acceptance criteria of $\pm 30\%$ of the expected value.

Linear calibration curve (linear regression) is calculated as follows:

1. Plot all x,y pairs;
2. $y = mx + b$ where:
 - m = slope
 - x = concentration
 - y = instrument response

An example of the RLS used as the lowest concentration calibration standard is shown below:

Contaminant	RRL (mg/L)	Date of Analysis	Graph Axis	STD#1	STD#2	STD#3	STD#4	STD#5
Cadmium	0.001	6/17/2011	Conc (x)	0.001	0.010	0.020	0.100	0.200
			Response (y)	91	1010	2000	10150	19560



In the case above, if cadmium was not detected in the sample it would be reported using one of the following formats, for example:

Cadmium	<0.001 mg/L
Cadmium	ND 0.001 mg/L
Cadmium	BDL (0.001 mg/L)

NOTE: In this instance, the detection limit is equal to the required reporting limit and also equal to the lowest calibration standard concentration.

Laboratory Submission to DOW - Initial

Laboratories must submit the following results of the Initial Demonstration of Capability to DOW for approval prior to analyzing wastewater compliance/permit samples. The submission must include:

1. EPA reference method, including version OR Standard Methods method and edition;
2. Date of analysis;
3. Analyst's name performing the analysis;
4. Initial Demonstration of Capability (IDC) results showing the spiked concentration, units and percent recoveries of all four (4) fortified samples; the calculated mean of the percent recoveries; the calculated percent relative standard deviation (%RSD);
5. Minimum Detection Limit Study (MDL) results showing the spiked concentration, units and the concentrations found for each of the seven (7) replicates; the calculated variance; and the calculated MDL. Laboratories must ensure that the calculated MDL is less than 10 times the replicate spike concentration; and
6. Lowest Standard on the Initial Calibration Curve (ICAL) or the Required Reporting Limit Standard (RLS) results and raw data showing that a valid standard is at or below the minimum reporting limit (MRL) or the compliance/permit required reporting limit.

Laboratory Submission to DOW - Ongoing

Laboratories must submit the following results to DOW annually to maintain approval to utilize an EPA approved method for analyzing wastewater compliance/permit samples. The annual submission must include:

1. EPA reference method, including version OR Standard Methods method and edition;
2. Date of analysis;
3. Analyst's name performing the analysis;
4. Ongoing Demonstration of Capability (ODC) results showing the spiked concentration, units and percent recoveries of all four (4) fortified samples; the calculated mean of the percent recoveries; the calculated percent relative standard deviation (%RSD);
5. Annual Minimum Detection Limit Study (MDL) results showing the spiked concentration, units and the concentrations found for each of the seven (7) replicates; the calculated variance; and the calculated MDL. Laboratories must ensure that the calculated MDL is less than 10 times the replicate spike concentration.

DOW may, at any time, request that laboratories submit verification of the Required Reporting Limit Standard (RLS) for any day that compliance/permit samples were analyzed. The submission for verification of Initial Calibration Curve (ICAL) or Continuing Calibration Verification (CCV) includes results and raw data showing that a valid standard is at or below the minimum reporting limit (MRL) or the compliance/permit required reporting limit

Summary of Demonstration of Capability Requirements, Acceptance Criteria and Frequency

Demonstration	Parameter	Requirement	Frequency
IDC	IDC Replicates (4 mid-range LCS)	<ul style="list-style-type: none"> • Each must be within 80 to 120% of the mean value; • %RSD must be $\leq 15\%$. 	Initial and Annual
MDL	7 Replicates	<ul style="list-style-type: none"> • Replicates analyzed over 2 to 3 non-consecutive days; • Calculated MDL must be less than the RRL; • Spike concentration must be less than 10 times the calculated MDL. 	Initial and Annual
RRL	Lowest Standard of Initial Calibration Curve	<ul style="list-style-type: none"> • Must be used with the calibration, cannot be dropped from use; • Must be $\pm 30\%$ of the expected value; • Concentration must be \leq RRL. 	Initial and performed each day that samples are analyzed
RRL	Verification Standard	<ul style="list-style-type: none"> • Must be $\pm 30\%$ of the expected value; • Concentration must be \leq RRL. 	Performed each day that samples are analyzed

IDC / ODC Report Form

General Information

Compliance / Permit Information

Laboratory Name:	Program:
Address:	KPDES Permit Numbers:
City, State Zip Code:	DNR Permit Numbers:
Contact Name:	
Contact Phone:	
Contact Fax:	
Contact Email:	

IDC / ODC Results

Analysis Date:	Method Name:
Analyst:	Method Reference:
Instrument ID:	

Contaminant	RRL ¹	Units	Spike Conc	#1	#2	#3	#4	Mean	% Rec ² #1	% Rec #2	% Rec #3	% Rec #4	%RSD

1. RRL = Required Reporting Limit
2. % Rec = Percent Recovery [(known / expected)*100%]

Minimum Detection Limit Study (MDL)

General Information

Compliance / Permit Information

Laboratory Name:			Program:	
Address:			KPDES Permit Numbers:	
City, State Zip Code:			DNR Permit Numbers:	
Contact Name:				
Contact Phone:				
Contact Fax:				
Contact Email:				

Minimum Detection Limit (MDL) Results

Analyst:		Method Name:	
Instrument ID:		Method Reference:	

Date	====	====	=====	===➔	#1	#2	#3	#4	#5	#6	#7	Std. Dev.	MDL ²	MRL ³
Contaminant	RRL ¹	Units	Est. MDL	Spike Conc										

1. RRL = Required Reporting Limit
2. MDL = Minimum Detection Limit
3. MRL = Minimum Reporting Level

Reporting Limit Standard (RLS)

General Information

Compliance / Permit Information

Laboratory Name:		Program:	
Address:		KPDES Permit Numbers:	
City, State Zip Code:		DNR Permit Numbers:	
Contact Name:			
Contact Phone:			
Contact Fax:			
Contact Email:			

Analyst / Method Information

Analyst:		Method Name:	
Instrument ID:		Method Reference:	

ICAL with Reporting Limit Standard

Contaminant	RRL ¹	Units	Date of Analysis	Graph Axis	#1	#2	#3	#4	#5	#6	#7	#8
				Concentration (x)								
				Instr. Response (y)								

Percent Recovery (%REC) of RRL = _____

ICAL Statistics for Linear Calibration

Contaminant	Number of Points	Correlation Coefficient (R ²)	Y – intercept	Slope (m)	Acceptable? (according to QAP)

1. RRL = Required Reporting Limit

DEFINITIONS

Confirmation: verification of the presence of a component through the use of an analytical technique based on a different scientific principle from the original method (e.g., second column, alternate wavelength or detector, etc.).

Continuing Calibration Check Standard (CCC): is a standard containing one or more of the target analytes that is prepared from the same standards used to calibrate the instrument. This standard is used to verify the calibration curve at the beginning of each analytical sequence. It may also be analyzed throughout and at the end of the sequence. The concentration of continuing standards may be varied, when prescribed by the reference method, so that the range of the calibration curve is verified on a regular basis.

Continuing Calibration Verification (CCV): see Continuing Calibration Check Standard (CCC).

Compliance sample: any sample submitted to DOW under a permitting program to fulfill requirements of a permit. Results of sample should usually meet a defined standard as stated in the permit.

DOW: Kentucky's Division of Water.

EPA: Environmental Protection Agency.

Initial Calibration Check Standard (ICCS): see Reporting Limit Standard (RLS).

Initial Calibration Standard (ICAL): a solution prepared from the primary dilution standard solution or stock standard solutions and diluted as needed to prepare an initial calibration curve.

Initial Calibration Verification Standard (ICV): see Continuing Calibration Check Standard (CCC).

Laboratory Fortified Blank (LFB): (Spike) is an aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

Minimum Detection Limit (MDL): the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing this analyte. See 40 CFR 136 App. B.

Minimum Reporting Limit (MRL): the lowest concentration that is reported by the laboratory.

Permit effluent sample: a sample submitted under a permitting program that relates directly to a permitted discharge.

Reporting Limit Standard (RLS): is a standard that is analyzed each day to evaluate instrument performance at or below the minimum reporting limit.

Kentucky Division of Water
Coal Mining Permit Requirements Reporting Limits
Revised: September 13, 2011

Group	Parameter	Method	Units	RRL
Groundwater	Iron, Total Dissolved	DOC	ug/L	210
Groundwater	Manganese, Total Dissolved	DOC	ug/L	210
Total Recoverable Metals	Antimony	DOC	ug/L	3.92
Total Recoverable Metals	Arsenic	DOC	ug/L	7
Total Recoverable Metals	Beryllium	DOC	ug/L	2.8
Total Recoverable Metals	Cadmium	DOC	ug/L	0.19
Total Recoverable Metals	Chromium	DOC	ug/L	70
Total Recoverable Metals	Copper	DOC	ug/L	6.54
Total Recoverable Metals	Lead	DOC	ug/L	2.23
Total Recoverable Metals	Mercury	DOC	ug/L	0.036
Total Recoverable Metals	Nickel	DOC	ug/L	36.6
Total Recoverable Metals	Selenium	DOC	ug/L	3.5
Total Recoverable Metals	Silver	DOC	ug/L	2.65
Total Recoverable Metals	Thallium	DOC	ug/L	0.168
Total Recoverable Metals	Zinc	DOC	ug/L	83.9
Other Parameters	Aluminum, Total Recoverable	DOC	mg/L	20
Other Parameters	Cyanide, Free	DOC	ug/L	3.64
Other Parameters	Hardness	DOC	mg/L as CaCO3	N/A
Other Parameters	Oxygen, Dissolved	DOC	mg/L	N/A
Other Parameters	Phenol, Total	DOC	mg/L	14.7
Other Parameters	Solids, Total Settleable (SS)	DOC	mL/L	2
Other Parameters	Turbidity	DOC	NTU	N/A
Other Parameters	WET	DOC	TU	N/A
Salts	Calcium, Total	DOC	mg/L	0.5
Salts	Chloride, Total	DOC	mg/L	175
Salts	Magnesium, Total	DOC	mg/L	0.2
Salts	Potassium, Total	DOC	mg/L	0.5
Salts	Sodium, Total	DOC	mg/L	2
General Permit	Acidity	DOC	mg/L	10
SMCRA	Alkalinity, Bicarbonate	DOC	mg/L as CaCO3	10
SMCRA	Conductance, Specific	DOC	uS/cm	N/A
SMCRA	Iron, Total Recoverable	DOC	ug/L	210
SMCRA	Manganese, Total Recoverable	DOC	ug/L	210
SMCRA	pH	Approved	S.U.	N/A
SMCRA	Solids, Total Dissolved (TDS)	DOC	mg/L	175
SMCRA	Solids, Total Suspended (TSS)	DOC	mg/L	10
SMCRA	Sulfate, Total	DOC	mg/L as SO4	175
SMCRA	Temperature	Approved	degrees C	N/A