THE EPA'S NEW MDL PROCEDURE: WHAT IS IT, AND WHERE DID IT COME FROM?

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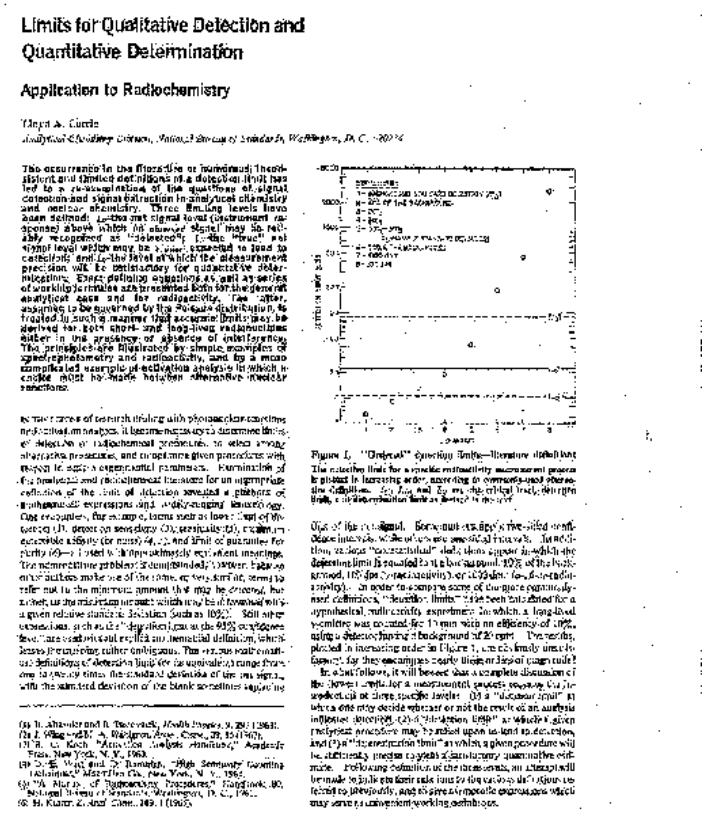
ENVIRONMENTAL SERVICES
CITY OF PORTLAND

WE BEGIN WITH THE CONCEPT OF DETECTION LIMITS…….

LLOYD CURRIE. 1968. *ANALYTICAL CHEMISTRY.* 40(3): 586-593.



Limits for Qualitative Detection and Quantitative Determination

Application to Radiochemistry

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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, correction and signal extraction in analytical chemistry and nuclear chemistry. Three limiting levels have been defined: (a) the net signal level (instrument response) above which an observed signal may be reliably recognized as "detected"; for this "first" net signal level uplift may be zero; (b) the level at which the measurement precision will be satisfactory for quantitative determinations. Exact defining equations are given for the generally applicable cases and for radioactivity. The latter, assumed to be governed by the Poisson distribution, is treated in such a manner that accurate limits may be derived for both short- and long-lived radionuclides either in the presence or absence of interference. The principles are illustrated by simple examples of signal-replasmametry and radioactivity, and by a more complicated example of activation analysis in which interfering nuclides must be taken into account. Alternative nuclear reactions

In many areas of research dealing with phenomena near the limits of detection or measurability, it becomes necessary to determine limits of detection or measurement, to select among alternative processes, and to optimize given procedures with respect to experimental parameters. Formulation of the analytical and radiochemical literature for an appropriate definition of the limit of detection revealed a plethora of mathematical expressions and widely-ranging terminology. One encounters, for example, terms such as lower limit of detection (1), power of sensitivity (2), sensitivity (3), minimum detectable activity (or mass) (4, 5), and limit of quantitative sensitivity (6–8). Used with approximately equivalent meanings, the nomenclature problem is demonstrated (9) when, in an article entitled "The Limit of Detection," we are told that "it is not our purpose to refer not to the numerical amount that may be detected, but rather, to the minimum amount which may be determined with a given relative statistical precision (such as 10%)." Still other connotations, such as the "significant zero at the 95% confidence level," are readily found, each with an immaterial definition, which leaves the meaning either ambiguous. The various contemporary definitions of detection limit (or its equivalent) range from zero to many times the standard deviation of the measurement, with the standard deviation of the blank sometimes appearing

(1) H. Ahlstrom and B. Bouchard, *Health Physics*, 9, 291 (1963).
(2) J. Wing and J. A. Wahgren, *Anal. Chem.*, 37, 1544 (1965).
(3) R. C. Koch, "Activation Analysis Handbook," Academic Press, New York, N. Y., 1960.
(4) D. E. Watt and D. Ramaiah, "High Sensitivity Counting," Tallahassee Mimeo Co., Inc., Tallahassee, Fla., 1965.
(5) "A Manual of Radioactivity Procedures," Handbook 80, National Bureau of Standards, Washington, D. C., 1961.
(6) H. Kiister, *Z. Anal. Chem.*, 189, 1 (1962).

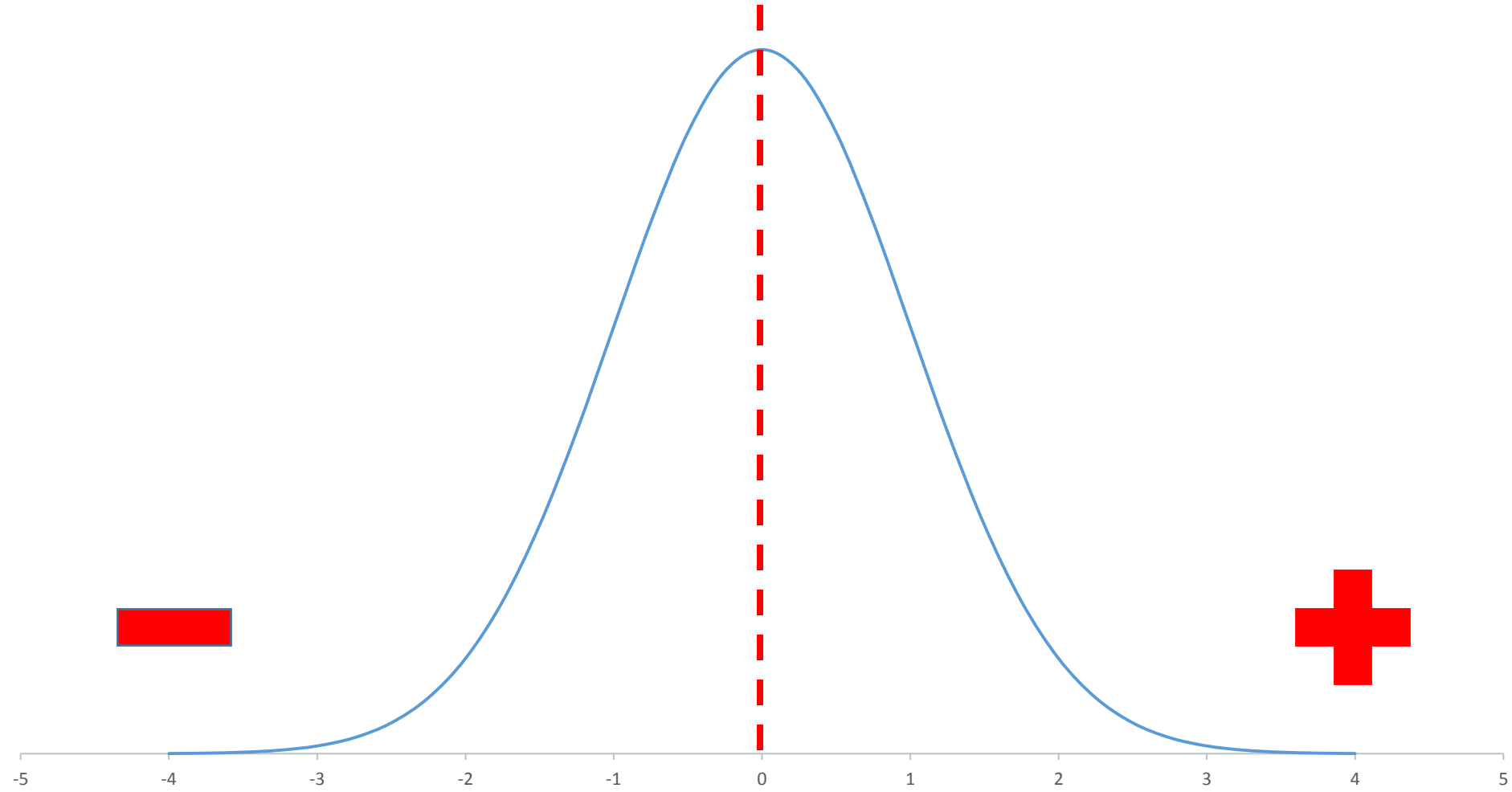
Figure 1. "Original" detection limits—literature definitions

The detection limits for a specific radioactivity measurement process is plotted in increasing order, according to commonly used terminology. See Eqs. and Eq. are the critical level, decision limit, and determination limit as discussed in the text

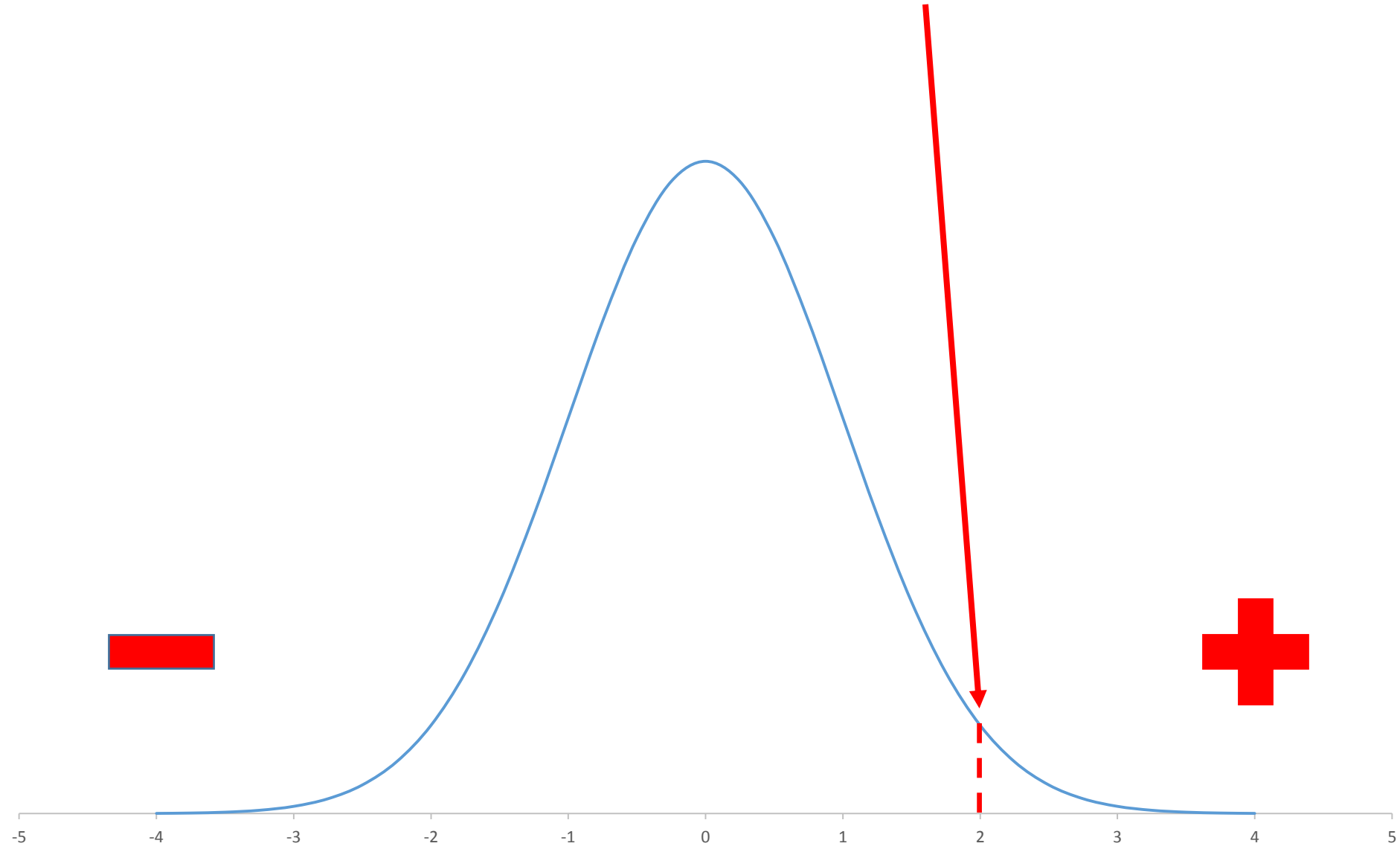
One of the principal factors governing the five-fold confusion in the literature is the failure to distinguish between the concepts of "detection" and "determination." In addition, we have "theoretical" limits, those appropriate to which the detection limit is assumed to be a known quantity (100% of the background, 100% power of sensitivity, or 100% confidence level), and "empirical" limits, those based on experimental results. In order to compare some of the more commonly used definitions, "detection limits" have been calculated for a hypothetical, multi-channel experiment in which a long-lived γ-emitter was counted for 10 min with an efficiency of 10%, using a detector having a background of 25 cpm. The results, plotted in increasing order in Figure 1, are self-explanatory. As they encompass nearly three orders of magnitude, the importance of proper definition is clear.

In what follows, it will be seen that a complete discussion of the chosen limits for a measurement process requires consideration of three specific levels: (1) a "decision signal" at which a decision may be made whether or not the result of an analysis indicates detection, (2) a "detection limit" at which a given analytical procedure may be relied upon to lead to detection, and (3) a "determination limit" at which a given procedure will be sufficiently precise to yield a satisfactory quantitative estimate. Following definition of the three levels, an attempt will be made to illustrate their relationship to the various limits reported previously, and to give asymptotic expressions which may serve as convenient working definitions.

CURRIE WAS EXAMINING DATA FROM RADIOCHEMISTRY. THE DETERMINATIVE TECHNIQUE HAD THE ABILITY TO GIVE POSITIVE AND NEGATIVE NUMBERS. FOR A BLANK:



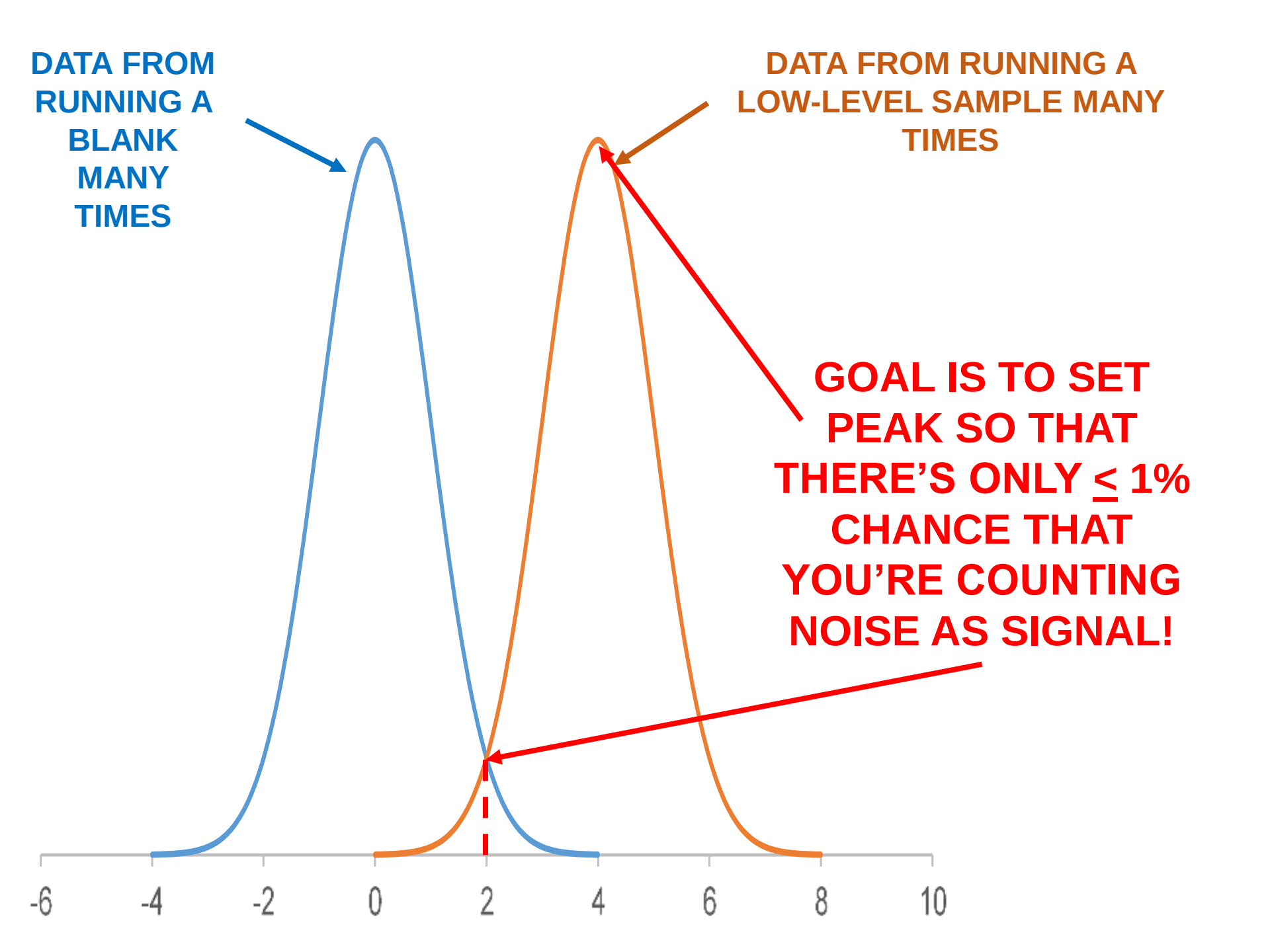
HE CALLED THE POINT WHERE THE CHANCE OF A RANDOM FALSE POSITIVE WAS ≤ 1% THE *CRITICAL LEVEL*.



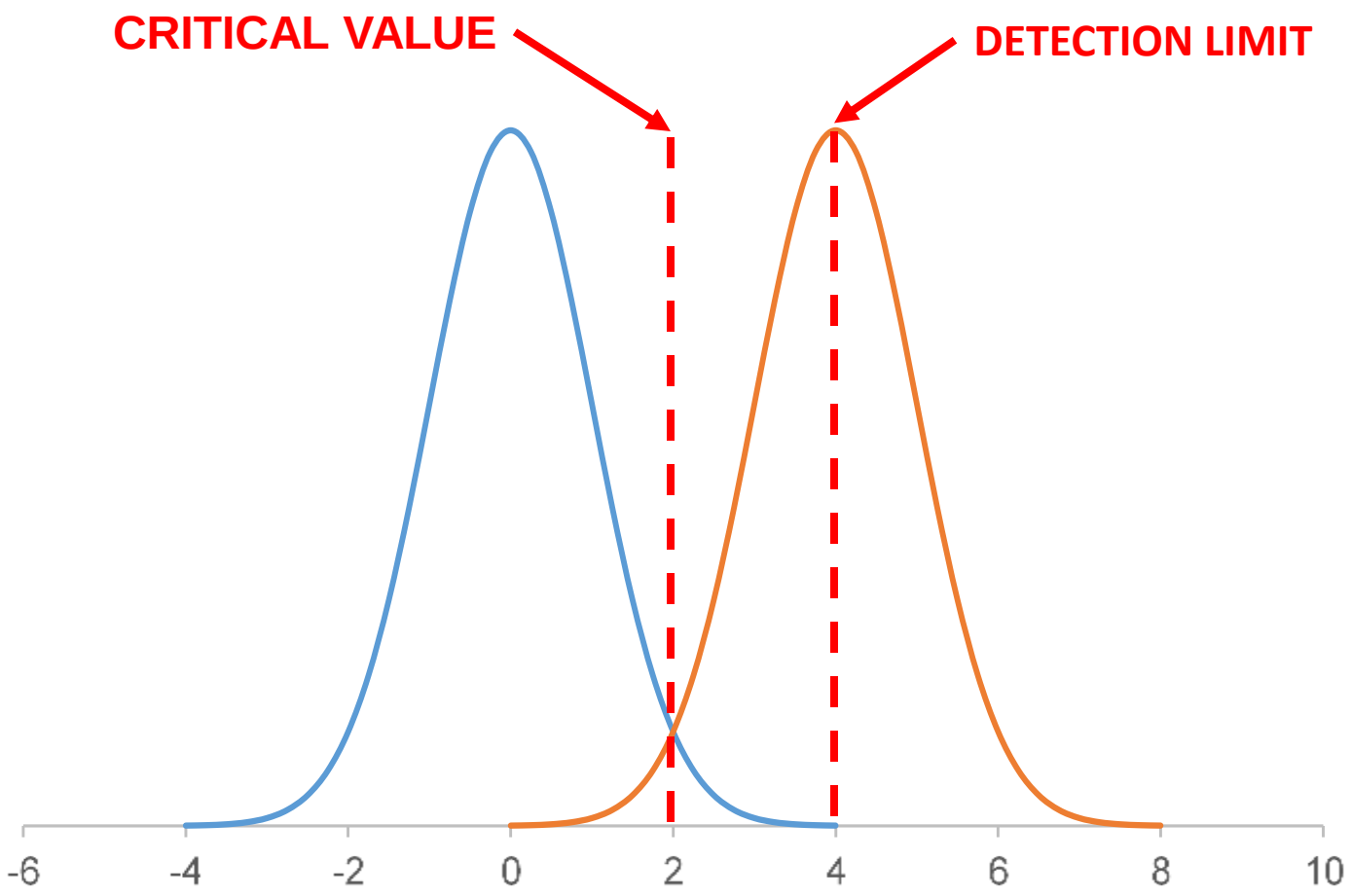
THE SAME BELL-SHAPED DISTRIBUTION WILL OCCUR WHEN ANALYZING A SAMPLE MANY TIMES.

THE “TRICK” IS TO FIND OUT HOW LOW YOU CAN GO BEFORE YOU START COUNTING NOISE AS ANALYTE.

CURRIE SHOWED IT GRAPHICALLY LIKE THIS…


DATA FROM RUNNING A BLANK MANY TIMES
DATA FROM RUNNING A LOW-LEVEL SAMPLE MANY TIMES
GOAL IS TO SET PEAK SO THAT THERE'S ONLY ≤ 1% CHANCE THAT YOU'RE COUNTING NOISE AS SIGNAL!
-6
-4
-2
0
2
4
6
8
10

CURRIE CALLED THIS LOWER VALUE FOR SAMPLES THE *DETECTION LIMIT*.



IMPORTANT POINT TO REMEMBER:

CURRIE'S APPROACH WAS TO

MINIMIZE FALSE POSITIVES

YOU CAN CALCULATE CURRIE'S CRITICAL VALUE AND OTHER PARAMETERS BECAUSE THE NORMAL DISTRIBUTION IS WELL-CHARACTERIZED…

$$y = \frac{1}{\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma}$$

$\mu =$ Mean

$\sigma =$ Standard Deviation

$\pi \approx 3.14159$

$e \approx 2.71828$

CURRIE ALSO CAME UP WITH THE IDEA OF A QUANTITATION LIMIT……

BASICALLY, IT WAS AN ATTEMPT TO MOVE THE DETECTION LIMIT HIGHER UNTIL THE CHANCE OF A FALSE POSITIVE APPROACHED ZERO.

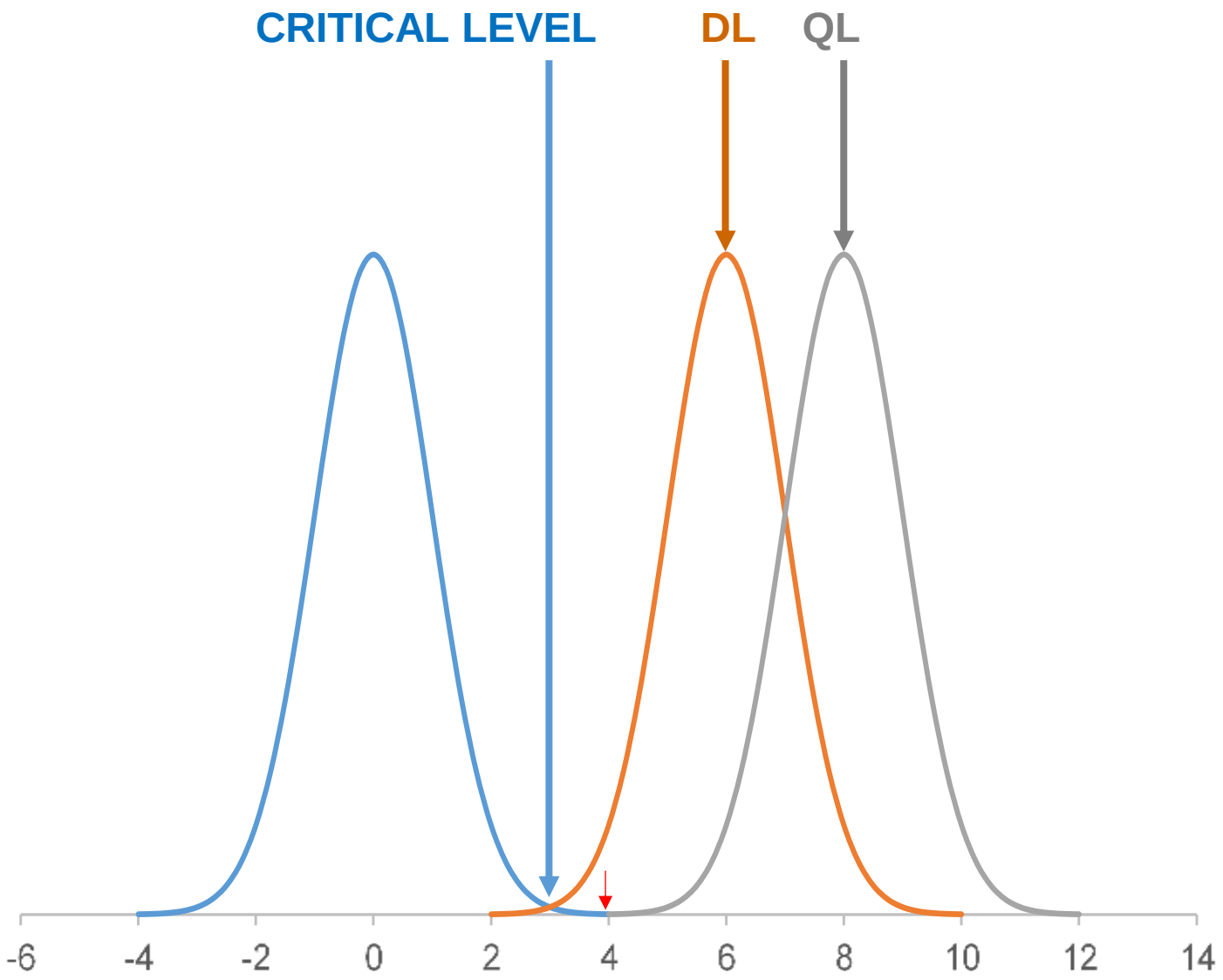
ALTHOUGH BACKED BY A LOT OF STATISTICS, THE FINAL RESULT WAS SIMPLE:

$$QL = 10s$$

WHERE S = THE STD. DEV. FROM THE ANALYSIS OF A BUNCH OF LOW-LEVEL SPIKED BLANKS.

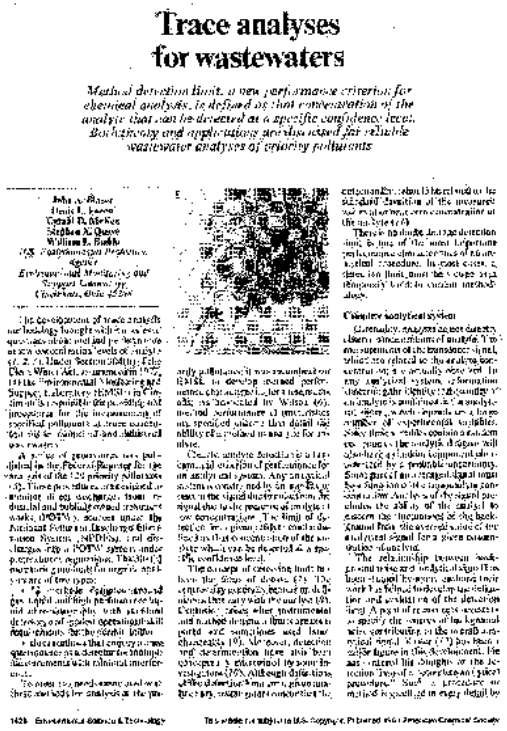
WHAT CURRIE WAS GETTING AT IS ILLUSTRATED IN THE FOLLOWING GRAPH…..

NOTE WHERE CURRIE'S QL APPROACHES ZERO ON THE DOWN SIDE (↓)



THIRTEEN YEARS LATER, THE EPA GOT INTO THE ACT WITH A PAPER OUT OF THE EPA EMSL LAB IN CINCINNATI, OHIO

GLAZER *et al.* 1981. *ENV. SCI. & TECHN*. 15: 1426-1435.



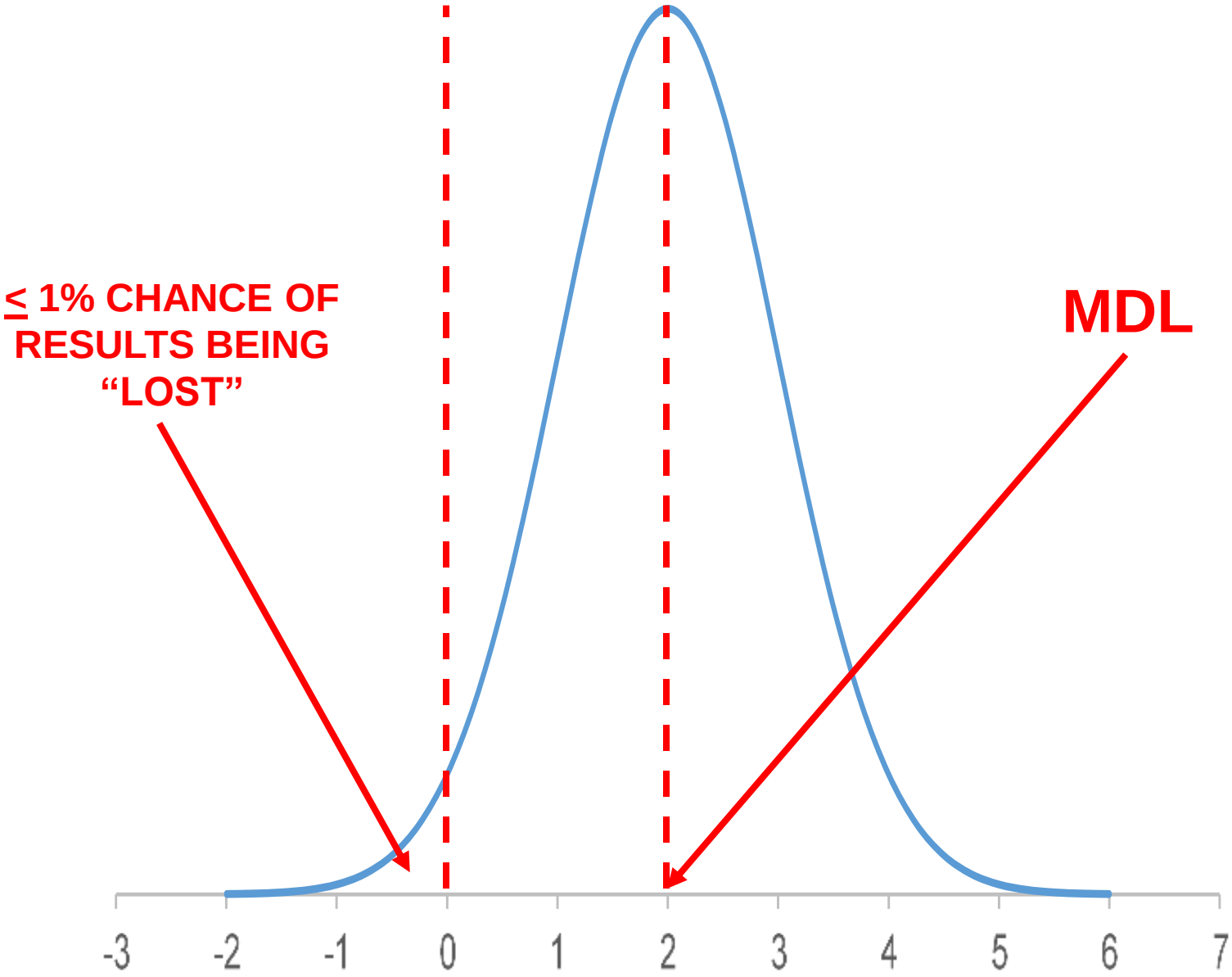
Trace analyses for wastewaters

Method detection limit, a new performance criterion for chemical analysis, is defined as that concentration of the analyte that can be detected at a specific confidence level. Both theory and applications are given to aid in reliable wastewater analyses of priority pollutants

THEY WERE LOOKING AT 15 ORGANICS METHODS (GC, GC/MS, AND HPLC) FOR THE NPDES PROGRAM (WASTEWATER & INDUSTRIAL PRETREATMENT).

THESE METHODS DON'T GENERATE NEGATIVE NUMBERS.

SO THE EPA WANTED TO SET A LIMIT TO AVOID POSITIVE RESULTS "FALLING OFF THE CURVE" SO TO SPEAK.


≤ 1% CHANCE OF RESULTS BEING "LOST"
MDL
-3
-2
-1
0
1
2
3
4
5
6
7

THREE YEARS LATER, THE EPA PROMULGATED THIS NEW MDL CONCEPT AT 40 CFR 136 ON OCTOBER 26, 1984

AS A REGULATORY OPTION

THE CALCULATION IS VIA THE WELL-KNOWN EQUATION

$$MDL = \left(t_{n-1,1-\alpha = 0.99} \right) \bullet s_n$$

IMPORTANT POINT TO REMEMBER:

THE EPA'S APPROACH WAS TO

MINIMIZE FALSE NEGATIVES

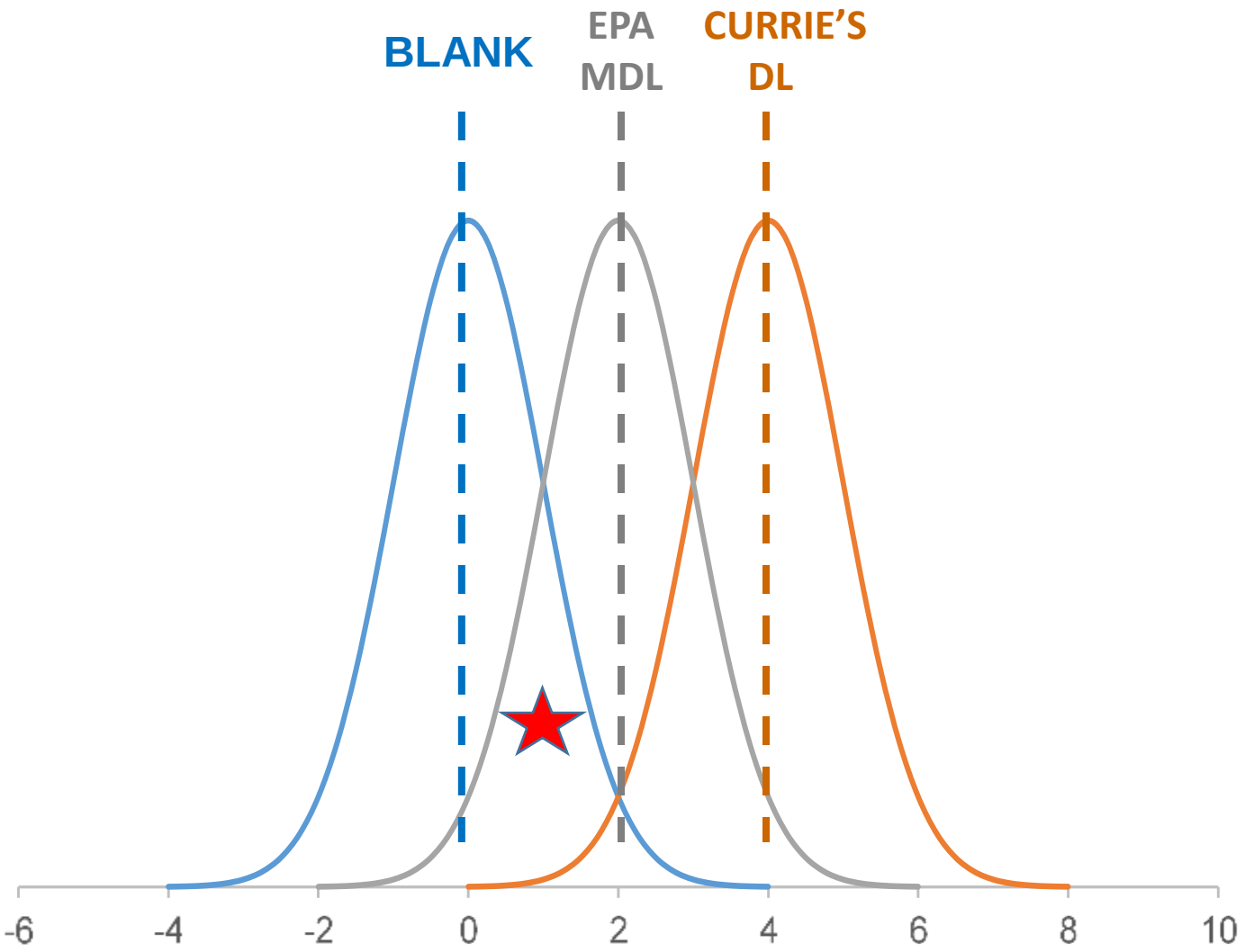
WHERE CURRIES' APPROACH WAS TO

MINIMIZE FALSE POSITIVES

WHEN YOU COMPARE THE EPA MDL WITH CURRIE'S DL, EPA MDL HAS A SIGNIFICANT POTENTIAL FOR INCLUDING NOISE IN THE SAMPLE SIGNAL

THIS WAS NOT CONSIDERED WHEN DEVELOPING THE MDL!!

(AREA ★ BELOW)



IN OTHER WORDS, THE EPA MDL COULD COUNT NOISE AS A POSITIVE "HIT"

THIS IS CALLED A TYPE I ERROR AND IS A BIG CONCERN FOR ANY REGULATED ENTITY THAT COULD BE FINED OR SHUT DOWN BECAUSE OF "FINDING" CONTAMINANTS IN THEIR DICHARGE(S).

BUT…

THE NEW EPA MDL PROCEDURE WAS SO EASY, IT WAS PICKED UP FOR ALL KINDS OF ANALYSES BY….

EPA OGWDW (GROUND & DRINKING WATER)

EPA OSW (SOLID WASTE)

EPA OERR (EMERGENCY & REMEDIAL RESPONSE)

STANDARD METHODS

AND EVEN ASTM

LIFE WAS TRULY GREAT FOR THE EPA AND EVERYBODY ELSE.

AND EVERYBODY IGNORED THE ISSUE OF CURRIE'S CRITICAL VALUE.

THAT IS, UNTIL THE EPA PROMULGATED ITS MDL PROCEDURE AT THE SAME TIME AS ITS NEW, LOW-LEVEL MERCURY METHOD ON JUNE 8, 1999….

AND MADE IT GENERAL FOR ALL EPA METHODS

(BIG MISTAKE…..)

BECAUSE IT GOT

PROMPTLY SUED !!!

BY…

THE ALLIANCE OF AUTOMOBILE MANUFACTURERS

THE CHEMICAL MANUFACTURERS ASSOCIATION

THE UTILITY WATER ACT GROUP

THE AMERICAN FOREST & PAPER ASSOCIATION

FOR REQUIRING THE MDL PROCEDURE TO BE USED FOR INAPPROPRIATE METHODS (E.G., METALS)

THE QUEST FOR THE HOLY GRAIL OF A UNIVERSALLY APPLICABLE MDL PROCEDURE HAD BEEN GOING ON AND CONTINUED TO GO ON FOR THE NEXT 16 YEARS!!

AND EVERYBODY GOT INTO THE ACT:

ML: EPA METHODS 624, 1624, 625, 1625 (1980 – 1984)
REVISED MDL: EPA METHOD 1631B (1999)
PQL: EPA DRINKING WATER PROGRAM (1987)
EQL: EPA OFFICE OF SOLID WASTE (LATE 1980s)
LCMRL: EPA DRINKING WATER PROGRAM (2006)
CRDL/CRQL: EPA SUPERFUND CONTRACT LAB PROGRAM (??)
CMDL/CMQL: EPRI (1993)
AML: ACADEMIA (1997)
IDE/IQE: ASTM (2007)
LOD/LOQ: AMERICAN CHEMICAL SOCIETY (1983)
RDL/RQL: AMERICAN CHEMICAL SOCIETY (WITHDRAWN)
DL CASE I/DL CASE II: ACIL (2003)
LT-MDL: USGS (1999)

THE EPA CONVENED THE FEDERAL ADVISORY COMMITTEE ON DETECTION AND QUANTITATION (OR *FACDQ* FOR SHORT). THE WORK GROUP CAME UP WITH THE "DQFAC METHOD" AND SENT IT TO EPA IN DECEMBER 2007, EIGHT YEARS AFTER THE EPA HAD BEEN SUED.

THE EPA DECIDED THE PROPOSED MDL PROCEDURE WAS TOO CUMBERSOME, AND IT WAS PROMPTLY

REJECTED!

THE NELAP INSTITUTE (TNI) CHEMISTRY EXPERT COMMITTEE DEVELOPED A NEW MDL PROCEDURE UNDER CONTRACT TO THE EPA AND SENT THE DRAFT TO THE EPA ON MARCH 19, 2014

EPA PROPOSED THE NEW TNI MDL METHOD IN ITS LATEST METHOD UPDATE RULE THAT WAS PROPOSED ELEVEN MONTHS LATER IN FEBRUARY 2015.

THIS UPDATE WAS SIGNED BY THE EPA ADMINISTER ON DECEMBER 15, 2016.

THEN IN JANUARY, PRESIDENT TRUMP SIGNED AN EXECUTIVE ORDER FREEZING SPENDING, AND THE FEDERAL REGISTER CEASED PUBLISHING.

…….WE'RE STILL WAITING……

FEDERAL REGISTER

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Part II

Environmental Protection Agency

40 CFR Part 136
Clean Water Act Methods Update Rule for the Analysis of Effluent; Proposed Rule

IN A NUTSHELL, THE PROPOSED MDL PROCEDURE IS:

1) ANALYZE A BUNCH OF BLANKS AND SPIKED BLANKS

2) CALCULATE THE INITIAL MDL (MDL_s) USING THE SPIKES

3) IF NO BLANKS CAME UP POSITIVE, DISCARD THE BLANK DATA

4) IF THERE ARE <u>SOME</u> POSITIVE BLANKS, THE MDL_b IS THE HIGHEST BLANK
   (IF YOU HAPPEN TO HAVE > 100 BLANKS (!), SET THE $ML_b \geq$ THE 99^{TH} PERCENTILE)

5) IF ALL OF THE BLANKS ARE POSITIVE, CALCULATE THE ML_b JUST LIKE THE MDL_s

6) YOUR INITIAL MDL IS WHICHEVER IS GREATER: THE ML_s OR THE ML_b.

TNI MDL PROCEDURE ADOPTED BY THE EPA AND PROPOSED IN THE 2/29/15 METHOD UPDATE RULE FOR 40 CFR 136 APPENDIX B…

DOES NOT INCLUDE QLs!

HOWEVER, TNI DID INCLUDE A QL PROCEDURE IN THEIR PROPOSED NEW STANDARD

- **SELECT A TRIAL QL ≥ 3x WHAT YOU GUESS YOUR MDL WILL BE**

- **THE TRIAL QL HAS TO BE ≥ YOUR LOWEST CAL STANDARD**

- **PROCESS THREE SETS OF ≥ 7 BLANKS AND BLANKS SPIKED AT THE TRIAL QL LEVEL THROUGH ALL STEPS OF THE METHOD, EACH SET RUN ON A SEPARATE DAY**

- **CALCULATE THE MDL_s AND MDL_b AND CHOOSE**

- **IF THE TRIAL QL ≥ MDL, QL = SPIKE LEVEL**
  IF THE TRIAL QL < MDL, QL = 3x MDL

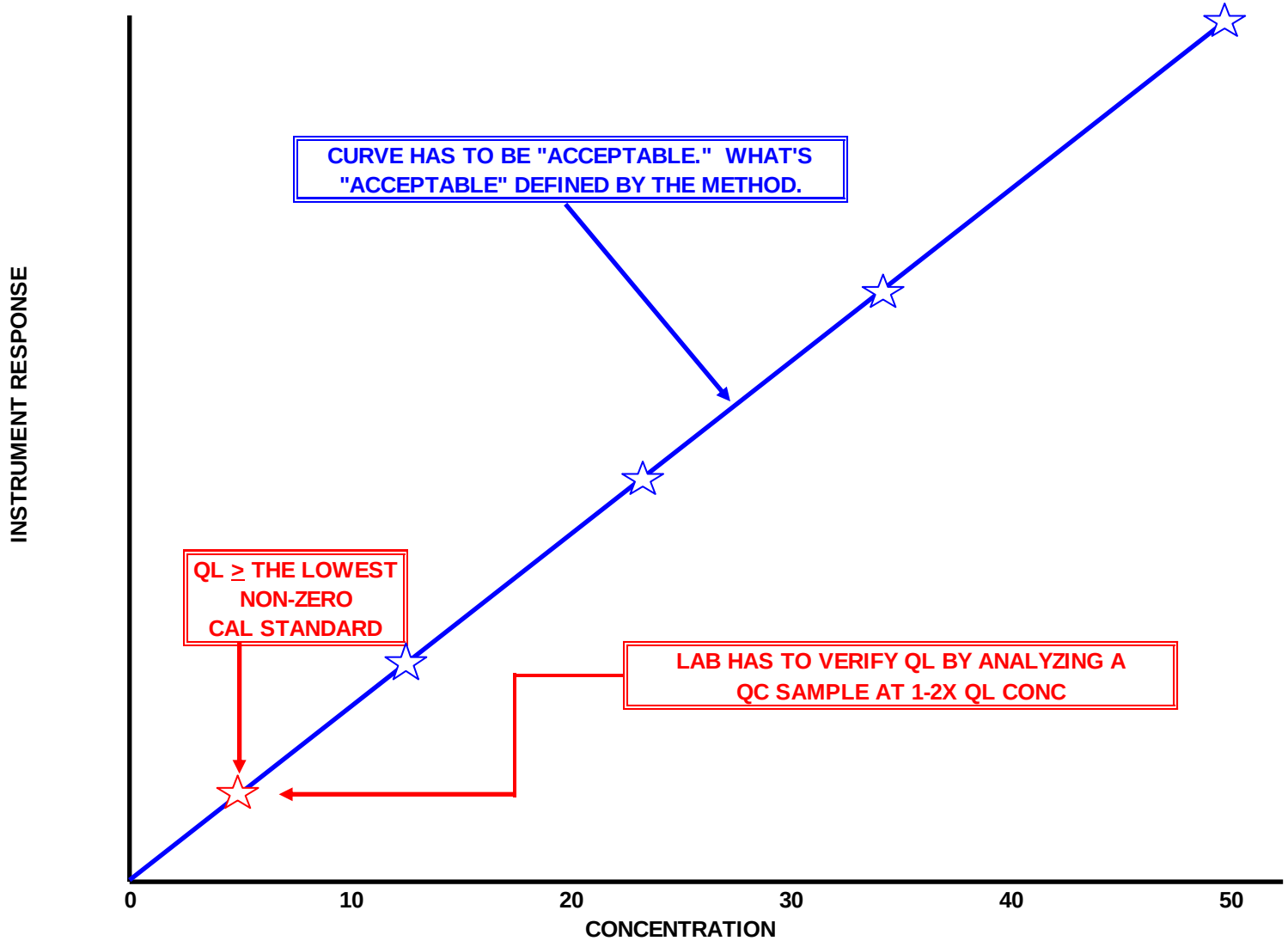
JUST SIX MONTHS LATER (8/13/15), EPA OSW PUBLISHED FINAL UPDATE V OF THE SW-846 COMPENDIUM…

- THE MDL WAS LITERALLY SCRAPPED AND REMOVED FROM CHAPTER ONE (QUALITY CONTROL)

- IN IT'S PLACE WAS PUT THE LLOQ, LOWER LIMIT OF QUANTIATION

- "…THE LOWEST POINT OF QUANTITATION, WHICH IN MOST CASES IS THE CONCENTRATION OF THE LOWEST CALIBRATION STANDARD IN THE CALIBRATION CURVE…"

- "AS THE REGULATONS ARE REVISED, THE RCRA PROGRAM WILL REMOVE THE MDL REFERENCE FROM THE MDPs [METHOD DEFINED PARAMETERS] AND REPLACE IT WITH THE LLOQ CONCEPT [sic] WHERE APPROPRIATE."


CURVE HAS TO BE "ACCEPTABLE." WHAT'S "ACCEPTABLE" DEFINED BY THE METHOD.
QL ≥ THE LOWEST NON-ZERO CAL STANDARD
LAB HAS TO VERIFY QL BY ANALYZING A QC SAMPLE AT 1-2X QL CONC
INSTRUMENT RESPONSE
0
10
20
30
40
50
CONCENTRATION

NO STEP-BY-STEP PROCEDURE IS GIVEN! YOU HAVE TO LOOK THROUGH VARIOUS SECTIONS OF CHAPTER ONE:

- **FIRST, THERE HAS TO BE A "DECISION LEVEL" OR "REGULATORY ACTION LEVEL". (AN EXAMPLE OF THE LATTER IS A STATE WATER QUALITY STANDARD.)**

- **CONSTRUCT YOUR CAL CURVE SO THAT YOUR LOWEST, NON-ZERO STANDARD IS AT OR BELOW THIS LEVEL.**

- **TEST YOUR CHOICE BY RUNNING WHAT IS ESSENTIALLY A LOW-LEVEL ICV AT THIS CONCENTRATION. INITIAL CONTROL LIMITS ARE $\pm$ 20% RECOVERY. CAN SET YOUR OWN AFTER DOING A LOT OF ANALYSES.**

- **IF THE ABOVE ARE SATISFIED, YOU HAVE YOUR LLOQ. IF NOT, YOU'LL HAVE TO RAISE YOUR CAL CURVE $\Rightarrow$ ITERATIVE PROCESS.**

HERE'S WHAT TO DO RIGHT NOW:

1) USE 40 CFR 136 FOR MDL (CURRENT VERSION, NOT "REVISION 2" BECAUSE IT'S NOT FINAL)

2) USE DEQ/STD. METHODS/CURRENT TNI FOR QL: THE LOWEST STANDARD USED IN A VALID CAL CURVE

3) KEEP A CLOSE EYE ON SW-846 METHOD REVISIONS AND SWITCH TO THE LLOQ WHEN CALLED FOR. NOTE THAT THIS SHOULD BE THE SAME AS THE QL IN #2, ABOVE!

The End