Title: Detection Limits

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Reference: EPA SW-846

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1.	01-05-94	Original Version
2.	11-13-03	Converted to LWP format. Deleted "Training Manual" from reference and added "EPA SW-846". Appendix added: Quiz Key.
3.		
4.		
5.		

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4.		11/30/06		11-30-06
5.		12/27/07		12-27-07
6.				
7.				
8.				

1.0 SCOPE AND APPLICATION

To set the policy and train personnel in how to express the limits of detection in reports.

2.0 DEFINITIONS

2.1 Detection Limit

To define a detection limit, the analyst must determine the minimum concentration of a substance (analyte) which could be observed in a sample with some degree of confidence if the analyte were present. Therefore the determination of detection limit requires (1) some degree of confidence (usually 99% confidence level) that the analyte is above a blank or background level and (2) that sample interferences are considered in this determination. There are many rigorous definitions for such limits; some are reviewed below.

2.2 Instrument Detection Limits (IDL) - not taking into consideration sample preparation.

According to EPA SW-846, inorganic IDL's must be determined by multiplying by three the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution at a concentration 3 to 5 times the IDL, with seven consecutive measurements per day.

Organic IDL's can be determined by multiplying by three the standard deviation obtained on three low level standards at a concentration approximately 10 times the IDL.

2.3 Method Detection Limit (MDL)

Method Detection Limit is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and sample preparation.

2.4 Sample Detection Limit (SDL)

The detection limit can vary from sample to sample depending upon interferences. Thus the DL is sample specific.

2.5 Limit of Quantitation (QL), Practical Quantitation Limit (PQL), Reliable Quantitation Limit (RQL)

This limit is usually higher than a detection limit, high enough where a quantitative value can be obtained. Quantitative measurements must have good reproducibility and relative standard deviations of 0-15%. For most analyses, as the concentration approaches a limit which you barely detect (detection limit) the reproducibility degrades. This generally occurs at 10X detection limit. Therefore, some analysts use a higher value to express a limit for obtaining good quantitative results, usually 3X to 10X MDL.

2.6 Reporting Limits (California DLR)

These limits are usually defined by a regulatory agency based on their needs. It is usually higher than an IDL or MDL, and the agency requires that a result be reported as not detected if below this limit.

In general: IDL < MDL = SDL < QL < Reporting Limits.

3.0 WCAS DETECTION LIMIT POLICY (Sample Detection Limit)

In general, for commercial work, detection limits are reported which are sample specific, i.e. sample detection limits. These will take into account the instrument sensitivity, sample preparation variables, and sample interferences. In determining this limit, simply remember to determine the minimum amount of analyte that you could confidently observe in a particular sample, if it were present. In general we use the approach described in SW-846 for Method Detection Limits (MDL), increasing this limit if interferences are present in the sample.

4.0 DETERMINING METHOD DETECTION LIMITS (Example)

Estimate the detection limit based on instrument and sample preparation variables. Prepare 3-7 replicate blank samples spiked with 5-10 times the estimated detection limit. The detection limit barring sample interference will be the value of 3 times the standard deviation (n-1).

For example, we estimate the detection limit for benzene in drinking water to be 1 ug/L. Seven replicates are prepared at 5 ug/L and analyzed. Results are as follows:

1.	7
2.	5
3.	5
4.	6
5.	5
6.	4
7.	5

Average = 5.29
Standard Deviation (n-1) = 0.95
Detection Limit (3SD) = 3

5.0 ALTERNATE METHODS

In some cases, sample detection limits are limited by blank or background concentration. A good example is ICPMS. Blank deionized high purity water contains some analytes at 0.01 to 1 ug/L. In this case detection limits can be determined by 3 standard deviations of the blank.

An even simpler approach has been found to work in these cases by using some multiple of the blank level depending on how the blank varies. For example, in ICPMS blank detection limits are calculated as twice the background or blank level. At these concentration levels, standard deviations are approximately 30%. Therefore 3 standard deviations is approximately the same as twice the background.

6.0 ESTIMATES FOR NON-ROUTINE ANALYSIS

For non-routine chromatographic analysis where it is not practical to spend so much time determining a detection limit, the analyst should estimate the limit based on the sensitivity multiplied by the minimum area. For example, if a benzene standard of 1 ug/L gives an area response of 100000 counts and the minimum area is set at 1000, the detection limit is approximately:

$$\frac{1000}{100000} \quad \text{x} \quad 1 \text{ ug/L} \quad = \quad 0.01 \text{ ug/L}$$

The calculation may be more complicated if internal standards are used.

7.0 REPORTING TRACE LEVELS

7.1 If a compound or element is found to be below the determined detection limit yet above the Method Blank, the compound is reported as trace. For example: TR<5 if 5 were the detection limit for the analysis.

7.2 The error in trying to accurately quantitate a value below the detection limit is very high, therefore it is better to indicate a trace amount rather than an estimated value.

8.0 DILUTION FACTORS AND DETECTION LIMITS

If the analyst is performing a multi-component analysis such as CAM Metals or Volatile Organics, and the sample must be diluted for practical reasons to prevent harm to the instrument, the detection limit for the sample is calculated as the lowest dilution-factor times the detection limit. For example, a sample contains 1000 PPM of trichloroethylene (TCE), and it must be diluted 1:1000 to prevent detector saturation or carryover into other samples, and 1:1000 dilution was the lowest dilution factor used for the analysis, all other detection limits in the sample must be multiplied by 1000. However, if the sample was unknowingly analyzed without dilution and the data for other analytes besides TCE (TCE might be outside calibration or saturated) is usable, the analyst can claim undiluted detection limits.

On the other hand, if the analyst is performing a single component analysis such as cyanide, never raise the detection limit based on the dilution factor. Remember, the detection limit is the minimum amount you could have seen if it were present. Therefore, the detection limit for a sample requiring 1:100 dilution is still the undiluted detection limit because had it been present at the lower levels, you could have detected it. You would not have diluted the sample had it been present at low concentration. Detection limits can be raised if the dilution was performed because of matrix interferences (e.g., consumption of derivatizing agent in formaldehyde analysis).

9.0 SAMPLE INTERFERENCES

If an interference is present in the sample giving a response near where the analyte would respond, the analyst must increase the detection limit to compensate for this interference. It is very difficult to determine exactly how much to adjust the detection limit. A good general conservative rule of thumb is to elevate the detection limit to the level calculated for the analyte given the interference response. For example, if a sample has a peak close to where benzene elutes, and the height of the peak is 1/3 of the 1 ug/L benzene standard at the benzene retention time, the detection limit can be estimated to be 0.3 ug/L in the sample.

The following people have read this SOP and are currently using these procedures in the laboratory:

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Todd Munoz	12-15-03
	12-15-03
	12-16-03
Louis Albanese	12-17-03
Robert Steed	12-19-03
Mary Mulcahy	12-22-03
	6-28-04
	08-16-04
	10/25/04
	11/23/04
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Janet L. Havey	10-5-05
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	12/15/06
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	06-14-07

APPENDIX
DETECTION LIMIT QUIZ 2/2/99
KEY

Name________________________________ Date______________

Below are listed some typical lab data. Review the data and determine the best sample detection limit to use in a report. Show all your work (partial credit may be given).

1. In an analysis that we don't perform very often, a well behaved compound, benzophenone, was determined by reverse phase HPLC. By well behaved, we mean that the peak was symmetrical without tailing and the response was very linear. The sample was prepared by extracting 1 g of sample into a final volume of 10 mL of methanol. Standards were analyzed at 1, 10, and 100 ug/mL. The 1 ug/mL standard gave a response of 4500 area counts, and the minimum peak area was set to 1000. The instrument had a signal/noise (S/N) ratio equivalent to 0.01 ug/mL.

The detection limit on the report should be ______2 ug/g___________. (don't forget units)

The limiting factor here is the minimum area. Well behaved compounds may be detectable below the minimum area. The S/N is not the limiting factor because this has nothing to do with the chromatographic system or data system's ability to detect an actual chromatographic peak.

min area X std conc X sample DF =

$$\frac{1000}{4500} \times 1\ \text{ug/mL} \times \frac{10\ \text{mL}}{1\ \text{g}} = 2.2\ \text{ug/g}$$

2. In an analysis that we don't perform very often, a not so well behaved compound, 2,4-dinitrophenol, was determined by gas chromatography. The compound tailed, and response was not linear especially at the low end. All other parameters were the same as example #1, except that the 1 ug/mL standard appears to be the lowest standard that we could see with any certainty.

The detection limit on the report should be ______10 ug/g____________.

Since the lowest standard that could be seen with any certainty was 1 ug/mL, this appears to be the limiting factor. 1 ug/mL X 10 mL/1 g = 10 ug/g.

Note that this is not a very common case. If you base a DL on standards, it should be done with some emphasis on finding a lowest possible concentration. To often I see analysts claiming the low standard when they could actually see much lower.

Also note in these examples, that the extraction efficiency was not taken into account. Such information may raise the DL if extraction is poor.

3. In determining Pb by ICPMS, standards are run at 1, 10, and 100 ug/L. The sample (0.5 g) was digested and made up to a final volume of 100 mL. Seven calibration blanks show an average background equivalent concentration of 0.01 ug/L and a standard deviation equivalent to 0.003 ug/L. The blank prepared with the sample contained 0.026 ug/L.

The detection limit on the report should be ________0.005 ug/g___________.

The limiting factor here is the concentration in the prep blank.

0.026 ug/L X 0.1L/0.5g = 0.0052 ug/g

4. In determining Au by ICPMS, standards are run at 1, 10, and 100 ug/L. The sample (0.5 g) was digested and made up to a final volume of 100 mL. Seven calibration blanks show an average background equivalent concentration of 0.02 ug/L and a standard deviation equivalent to 0.002 ug/L. The blank prepared with the sample also contained 0.02 ug/L.

The detection limit on the report should be _________0.001 ug/g__________.

Because the average background is statistically very reproducible, this is a good candidate for background subtraction of the average background. The detection limit would then be calculated as 3 X std dev (n-1) (3 X 0.002 ug/L X 0.1L/0.5 g = 0.0012 ug/g).

The samples would then be calculated as normal, and finally the average background subtracted to get the final answer. For example:

calculated sample conc (0.36 ug/L) - background (0.02 ug/L) = 0.34 ug/L

0.34 ug/L X 0.1L/0.5g = 0.068 ug/g in sample with a DL of 0.001 ug/g

5. In determining DDT by EPA Method 8080, 50 g of sample are extracted to a final volume of 10 mL in hexane. Standards are analyzed 5, 25, and 75 ug/L. An MDL study previously resulted in a standard deviation of 0.006 ug/kg. The instrument is currently performing as well as it did in the MDL study, and the sample was extracted just as in the MDL study.

The detection limit on the report should be ______0.02 ug/kg___________.

3 X SD = 0.018 ug/kg