DETECTION LIMITS: THE GOOD, THE BAD, AND THE UGLY

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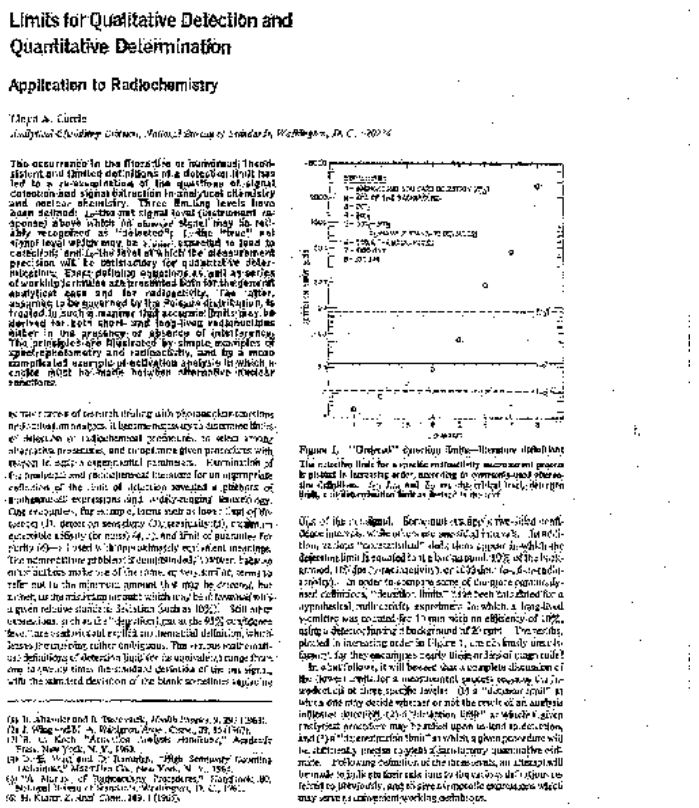
PACIFIC NW PRETREATMENT WORKSHOP
21ST ANNUAL MEETING
SEPTEMBER 15, 2014

ENVIRONMENTAL SERVICES
CITY OF PORTLAND

“TO BEGIN…AT THE BEGINNING…”

(*Dylan Thomas, Under Milkwood*)

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



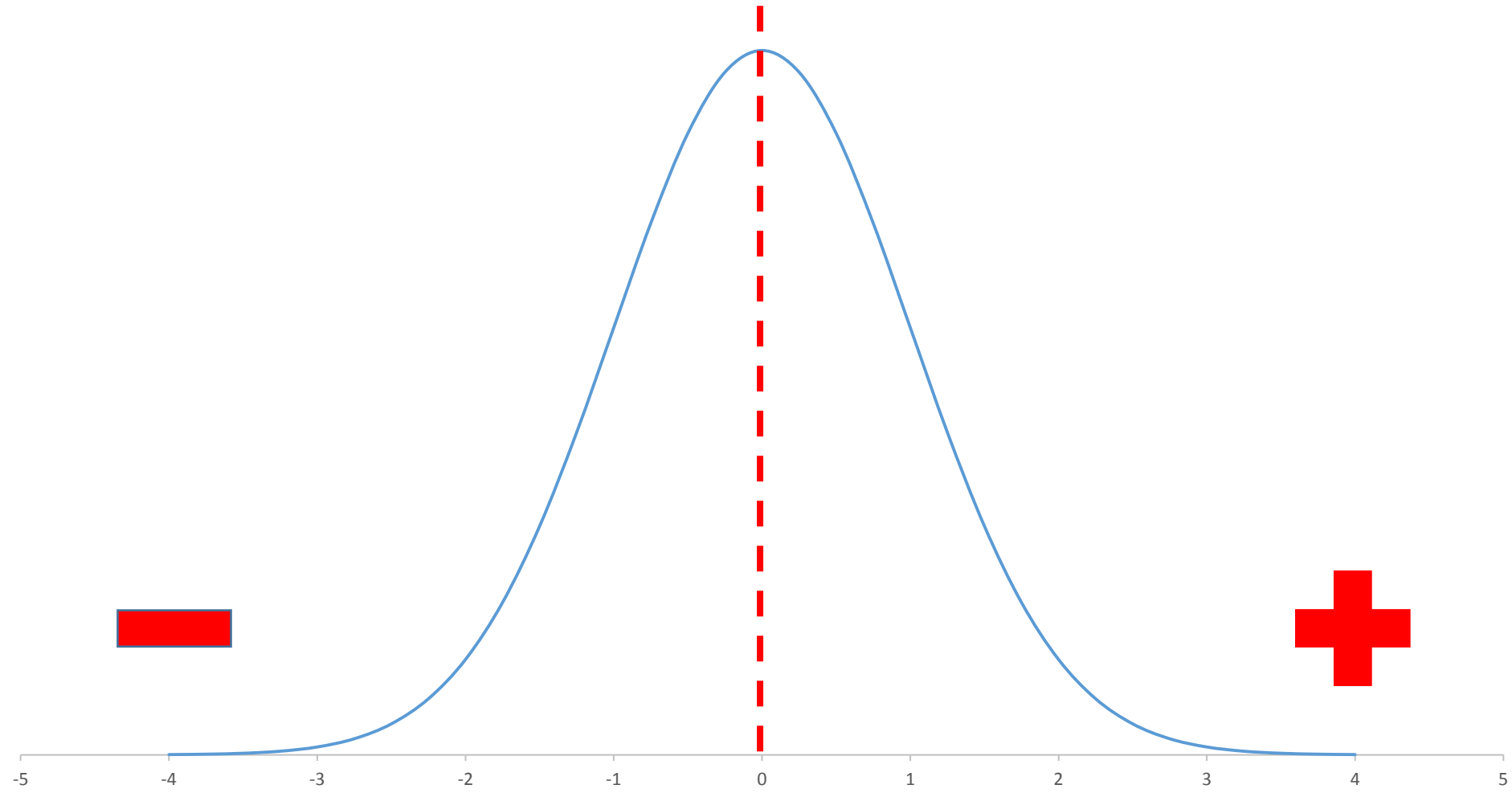
Limits for Qualitative Detection and Quantitative Determination

Application to Radiochemistry

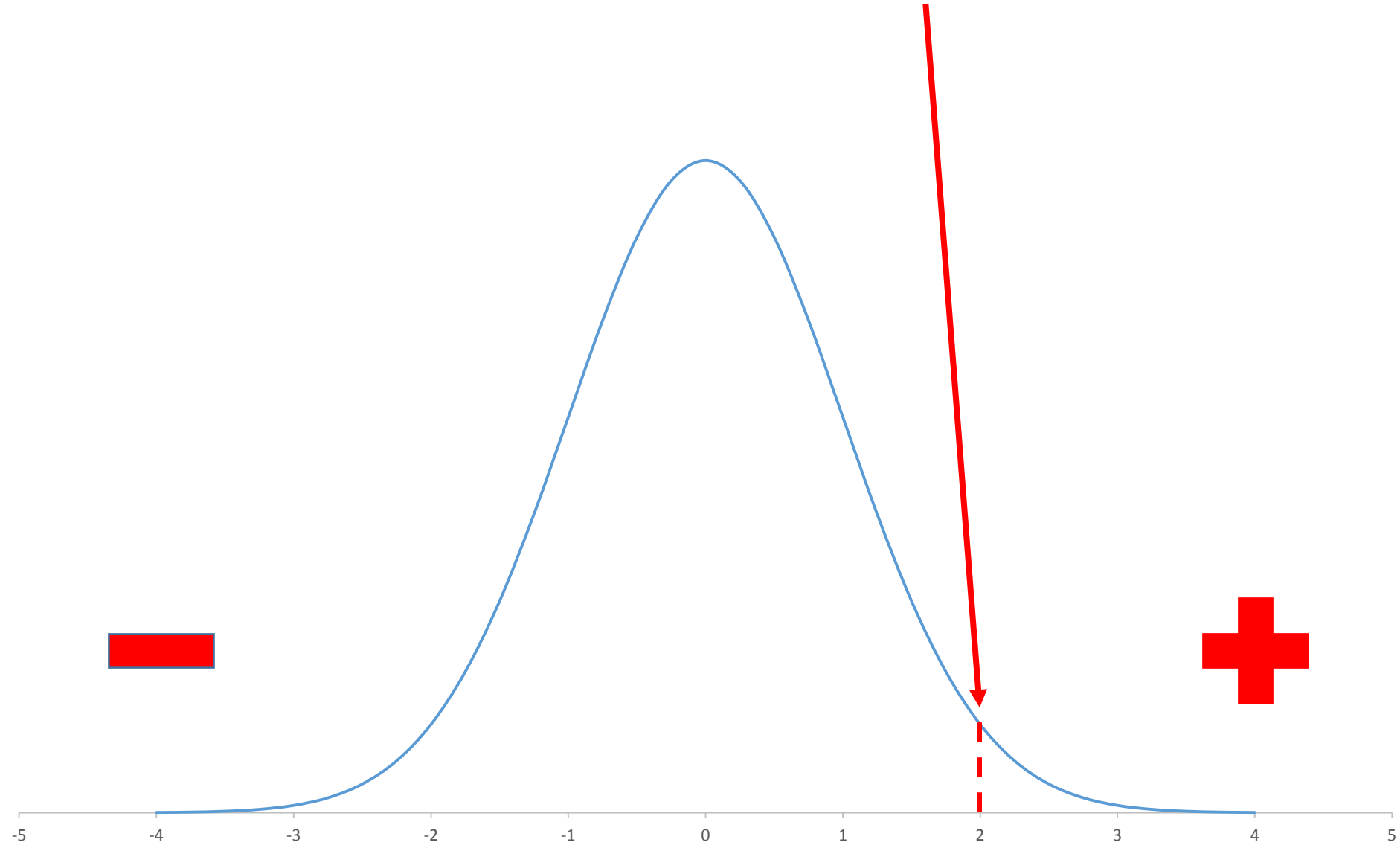
Lloyd A. Currie

Analytical Chemistry Division, National Bureau of Standards, Washington, D. C. 20234

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



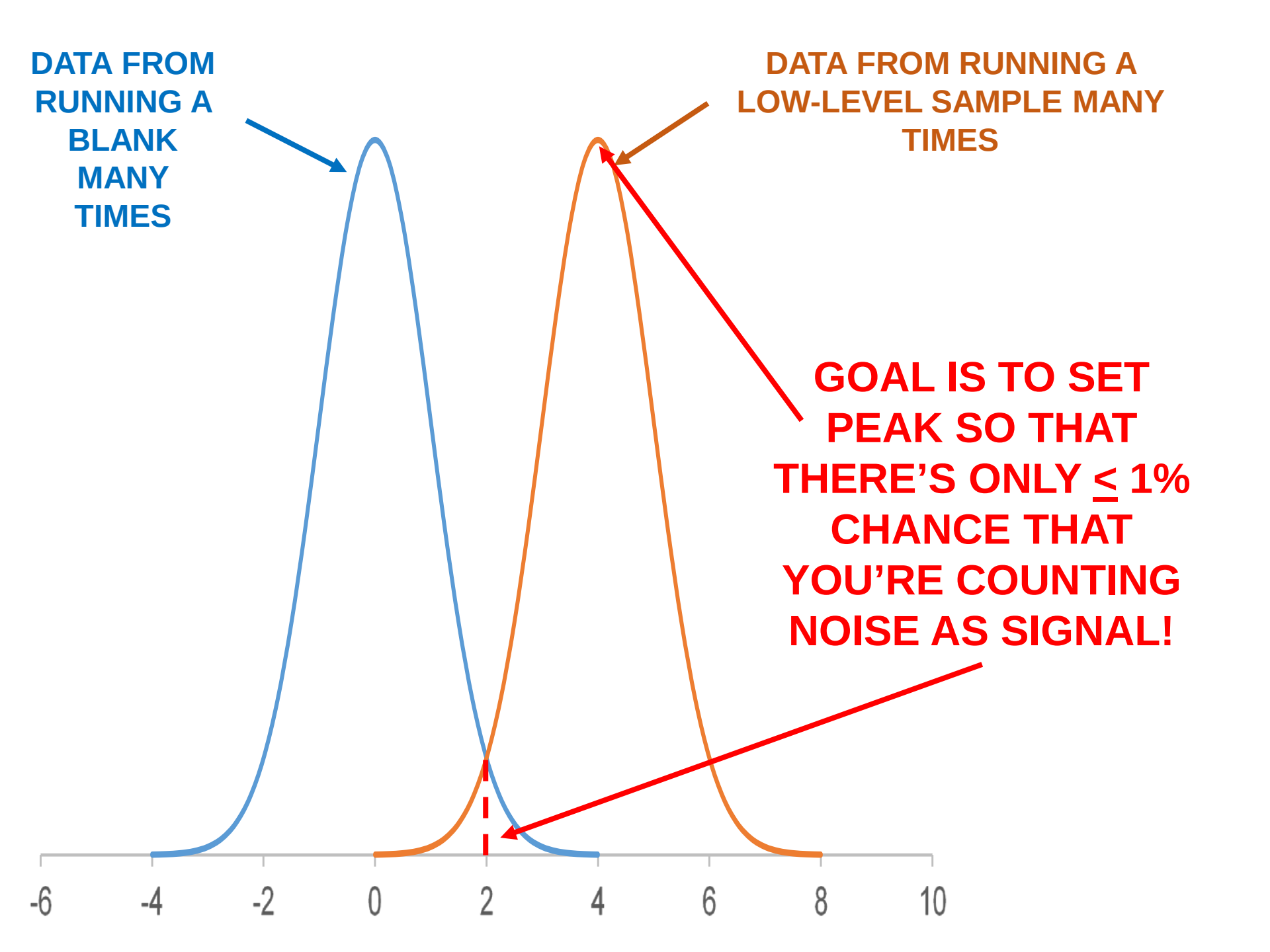
HE CALLED THE POINT WHERE THE CHANCE OF A RANDOM FALSE POSITIVE WAS ≤ 1% THE *CRITICAL LEVEL*.



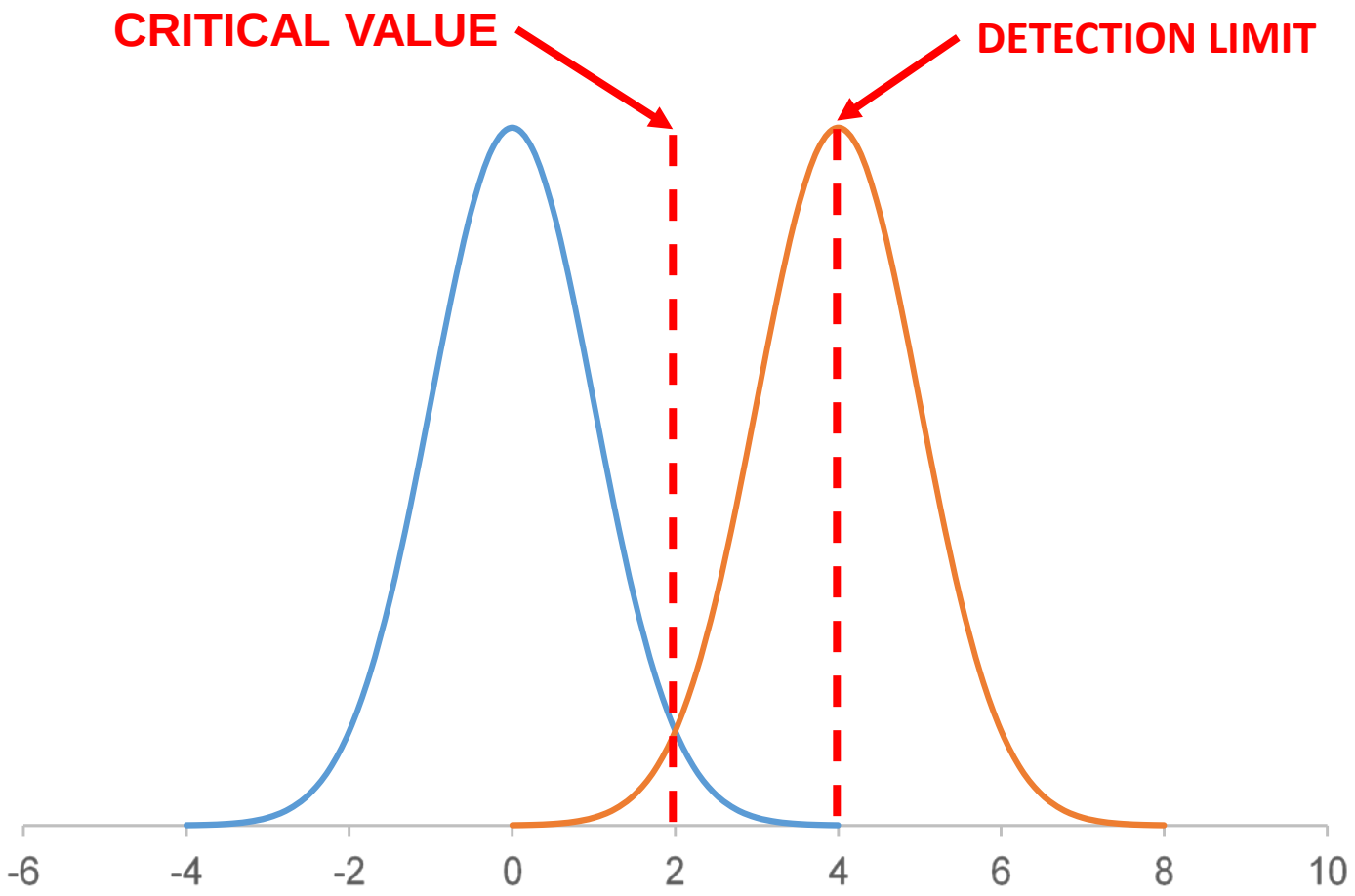
THE SAME BELL-SHAPED DISTRIBUTION WILL OCCUR WHEN ANALYZING A SAMPLE MANY TIMES.

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

$\pi \approx 3.14159$

$e \approx 2.71828$

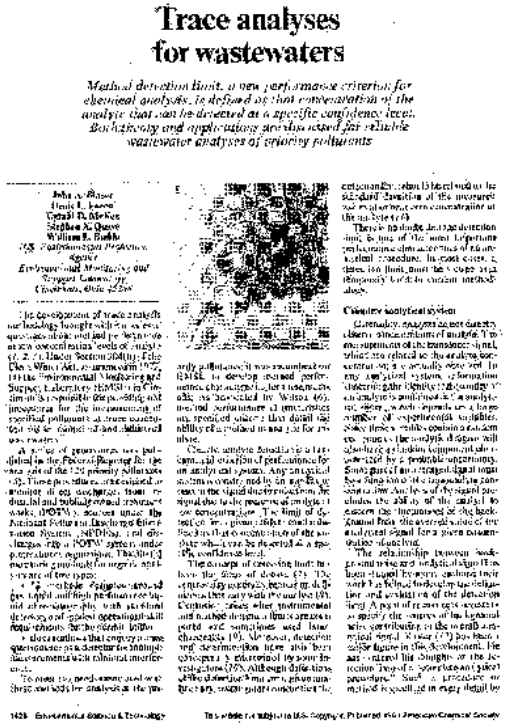
BUT!

TO CALCULATE CURRIE'S DETECTION LIMIT, YOU FIRST HAVE TO GENERATE THE PROBABILITY FUNCTION FROM ANALYZING A WHOLE LOT OF BLANKS SO YOU CAN CALCULATE THE CRITICAL VALUE.

SO HOW DID WE GET FROM CURRIE'S DETECTION LIMIT TO THE EPA MDL PROCEDURE AT 40 CFR 136???

IT ALL BEGAN IN 1981 WITH A PAPER OUT OF THE EPA EMSL LAB IN CINCINNATI, OHIO

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



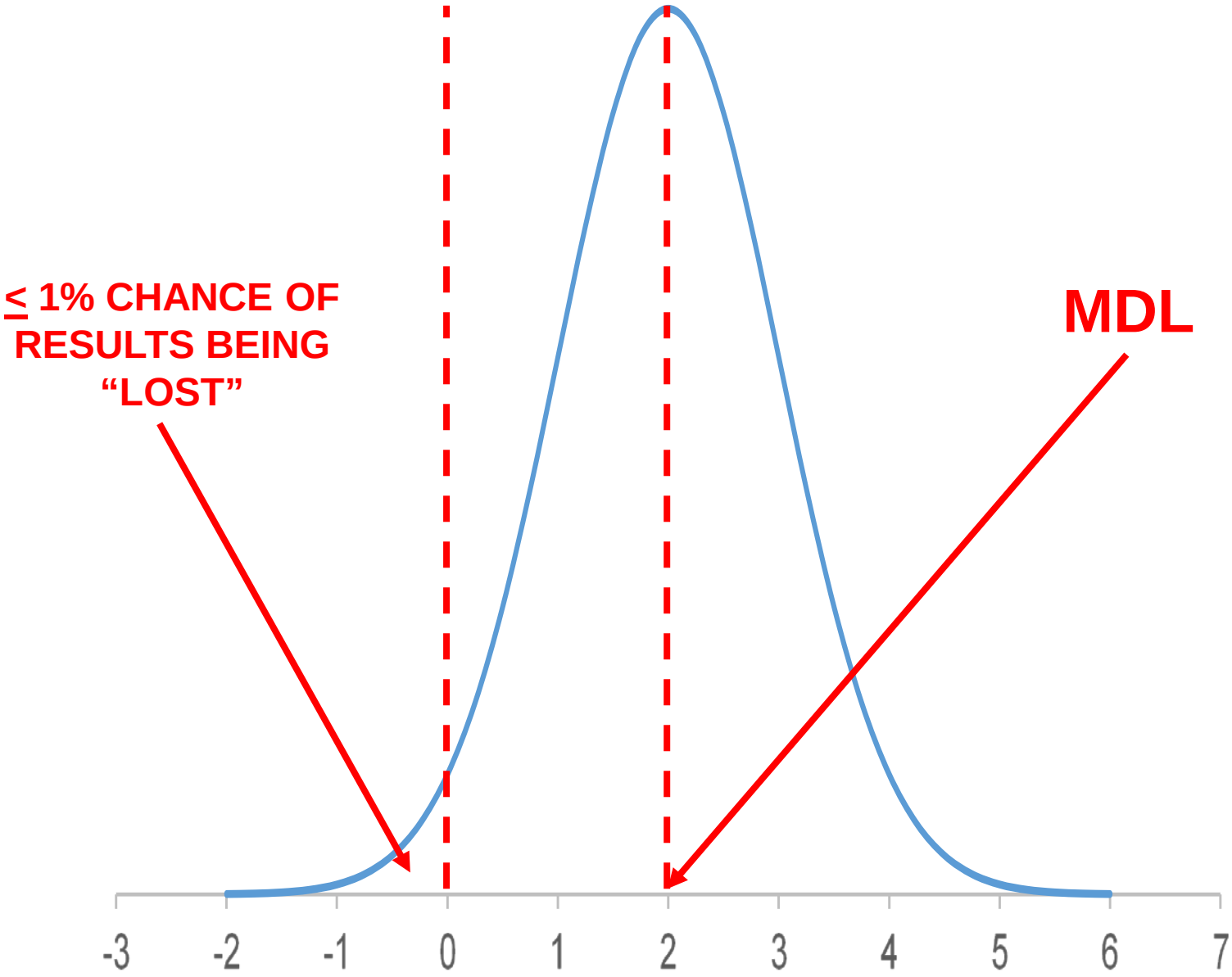
Trace analyses for wastewaters

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).

BIG PROBLEM:

THESE METHODS DON'T GENERATE NEGATIVE NUMBERS. 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

THE EPA PROMULGATED THEIR NEW MDL CONCEPT AT 40 CFR 136 ON OCTOBER 26, 1984 *AS A REGULATORY OPTION*

THE CALCULATION IS VIA THE WELL-KNOWN EQUATION

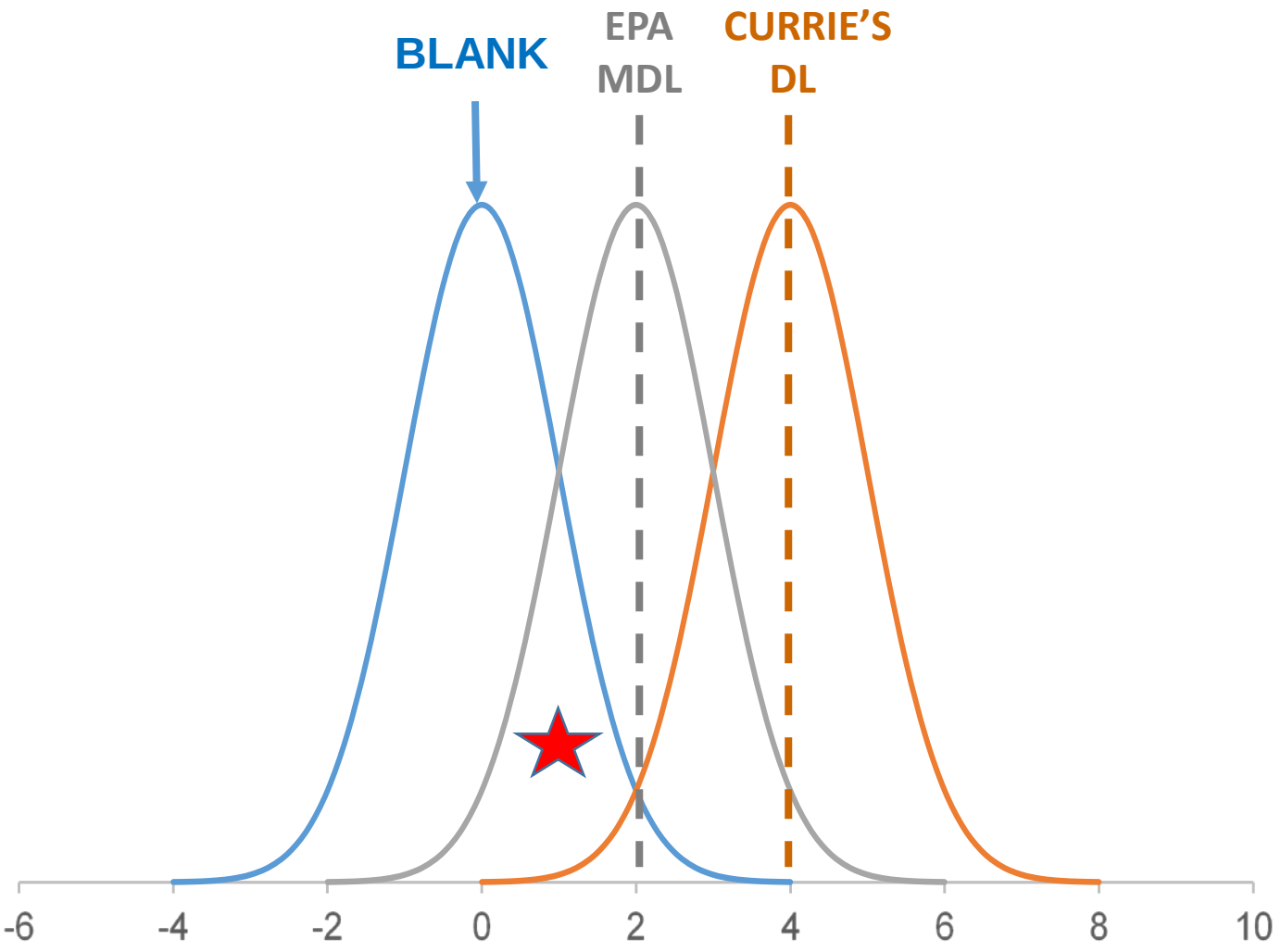
$$MDL = (t_{n-1,1-\alpha = 0.99}) \bullet s_n$$

IMPORTANT POINT TO REMEMBER:

THE EPA'S APPROACH WAS TO

MINIMIZE FALSE NEGATIVES

THE EPA MDL PROCEDURE CREATES AN ARTIFICALLY LOW DETECTION LIMIT THAT HAS A SIGNIFICANT POTENTIAL FOR INCLUDING NOISE IN THE SAMPLE SIGNAL: AREA ★ BELOW.



IN OTHER WORDS, DATA COULD SHOW THE PRESENCE OF A CONTAMINANT WHEN THERE WAS ACTUALLY NOTHING THERE.

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 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 WITH ITS NEW, LOW-LEVEL MERCURY METHOD ON JUNE 8, 1999….

AND GOT PROMPTLY SUED !!!

BY…

THE ALLIANCE OF AUTOMOBILE MANUFACTURERS

THE CHEMICAL MANUFACTURERS ASSOCIATION

THE UTILITY WATER ACT GROUP

THE AMERICAN FOREST & PAPER ASSOCIATION

WHY???

REMEMBER THE SLIDE SHOWING THE MDL AND DL???

EPA MDL = 2

CURRIE DL = 4

SO. THE EPA STUDIED THE WHOLE ISSUE, LOOKED AT EVERY DETECTION LIMIT PAPER/METHOD EXTANT, EVEN CONVENED A HIGH-POWERED WORK GROUP TO COME UP WITH A SOLUTION. THE BIG EPA DRAFT REPORT CAME OUT IN OCTOBER 2004, WAY BEFORE THEIR WORK GROUP WAS FINISHED.

BUT...

THE EPA FELT THAT THINGS LOOKED PROMISING.

THE WORK GROUP WAS CALLED THE FEDERAL ADVISORY COMMITTEE ON DECTECTION AND QUANTITATION (OR *FACDQ* FOR SHORT). THE WORK GROUP CAME UP WITH THE DQFAC METHOD AND SENT IT TO EPA IN DECEMBER 2007.

(NOTE THAT THIS WAS EIGHT YEARS AFTER THE ROD WAS SIGNED BY THE EPA THAT ORDERED THEM TO REDO THE OLD MDL PROCEDURE!)

IT: 1) REQUIRES ANALYZING A LOT OF BLANKS AND SPIKED BLANKS

2) INVOLVES THE USE OF A LOT OF STATISTICS

AND WAS PROMPTLY

REJECTED

BY THE EPA

(MUCH TO THE CONSTERNATION OF THE WORK GROUP, WHICH WORKED FOR SEVERAL YEARS DEVELOPING THE METHOD)

HERE'S A HINT WHY IT DIDN'T MAKE THE GRADE……..

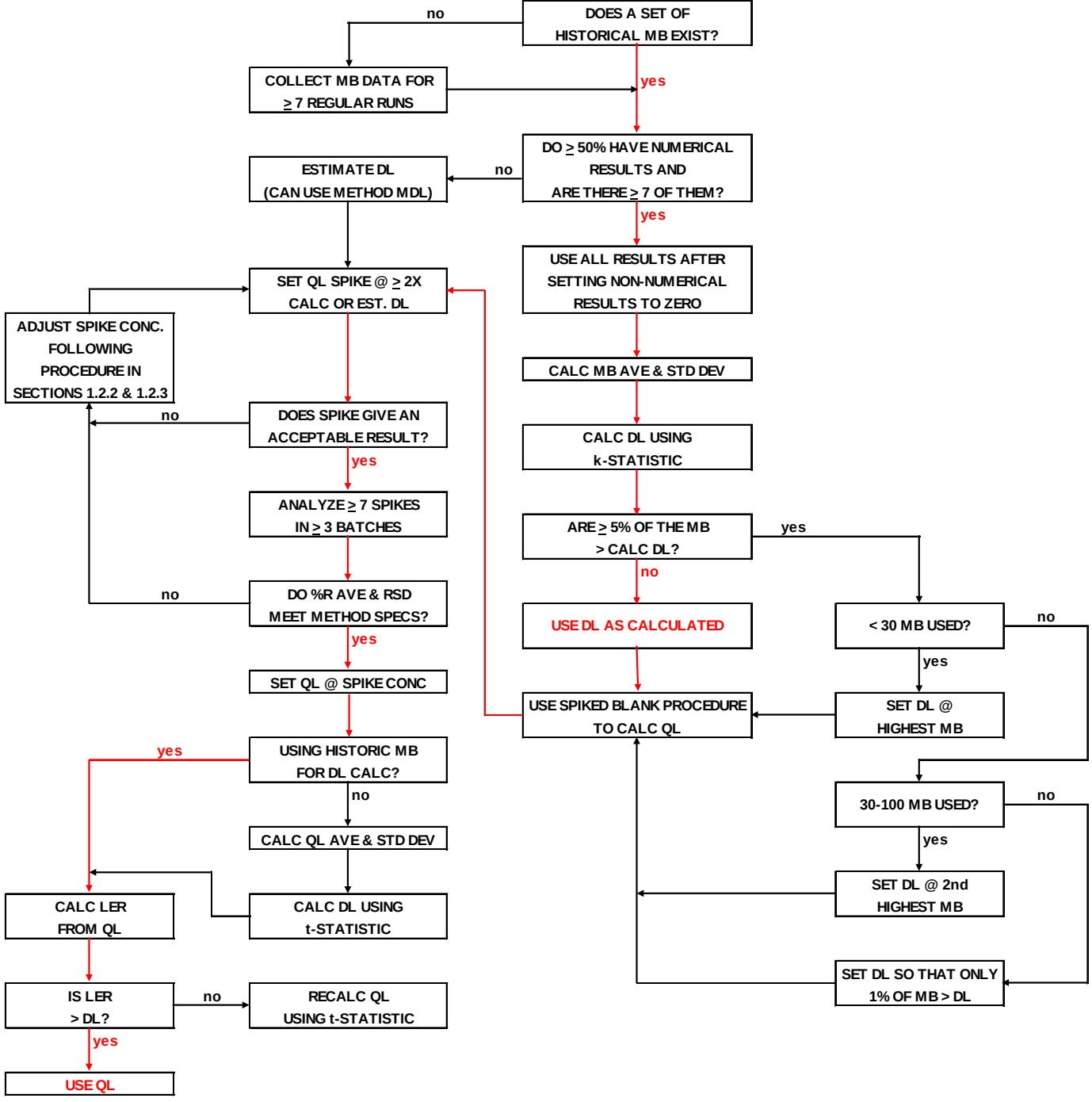

DOES A SET OF HISTORICAL MB EXIST?
no
COLLECT MB DATA FOR ≥ 7 REGULAR RUNS
yes
DO ≥ 50% HAVE NUMERICAL RESULTS AND ARE THERE ≥ 7 OF THEM?
no
ESTIMATE DL (CAN USE METHOD MDL)
yes
USE ALL RESULTS AFTER SETTING NON-NUMERICAL RESULTS TO ZERO
SET QL SPIKE @ ≥ 2X CALC OR EST. DL
ADJUST SPIKE CONC. FOLLOWING PROCEDURE IN SECTIONS 1.2.2 & 1.2.3
CALC MB AVE & STD DEV
DOES SPIKE GIVE AN ACCEPTABLE RESULT?
no
yes
CALC DL USING k-STATISTIC
ANALYZE ≥ 7 SPIKES IN ≥ 3 BATCHES
ARE ≥ 5% OF THE MB > CALC DL?
yes
no
DO %R AVE & RSD MEET METHOD SPECS?
no
USE DL AS CALCULATED
< 30 MB USED?
no
yes
SET QL @ SPIKE CONC
USE SPIKED BLANK PROCEDURE TO CALC QL
SET DL @ HIGHEST MB
yes
USING HISTORIC MB FOR DL CALC?
30-100 MB USED?
no
no
yes
CALC QL AVE & STD DEV
SET DL @ 2nd HIGHEST MB
CALC LER FROM QL
CALC DL USING t-STATISTIC
SET DL SO THAT ONLY 1% OF MB > DL
IS LER > DL?
no
RECALC QL USING t-STATISTIC
yes
USE QL

Table 2 -- Data And Calculated Results For The DL-QL & L_C-L_D Methods

	METHOD BLANK DATA SETS		
	LOW LEVEL	HIGH LEVEL	COMBINED
I METHOD BLANK DATA			
n	43	29	72
X_{mean} (ng/L)	0.192	0.636	0.371
s	0.233	0.422	0.388
II DL CALCULATION			
$k_{n-1,\ 0.99}$	3.112	3.368	2.877
$DL_{(ng/L)} = X_{mean} + (k_{n-1,\ 0.99} \bullet s) =$	**0.917**	**2.057**	**1.487**
III QL SET POINT			
2 • DL =	1.84	4.12	2.98
QL Spike Concentration (ng/L)	2.0	4.2	3.0
IV QL STUDY DATA			
n	25	28	30
X_{mean} (ng/L)	2.212	4.136	2.943
s	0.118	0.196	0.266
V QL DATA AS PERCENT RECOVERY			
RANGE	96.5 - 120	91.0 - 109	89.2 - 107
MEAN	110.6 ± 11.8	98.5 ± 4.7	98.1 ± 8.9
EPA 1631E IPR %R CONTROL LIMITS		**------ 79 - 121 ------**	
RSD	10.7	4.8	9.1
EPA 1631E IPR RSD CONTROL LIMIT		**---------- 21 ----------**	
VI LER CALCULATION			
$t_{n-1,\ 0.95}$	1.711	1.706	1.699
$LER_{(ng/L)} = X_{mean} - (t_{n-1,\ 0.95} \bullet s) =$	2.01	3.8	2.49
LER / DL =	2.18	1.85	1.67
LER > DL ⇒ $QL_{(ng/L)}$ =	**2.0**	**4.2**	**3.0**
VII L_C CALCULATION (USES METHOD BLANK DATA)			
$Z_{0.99}$		--------- 2.33 ---------	
$CHI\text{-}SQUARED_{n-1,\ 0.99}$	23.65	13.56	45.44
$LC_{(ng/L)} = Z_{0.99} \bullet [(n\text{-}1)/CHI\text{-}SQUARED_{n-1,\ 0.99}]^{1/2} \bullet s =$	0.724	1.41	1.13
WORKING $LC_{(ng/L)}$	**0.7**	**1.4**	**1.1**
2 • LC_{calc} =	1.45	2.82	2.26
$LD_{(ng/L)}$ = QL =	**2.0**	**3.0**	**3.0**

WHICH IS NOT TO SAY THAT THE EPA AND OTHERS HADN'T BEEN BUSY.

YES, THE EPA AND EVERYBODY ELSE HAD BEEN WORKING OVERTIME PROPOSING ENDLESS DETECTION LIMIT REGIMES FOR SPECIFIC METHODS, FOR USE IN SPECIFIC PROGRAMS OR OFFICES…A TOWER OF DETECTION BABEL THAT ALSO INCLUDED ATTEMPTS AT ESTABLISHING QUANTITATION LIMITS.

????

UH, WE HAVEN'T EVEN COVERED THAT IDEA.

SIDEBAR SLIDE #1:

CURRIE CAME UP WITH THE IDEA OF A QUANTITATION LIMIT BACK IN HIS 1968 PAPER.

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

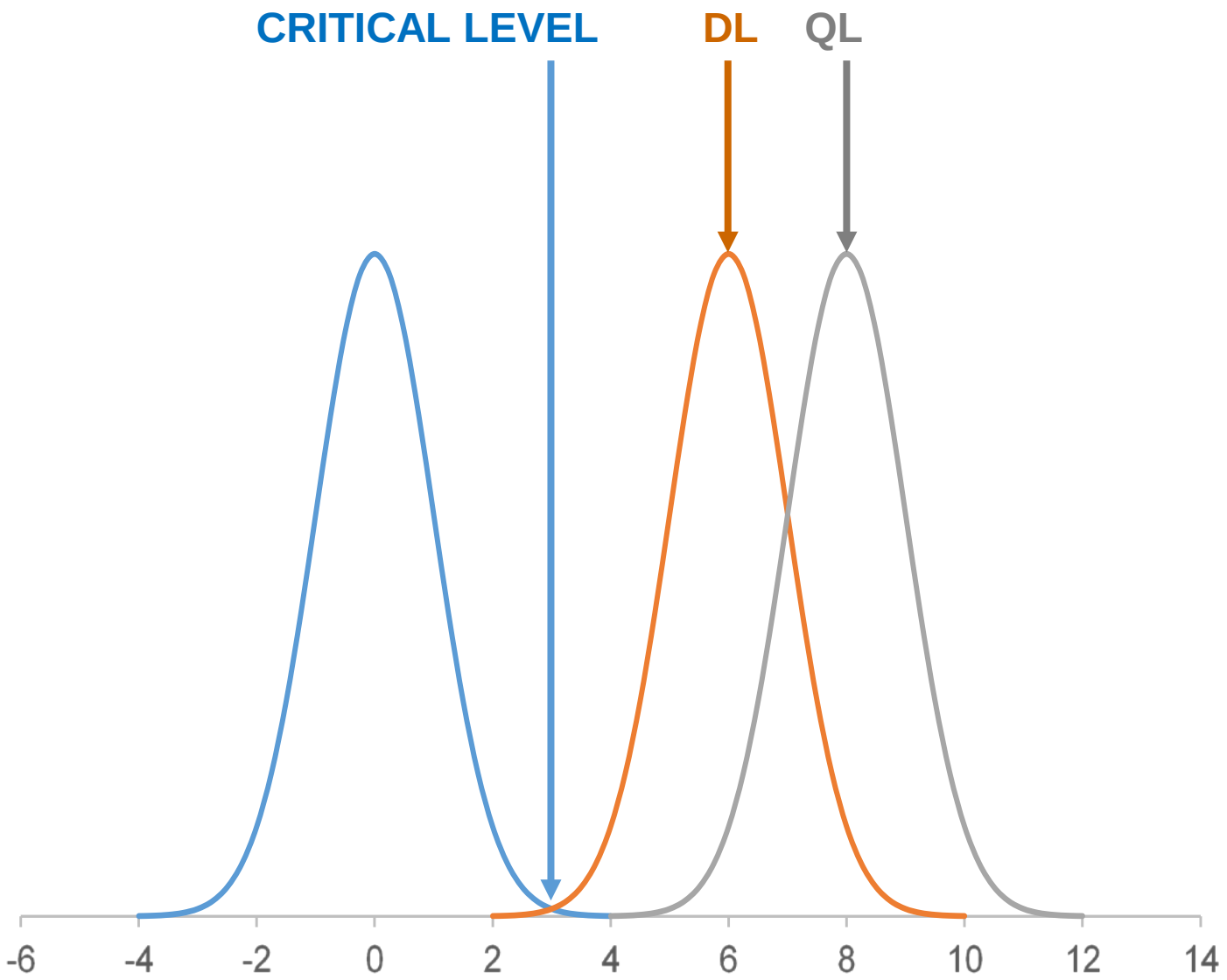
ALTHOUGH BACKED BY A LOT OF STATISTICS, THE FINAL RESULT WAS SIMPLE:

$$QL = 10s$$

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…..

SIDEBAR SLIDE #2



OKAY, BACK TO THE MAIN THREAD OF THE PRESENTATION. HERE'S WHAT WAS GOING ON AT THE EPA AND AT OTHER ORGANIZATIONS:

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)

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THE TNI CHEMISTRY EXPERT COMMITTEE (UNDER CONTRACT TO THE EPA) SENT ITS OWN MDL METHOD TO EPA ON MARCH 19, 2014.

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 SOME 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.

SO WHERE ARE WE???

- THE EPA HAS YET TO COME UP WITH A SUBSTITUTE FOR THE ORIGNAL MDL METHOD AT 40 CFR 136(b)
- TNI HAS PROPOSED AN MDL METHOD. WHO KNOWS WHAT THE EPA WILL DO WITH IT?
- THERE IS CURRENTLY NO CONSENSUS ON HOW TO ARRIVE AT THE QL
- MOST OF THE QL METHODS BEING SUGGESTED ARE VERY COMPLEX AND REQUIRE A SUBSTANTIAL AMOUNT OF DATA (BLANKS, SPIKED BLANKS, ETC.)

IF THAT ISN'T ENOUGH, FOR YEARS STATISTICIANS HAVE BEEN SAYING THAT THE ENTIRE CONCEPT OF DETECTION LIMITS IS BAD.

THERE IS AN ENTIRE LITERATURE ON ESTIMATING POPULATION STATISTICS OF LARGE DATA SETS THAT HAVE BEEN "ARTIFICIALLY" CENSORED BY USING DETECTION LIMITS!

IN COUNTRIES UNDER ISO, PRECISION AND BIAS ESTIMATES ARE USED, NOT DETECTION LIMITS.

ON THE "FOLLY" OF DETECTION LIMITS:

NOEL CRESSIE. *LIMITS OF DETECTION*. CHEMOMETRICS AND INTELLIGENT LABORATORY SYSTEMS. 22: 161-163, 1994.

ON "RESTORING" LARGE DATA SETS CONTAINING CENSORED DATA:

DENNIS HELSEL. *NONDETECTS AND DATA ANALYSIS: STATISTICS FOR CENSORED ENVIRONMENTAL DATA*. NEW YORK: WILEY, 2005.

DENNIS HELSEL. *MORE THAN OBVIOUS: BETTER METHODS FOR INTERPRETING NONDETECT DATA*. ENV. SCI. TECHN. 39: 419A-425A, 2005.

ON USING PRECISION & BIAS ESTIMATES RATHER THAN DETECTION LIMITS:

BERTIL MAGNUSSON et al. *HANDBOOK FOR CALCULATION OF MEASUREMENT UNCERTAINTY IN ENVIRONMENTAL LABORATORIES. VERSION 3.1*. *NORDTEST PROJECT 1589-02*. OSLO: NORDIC INNOVATION, 2012.

OUR OWN WORK RUNNING ~75 Hg BLANKS AND SPIKES THROUGH FOUR DETECTION/QUANTITATION SCHEMES AND FINDING NO REAL DIFFERENCES:

CHARLES LYTLE et al. *NEW DETECTION LIMIT PROCEDURES: IS THERE A CLEAR WINNER?* WEF LABORATORY SOLUTIONS. 15(3): 1-8, 2008.

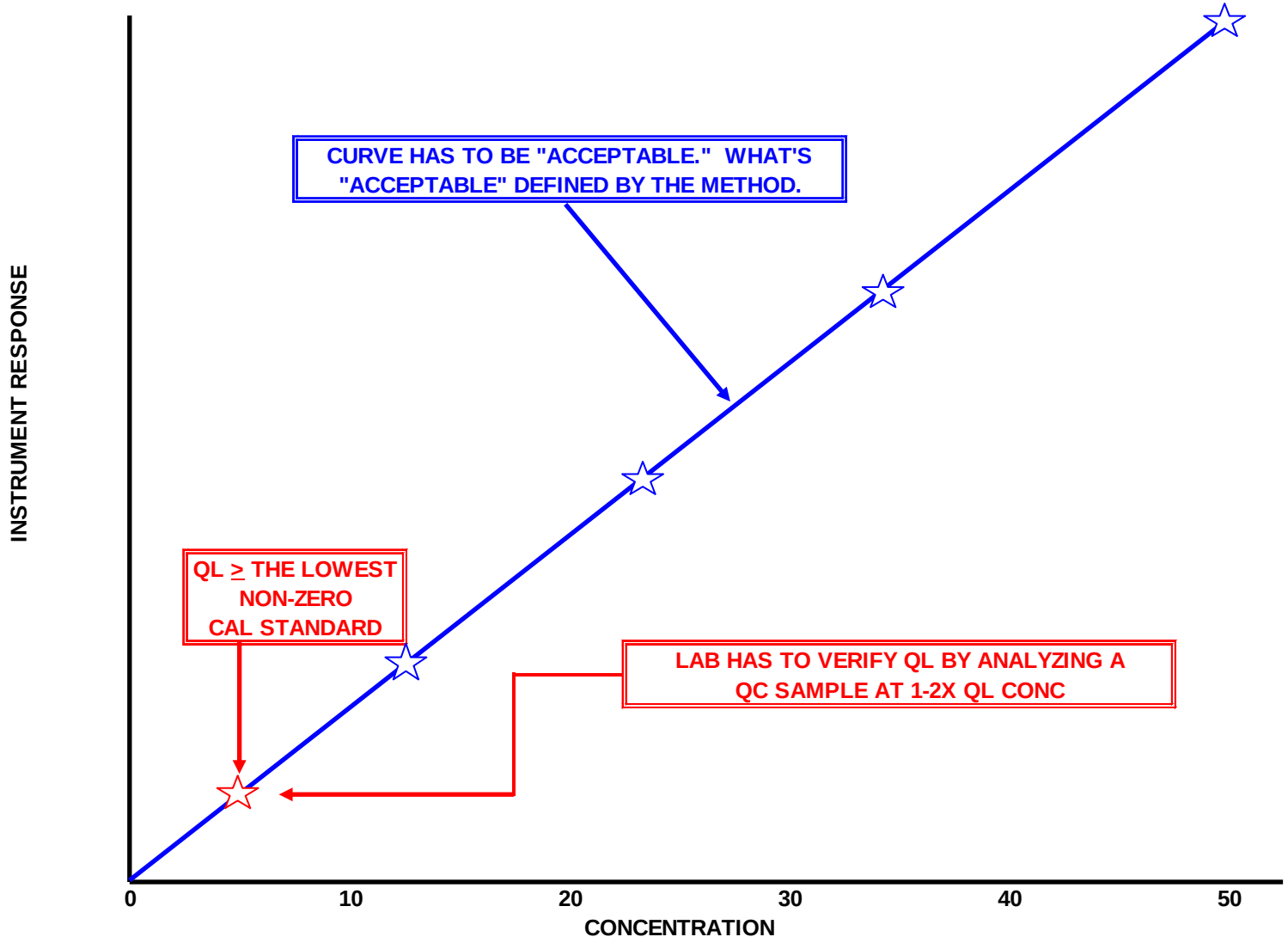
“THERE’S NO WAY OUTTA HERE…”

(BOB DYLAN, ALL ALONG THE WATCHTOWER)

HERE’S WHAT WE DO AT WPCL:

1) 40 CFR 136 FOR MDL (BECAUSE WE HAVE TO)

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


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

SIMPLE!!
EASY!!
NOT HARD TO UNDERSTAND!!

- BE SURE YOU REALLY UNDERSTAND WHAT MAKES A CAL CURVE "ACCEPTABLE" (HINT: YOUR CURVE CAN'T BE HETEROSCEDASTIC)
- THERE'S A LOT OF RESISTANCE TO USING THIS METHOD
  - SETTING THE LOWEST CAL STD CAN BE ARBITRARY
  - CALIBRATION IS DONE ON CLEAN SPIKES (NO MATRIX EFFECTS)
  - CALIBRATION AND THUS THE QL CAN CHANGE

I'VE BEEN ASKED TO ADD THE FOLLOWING AS A POSTSCRIPT

- DILUTING AN EXTRACT OR DIGESTATE DOES NOT CHANGE YOUR QL
- IT CHANGES YOUR REPORTING LIMIT
- DILUTION DOES NOT CHANGE YOUR CAL CURVE
- THUS, YOUR QL DOESN'T CHANGE BECAUSE IT CAN'T!

DILUTION OF AN EXTRACT OR DIGESTATE

- DOESN'T CHANGE YOUR IDL
- DOESN'T CHANGE YOUR MDL
- DOESN'T CHANGE YOUR QL

IT CHANGES YOUR REPORTING LIMIT:

IDL < MDL < QL ≤ MRL

IMAGINE YOU OWN A NEW CELESTRON 14-INCH SCT THAT IS SO SENSITIVE YOU CAN SEE THE LUNAR ROVER MOVING AROUND ON THE MOON.

THE NIGHT TURNS HAZY; EVERYTHING GETS BLURRY; YOU CAN'T MAKE OUT THE ROVER.

THE TELESCOPE IS NOT BROKEN. IT HAS NOT LOST ITS ABILITY TO SEE TINY THINGS ON THE MOON. THE AIR "MATRIX" IS INTERFERING. UNFORTUNATELY, YOU CAN'T "DILUTE" THE HAZE. YOU'RE STUCK.

YOU CAN'T VERIFY A LAB'S ABILITY TO REACH OR MAINTAIN A QL THROUGH THE ANALYSIS OF REAL WORLD SAMPLES!

THE QL CAN ONLY BE VERIFIED BY THE ANALYSIS OF AN INDEPENDENT STANDARD AT OR NEAR THE QL.

THIS IS DONE PERIODICALLY, AND THE TNI CHEMISTRY EXPERT COMMITTEE IS CURRENTLY DEBATING WHAT FREQUENCY TO PUT INTO THE NEW STANDARD.

ACKNOWLEDGEMENTS:

JASON LAW, COP-BES, FOR HELPFUL DISCUSSIONS.

CHUNG-REI MAO, PhD, CHEMIST, ENVIRONMENTAL AND MUNITIONS CENTER OF EXPERTISE, US ARMY COE ENGINERING AND SUPPORT CENTER, HUNTSVILLE, AL, FOR REVIEWING THE ENTIRE PRESENTATION AND OFFERING CORRECTIONS AND SUGGESTIONS.

“DON’T BEAT IT TO DEATH…”

(PAUL NEWMAN, COOL HAND LUKE)

The End