

Should Term Limits Be Applied to Analytical Detection?

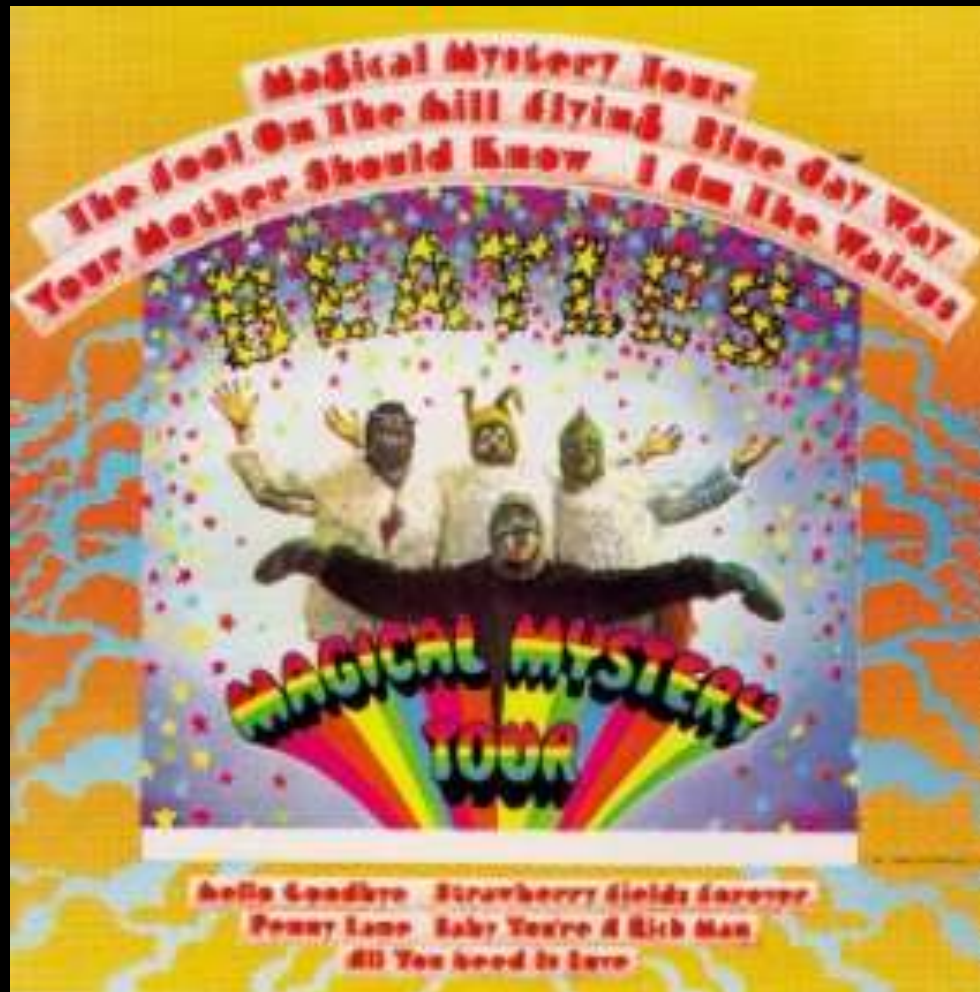
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**Do we have too many terms
for Detection Limits and
Quantitation Limits?**

What the “L” is the problem?

The Year Was 1968



Problems with Detection Limits

Concepts First Discussed in 1968

“The occurrence in the literature of numerous, inconsistent and limited definitions of a detection limit has led to a re-examination of the questions of signal detection and signal extraction in analytical chemistry and nuclear chemistry. “

- *Currie, L. A. (1968), “Limits for Qualitative Detection and Quantitative Determination,” Analytical Chemistry, 40, 586–593.*

Detection Limit Problems are compounded due to Regulatory Issues

“There is a urgent need for answers...a growing number of regulations and recommendations of the European Community concerning limits for trace constituents in food, water, air, and soil... have methods that lack reliable background information on detection limits.”

(E. Hartmann, 1989. Detection capability of analytical methods, Fresenius Z. Anal. Chem., 335: 954-959)

Detection Limits still are a problem in the late 90s

“The meaning of 'detection limits' is perhaps clear to all, in a qualitative sense. That is, the detection limit is commonly accepted as the smallest amount or concentration of a particular substance that can be *reliably* detected in a given type of sample or medium by a specific measurement process. Within such a general definition, however, lurk many pitfalls in terminology, understanding, and formulation, that have led to several decades of miscommunication among scientists and between scientists and the public.”

(Currie 1997. Detection: International update, and some emerging di-lemmas involving calibration, the blank, and multiple detection decisions Chemometrics and Intelligent Laboratory Systems, 37 (1) 151-181)

Standard Methods 1997

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Detection Limit Assistance Chart



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standard in the laboratory's initial calibration curve adjusted for initial sample volume or weight.

What has happened in the last 10 years?

- Over 700 peer reviewed articles on detection limits in environmental, medical, forensic, statistical, and quality assurance journals.
- Dozens of new terms such as Characteristic Limit (the concentration where the variances of background noise and analytical error are equal; Berthouex and Gan 1993) were proposed.

What has happened in the last 10 years?

- At least 100 new statistical treatments for determining detection limits have been proposed (eg. Traldi 2006: quadratic calibration curves with inverse regressions; Parker 2002": root mean square method with multiple calibration curves; Yang et al. 2005: multipoint fitting of RSD at different concentrations; Daniels and Yin 2006: Bayesian statistics)

Detection Limit Procedure Development

Detection Limit Procedures rely on Models that:

- Are Based on Statistical Assumptions (normality, constant variance, sample size, etc)
- Are often developed and calibrated to specific data sets selected by the developer

You only need one or two data sets to publish a paper

Find a data set that does not fit, develop a new a new procedure for the data that works, publish another paper

The possibilities are endless!

Recent News on Models

- **Models of volcanic ash from the eruption in Iceland grounded air travel. Model data proven false by actual measurements.**
- **Hacked emails show that leading climate scientists “adjusted” temperature data to fit the model.**
- **New supercomputer studies suggest it is "very likely" ocean currents will carry oil from the Deepwater Horizon spill in the Gulf of Mexico around the tip of Florida and thousands of miles up the U.S. East Coast researchers announced Thursday. Using a \$100 million computer model of the world's ocean-circulation patterns, the simulations show a strong Loop Current almost inevitably will pull the oil into the powerful Gulf Stream. It would then travel up the Atlantic coast at a speed of about 100 miles a day**

Gulf Oil Simulation (The only thing likely is this will not be the actual outcome)



Moral of the Story

- Even the best and most advanced models are only as good as the assumptions made and the data used!

How do deal with the information overload on detection limits?



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A Better Approach



(One small bite at a time)

Why are detection limits a big deal?

- CWA, SDWA, and RCRA compliance decisions are based on the presence/absence of pollutants
- High costs associated with non compliance
- High costs to labs trying to comply with multiple programs with different detection limits
- No uniform statistical approach between regulatory programs

What makes detection limits a really big deal?

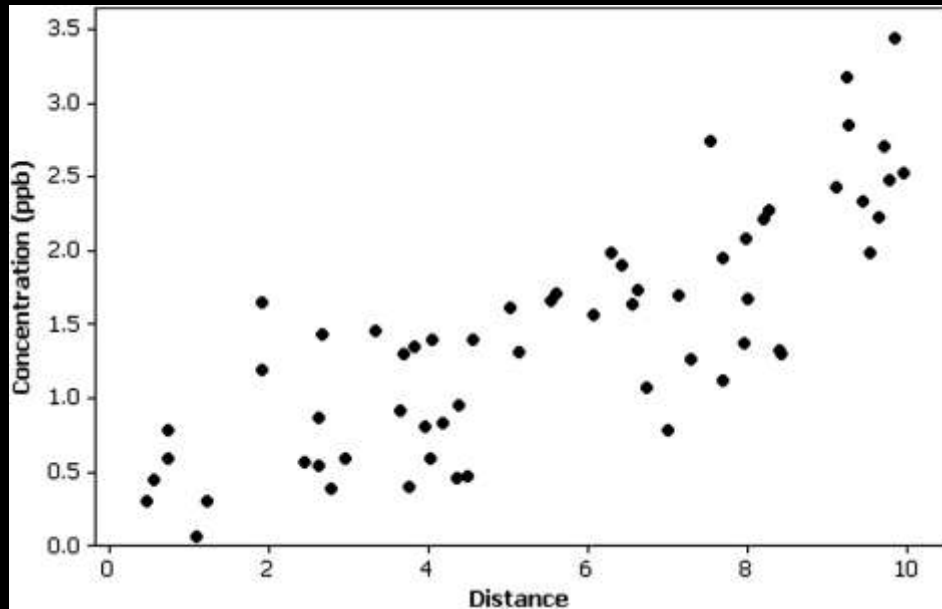
- **Parameters with low Water Quality Based Effluent Limits (eg PCBs and Hg) where no discharge is permitted (0).**
- **“In many cases the lay public believes, given sufficient effort or funding, that a concentration of zero may be detected and/or achieved. Not unlike the third law of thermodynamics, however, neither is possible, even in concept.”**
- **Currie 1998**

What makes detection limits a really big deal?

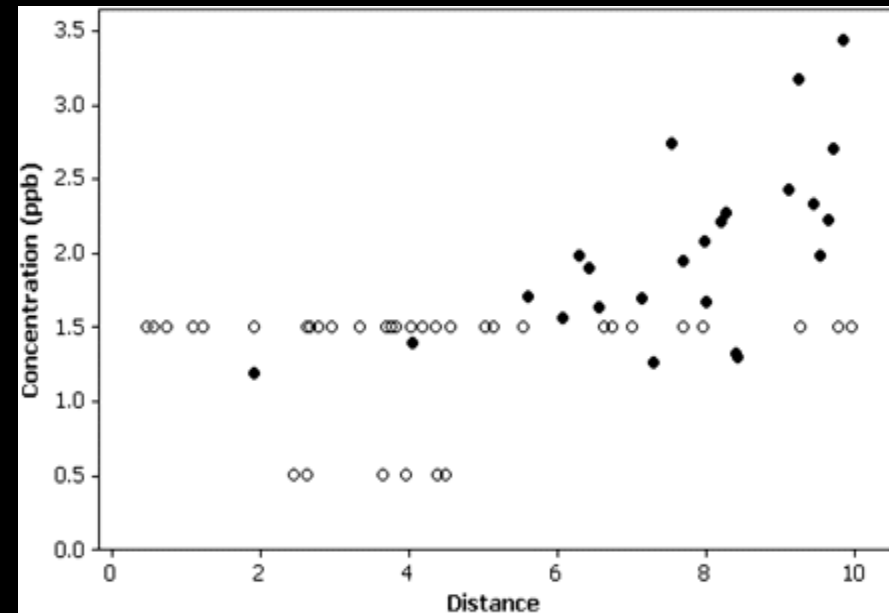
- **Censored results $< DL$ are problematic in the analysis of data in the fields of medicine, astronomy, occupational health, and environmental science**
- **The link between asbestos in brake linings and lung cancer in mechanics was missed because of censored detection limits.**

(Helsel D. 2010. Much ado about next to nothing: incorporating nondetects in science. Ann Occup Hyg 54:257–62.)

The Impact of Detection Limit Censoring



No DL censoring $r^2=0.81$



Censoring at DL of 1 and 3 ppb and substituting values of half DL shown as open circles. $r^2=0.55$

(Helsel 2010)

What should be Done

- **Let science be science and continue the discovery process. (Most academics need 2 publications per year to justify their existence)**
- **If and when a useful procedure is developed, it will need to go through many hoops to impact the analyst.**
- **Learn some basic statistics to understand the assumptions and uncertainties inherent in models.**
- **Focus on improvements to methods and QA/QC that enhance data quality,**

Regulatory and Bench Level Actions

Get rid of the 0 discharge expectation

- Recognize that a detection limit estimation procedure will not get you a lower reporting limit
- In fact most procedures that properly address statistical concerns and variability over time yield higher DLs than the MDL
- Invalid data between DL and QL serves no scientific purpose
- Labs should be reporting at a verifiable LOQ and not an annual MDL

Look to methods to provide lower DLs

- **Improvements to analytical methods such as cleanups, extraction and concentration techniques will get you part way**
- **Extracting acids first and/or using continuous L/L extraction greatly improves the recovery of phenols**
- **New technology will get you closer (Hg by Cold Vapor Atomic Absorption vs Atomic Fluorescence**

Replace PCB aroclor based methods with congener specific ones

- Pattern recognition adds considerable complexity to detection limits**
- PCBs are old compounds (banned for 40 years) and degradation/partitioning process continue to alter the aroclor pattern**
- Congener specific ECD, GC/MS-NCI, and GC/MS-high resolution have been in existence for 40 years and used worldwide in over 1000 peer reviewed journal articles**

Get rid of poor performing compounds that do not work with the method with which they are paired with

The Federal Advisory Committee recommended minimum Measurement Quality Objectives

- **Precision \leq 30% RSD**
- **Accuracy (measured as recovery for single determination) = 20-180%**
- **False Negative rate \leq 10%**
- **Ratio of Accuracy to Precision must be no less than 1.0**
- **EPA casted the only no vote???**

MDL Needs to be Replaced

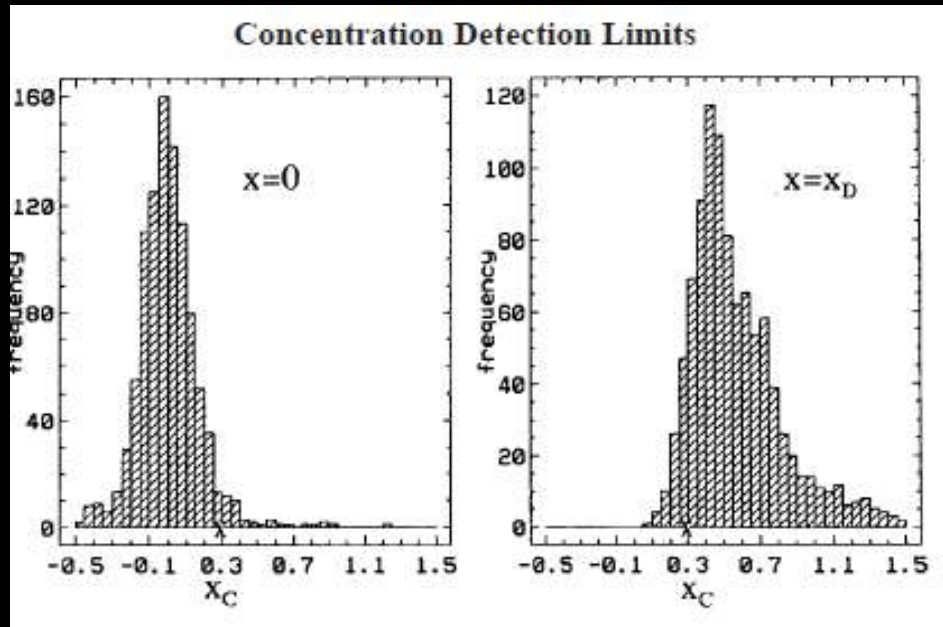
Assumes constant variance which often is not the case.

- Spike at a higher level with less variability, get a low MDL
- Spike at a low level with more variability and get high MDL.
- MDL studies can be artificially optimized using instrument conditions and spiking and preparation factors to provide very low MDLs.
- Just like calibration curves, they will vary over time.

MDL Needs to be Replaced

Assumes normality which often is not the case (Abby normal data).

- Most DL data is skewed right (Currie 1997)



MDL Needs to be Replaced

- **Can vary by instrument, analyst, lab, and over time**
- **Short term standard deviation is the same as long term standard deviation**
- **There is no blank contamination**
- **Performed in DI water and does not consider matrix effects**
- **Costly event that produces little meaningful data over**

Key Issues

- The MDL does not incorporate and apply Data Quality Objectives for bias, precision, representativeness, and comparability for lab and method performance at the detection and quantitation limits used in CWA programs, at all levels and frequencies of operations that can influence data use and interpretation relative to detection and quantitation limits.

Possible Replacements

NELAC 2009 TNI Standards

- LOD determinations when instrument conditions change
- LOQ verification as part of calibration curve and in each batch
- Still many details to work out

FACDQ Recommendations

Modified ACIL Single Lab Procedure

- **Demonstrates the laboratories performance at a specified level over time.**
- **Determines the lowest possible value achievable by the laboratory while meeting the Measurement Quality Objectives.**

Recognition of Method Types

- **Censored method – methods that produce no quantitative response below a certain signal threshold (Chromatographic methods)**
- **Uncensored method – methods that produce a quantitative response for each measurement regardless of concentration (ICP)**

We must chose wisely!

