



PROPOSED CHANGES TO REGULATION 153/04 AND POTENTIAL IMPACTS



ENVIRONMENTAL CHEMISTRY



TRIBOLOGY



OIL AND GAS CHEMISTRY



ULTRA TRACE CHEMISTRY



MINING GEOCHEMISTRY



RESERVOIR ENGINEERING

PRESENTED TO:



AIR QUALITY MONITORING



RESEARCH



OIL SANDS





PROPOSED CHANGES TO REGULATION 153/04 AND POTENTIAL IMPACTS

- CHANGES TO THE STANDARD
- THE ANALYTICAL PROTOCOL - HOW WE DO THINGS IN THE LAB - AND WHAT EFFECT THAT WILL HAVE
- THE SAMPLING PROTOCOL - CHANGES THAT MAY IMPACT FIELD APPROACHES





THE HISTORY OF THE STANDARD

- In the early 1980s clean-up of the Shell and Texaco refinery lands in Oakville and Port Credit led to numeric values that were used in “*Guideline for the Decommissioning and Clean-up of Sites in Ontario*” in 1989
- In 1991 a supporting document. “*Soil Clean-up Guidelines for Decommissioning of Industrial Lands: Background and Rational for Development*” was published, however, it remained difficult to determine how certain standards were determined.
- The Ministry of the Environment (MOE), in consultation with the Petroleum industry, developed “*Interim Guidelines for the Assessment and Management of Petroleum Contaminated Sites in Ontario*” in 1993. This document relied heavily on professional judgment and criteria derived in Alberta. The criteria were not always effect based and still uncertainty remained regarding the procedures for development.
- 1993 the MOE developed a new set of standards based on the Massachusetts Contingency Plan (MCP), an approach that was being used by the Massachusetts Department of Environmental Protection (MADEP). These numeric standards were published in 1996 in “*Guidelines for Use at Contaminated Sites in Ontario*”. Accompanying this document was “*Rationale for the Development and Application of Generic Soil, Groundwater and Sediment Criteria for Use at Contaminated Sites in Ontario*”.
- With the passing of amendments to the EPA through the Brownfields Statute Law Amendment Act 2001 and the subsequent passing of Regulation 153/04 in 2004, the 1996 soil and ground water criteria took effect in Ontario. Thus most of the standards that are currently being used in Ontario date back to between 1985 and 1996.



THE HISTORY OF THE STANDARD

-Reasons for the proposed amendments to Reg. 153/04



The Ministry and external stakeholders have identified several issues with the current criteria:

- The need for additional standards
- The use of outdated toxicity data and lack of transparency
- Address additional exposure pathways
- The lack of consideration of certain receptors for some contaminants
- Impractical/unrealistic settings for commercial/industrial land use
- Cross-media transfer of metals not adequately considered
- Degradation to vinyl chloride over time not adequately considered
- Models and settings for contaminant transport which do not represent best practice and are not transparent
- The need for an approach that is amenable to a “Tier 2” modified generic approach
- Models for human health exposure which are not consistent with practices in other jurisdictions
- Background standards which may be inequitable for some land uses



THE CURRENT STATUS



- SOME STANDARDS WENT UP, SOME STANDARDS WENT DOWN
- INITIALLY, MANY OF THE STANDARDS WERE SET BELOW LIMITS THAT WERE PRACTICALLY ACHIEVABLE FROM AN ANALYTICAL STANDPOINT
- THE “TECHNICAL ADVISORY GROUP” OR TAG ADVOCATED FOR STANDARDS THAT REFLECT THE CURRENT ANALYTICAL REALITY
- THROUGH DIALOGUE WITH MOE, STANDARDS ARE IN THE PROCESS OF BEING ADJUSTED TO ENSURE THEY CAN BE ACCURATELY MEASURED
- IN CONCERT WITH ADJUSTED STANDARDS, THE TECHNICAL ADVISORY GROUP ADVOCATED FOR STANDARD APPROACHES TO ANALYSIS
- THESE APPROACHES HAVE MATERIAL IMPACT ON END USERS OF THE DATA



AGAT Laboratories

THE CURRENT STATUS



● GUIDANCE DOCUMENTS CAN BE FOUND HERE:

http://www.ene.gov.on.ca/envision/env_reg/er/documents/2008/010-4642%202.pdf



THE ANALYTICAL PROTOCOL

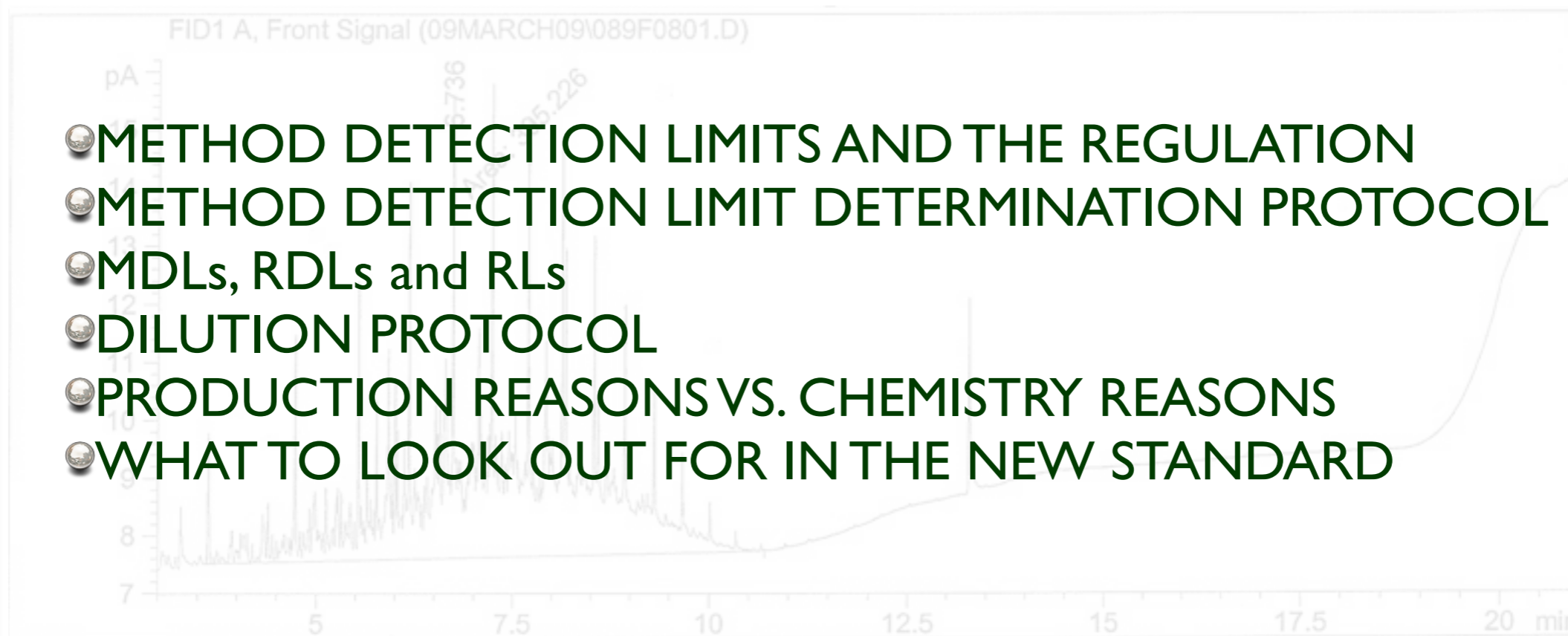
- DETECTION LIMITS (MDLs, RDLs, RLs)
- THE DILUTION PROTOCOL
- “MATRIX INTERFERENCE”





REGULATION 153/04 & DETECTION LIMITS

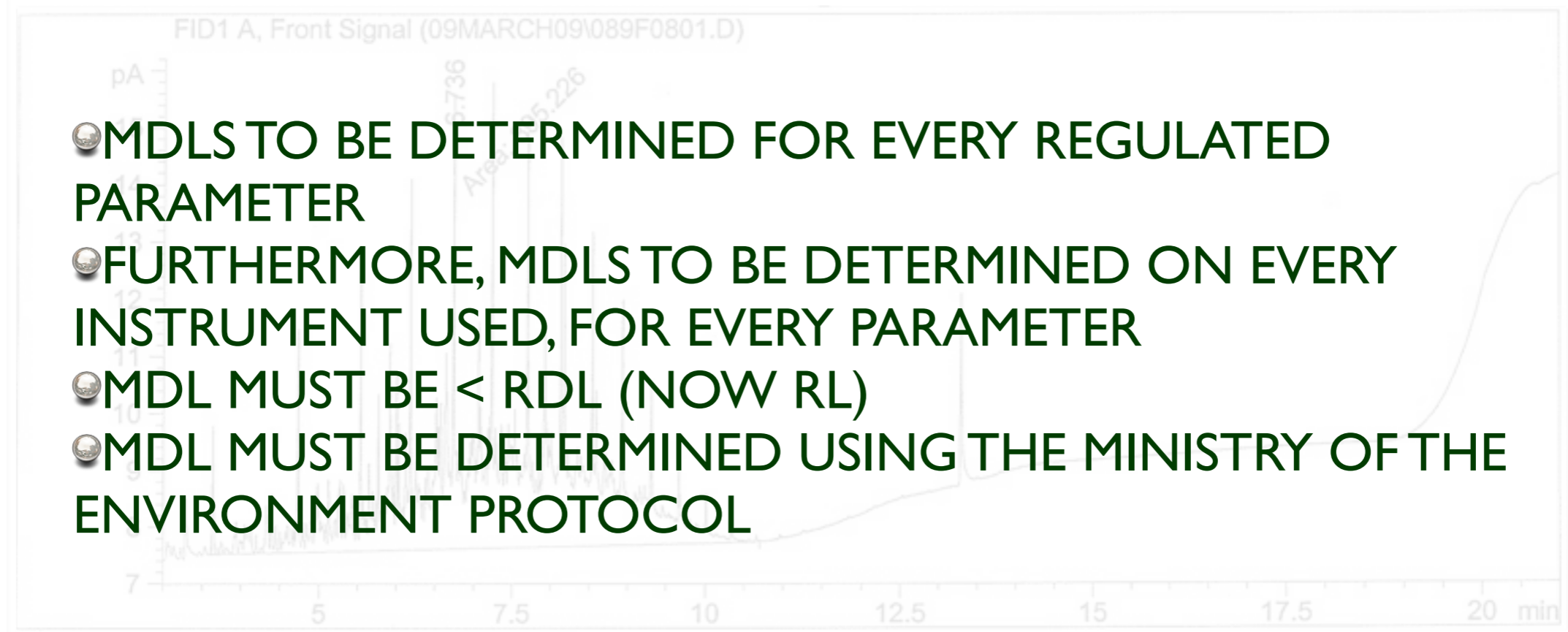
- METHOD DETECTION LIMITS AND THE REGULATION
- METHOD DETECTION LIMIT DETERMINATION PROTOCOL
- MDLs, RDLs and RLs
- DILUTION PROTOCOL
- PRODUCTION REASONS VS. CHEMISTRY REASONS
- WHAT TO LOOK OUT FOR IN THE NEW STANDARD





METHOD DETECTION LIMITS AND THE REGULATION

- MDLS TO BE DETERMINED FOR EVERY REGULATED PARAMETER
- FURTHERMORE, MDLS TO BE DETERMINED ON EVERY INSTRUMENT USED, FOR EVERY PARAMETER
- MDL MUST BE $<$ RDL (NOW RL)
- MDL MUST BE DETERMINED USING THE MINISTRY OF THE ENVIRONMENT PROTOCOL





MOE PROTOCOL FOR DETERMINATION OF METHOD DETECTION LIMITS

- PREPARE A SAMPLE (USUALLY WATER OR BLANK SOIL) FORTIFIED AT 1 - 10X THE EXPECTED MDL
- IF THE RESULTANT MDL DETERMINATION IS $< 10X$ THE SPIKE USED IN PREPARATION, THE PROCESS STARTS AGAIN
- 8 (OR MORE) ALIQUOTS OF SAMPLE ARE PROCESSED THROUGH THE ENTIRE METHOD.
- THE STANDARD DEVIATION OF THE SAMPLE SET IS CALCULATED



MOE PROTOCOL FOR DETERMINATION OF METHOD DETECTION LIMITS

- STANDARD DEVIATION CALCULATED AS FOLLOWS

$$\sigma = \sqrt{\frac{\sum (x_i - m)^2}{n - 1}}$$





MOE PROTOCOL FOR DETERMINATION OF METHOD DETECTION LIMITS

● MDL IS CALCULATED AS $t * S$, WHERE:

NUMBER OF REPLICATES	DEGREE OF FREEDOM	<i>t</i>
7	6	3.143
8	7	2.998
9	8	2.897
10	9	2.821
11	10	2.764
16	15	2.603
21	20	2.528
26	25	2.485
31	30	2.457





METHOD DETECTION LIMIT FOR SUMMED PARAMETERS

- MDL IS CALCULATED AS SQUARE ROOT OF THE SUM OF SQUARES
- EX. TOTAL XYLENE AS A SUM OF o-XYLENE AND m&p-XYLENE
 - MDL o-XYLENE = 0.02
 - MDL m&p-XYLENE = 0.03
 - MDL FOR TOTAL XYLENE = $\text{SQRT}(0.0004 + 0.0009) = 0.035$





MDL, RDL AND RL



MDL - THE MDL IS THE LOWEST CONCENTRATION AT WHICH AN ANALYTE CAN BE DISTINGUISHED FROM A BLANK WITH 99% CERTAINTY.

RDL - TYPICALLY SET AT 3 - 5X THE MDL, THE LOWEST CONCENTRATION AN ANALYTE CAN BE DETECTED IN A SAMPLE WITH A REASONABLE DEGREE OF ACCURACY AND PRECISION

RL - A PARAMETER THAT IS SET BY REGULATION FOR EACH REPORTABLE PARAMETER. IN THE CASE OF ONTARIO REGULATION 153 / 04, SOME RLs ARE SET AT OR ABOVE THE RDL, SOME ARE SET AT THE MDL.



MDL, RDL AND RL



MOST PARAMETERS LISTED FOR TABLE I HAVE STATISTICAL MDLs AT THE REPORTING LIMIT

THIS REPRESENTS A DANGER IN TERMS OF ACHIEVABILITY IN THE CASE OF CONTAMINATED SAMPLES

THEREFORE PRACTICAL MEASURES NEEDED TO BE BUILT INTO THE ANALYTICAL PROTOCOL FOR SAMPLES DESTINED FOR MULTI-COMPONENT SCANS WITH ONE OR MORE CONTAMINATING SUBSTANCES



SAMPLE DILUTION PROTOCOL

WHEN THE CONCENTRATION OF ONE OR MORE PARAMETERS IN A MULTICOMPONENT SCAN EXCEED THE CONCENTRATION OF THE HIGHEST CALIBRATION STANDARD, DILUTION IS REQUIRED

WHEN THIS IS REQUIRED THE RDL FOR EACH TARGET ANALYTE MUST BE ADJUSTED IN DIRECT PROPORTION TO THE DILUTION FACTOR, WHERE:

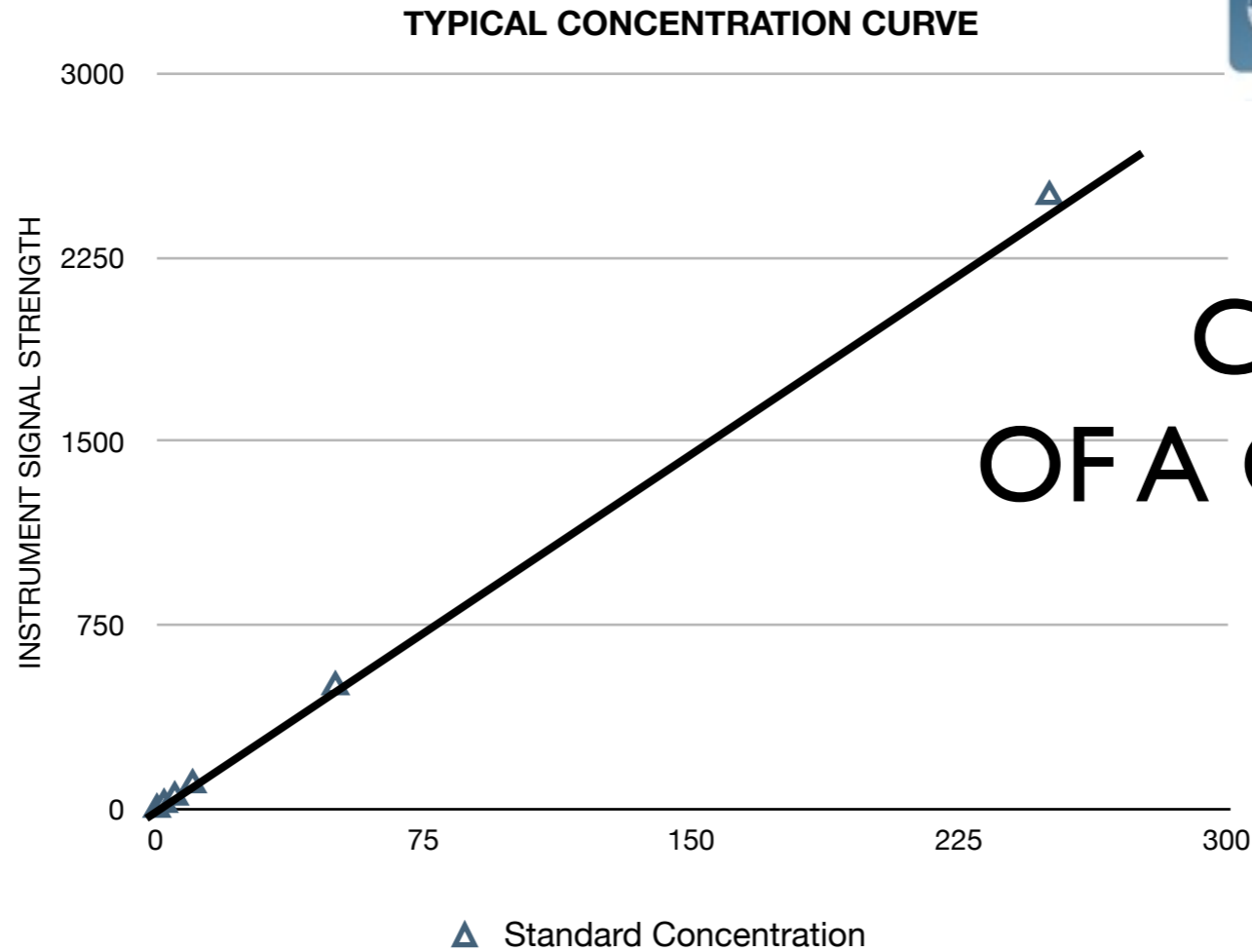
DILUTION FACTOR = $\frac{\text{FINAL VOLUME OF DILUTED SAMPLE}}{\text{SAMPLE ALIQUOT VOLUME}}$

RDL (REVISED) = DF X RDL





CALIBRATION STANDARDS

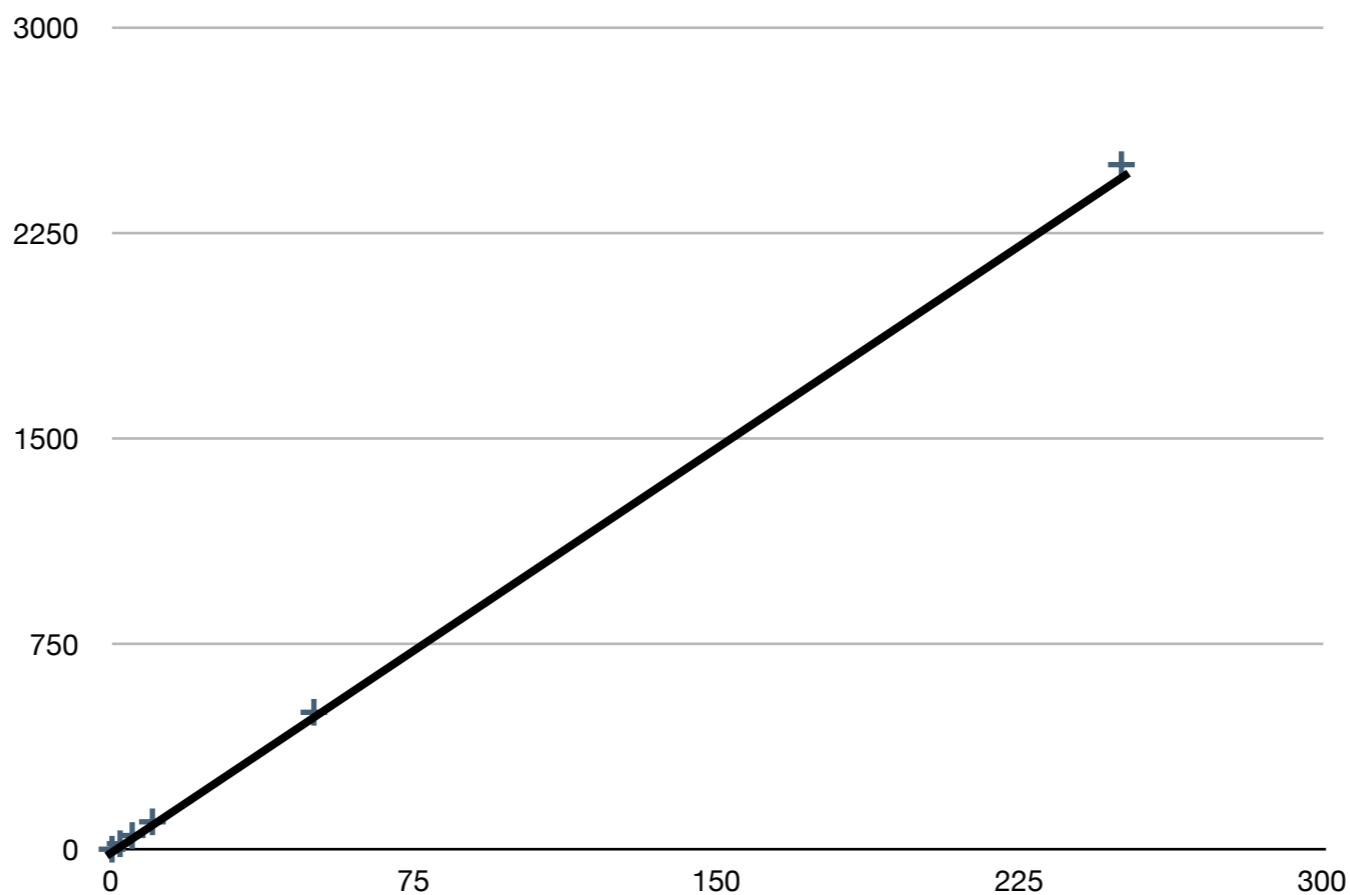


CREATION OF A CALIBRATION CURVE

CALIBRATION STANDARD CONCENTRATIONS	INSTRUMENT SIGNAL STRENGTH
0	0
2	20
5	50
10	100
50	500
250	2500

CALIBRATION / DILUTION

TYPICAL CONCENTRATION CURVE



+ Standard Concentration

ANALYTE CONCENTRATION	SIGNAL STRENGTH
0	0
2	20
5	50
10	100
50	500
250	2500

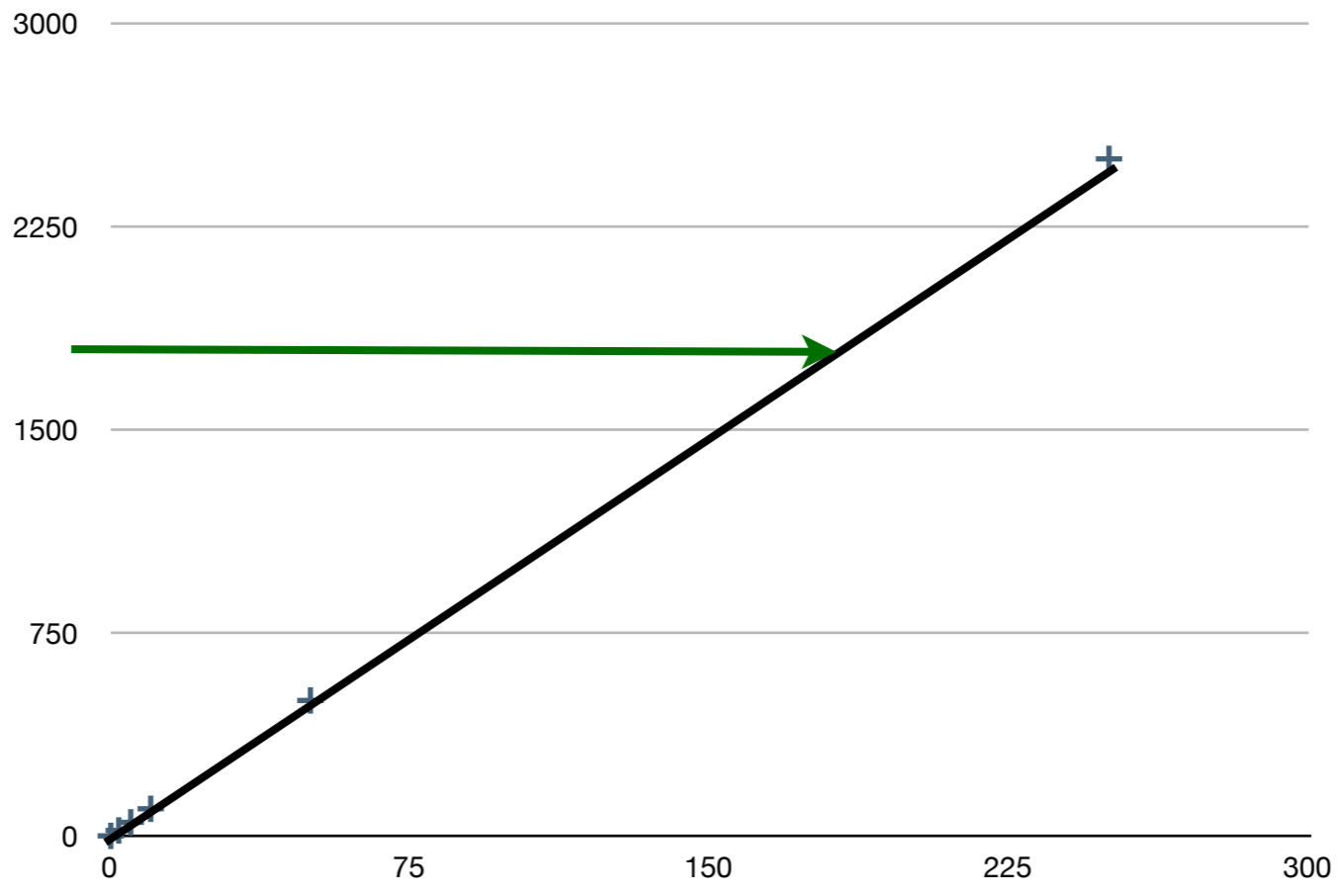


CALIBRATION / DILUTION



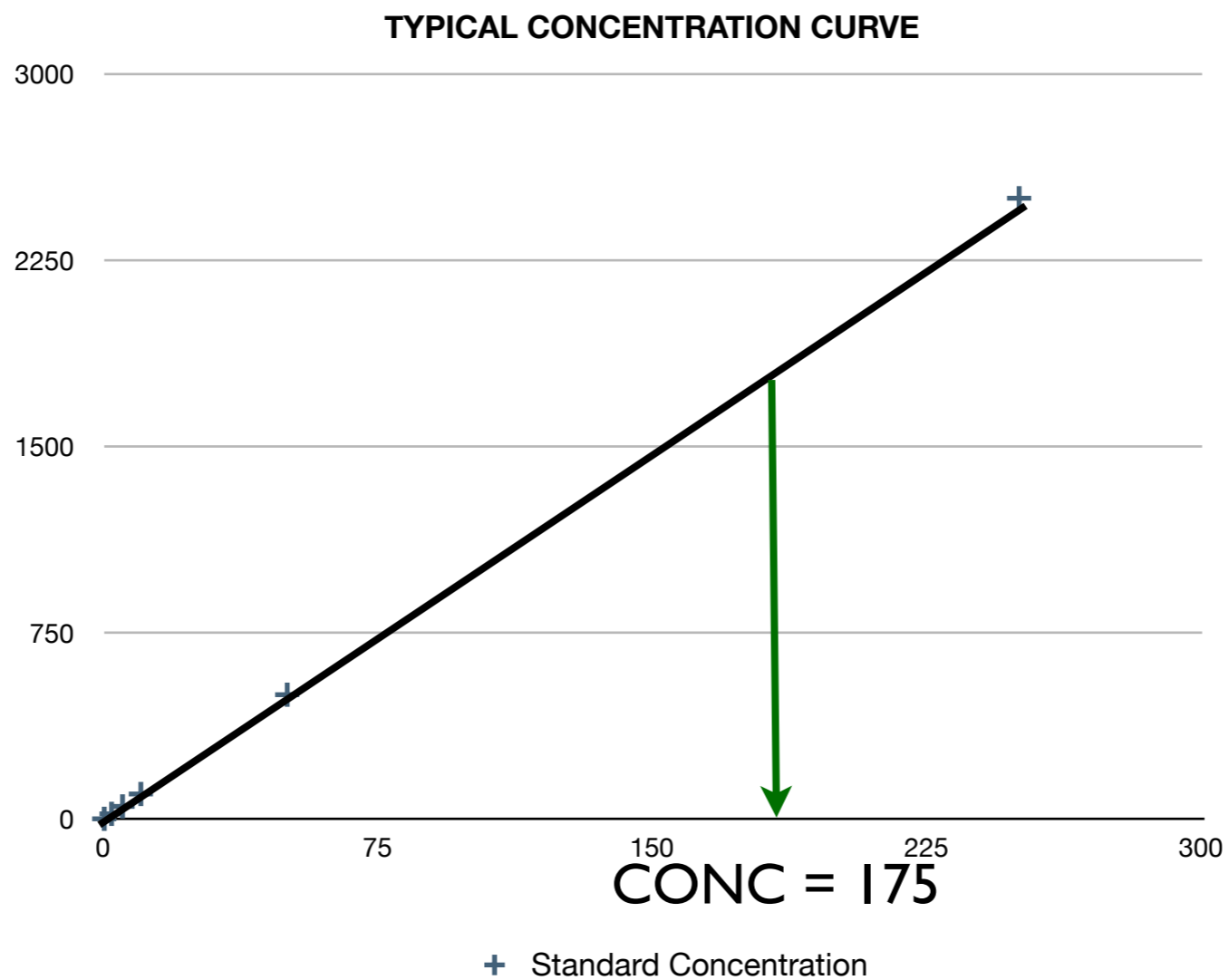
TYPICAL CONCENTRATION CURVE

SIGNAL
STRENGTH = 1750



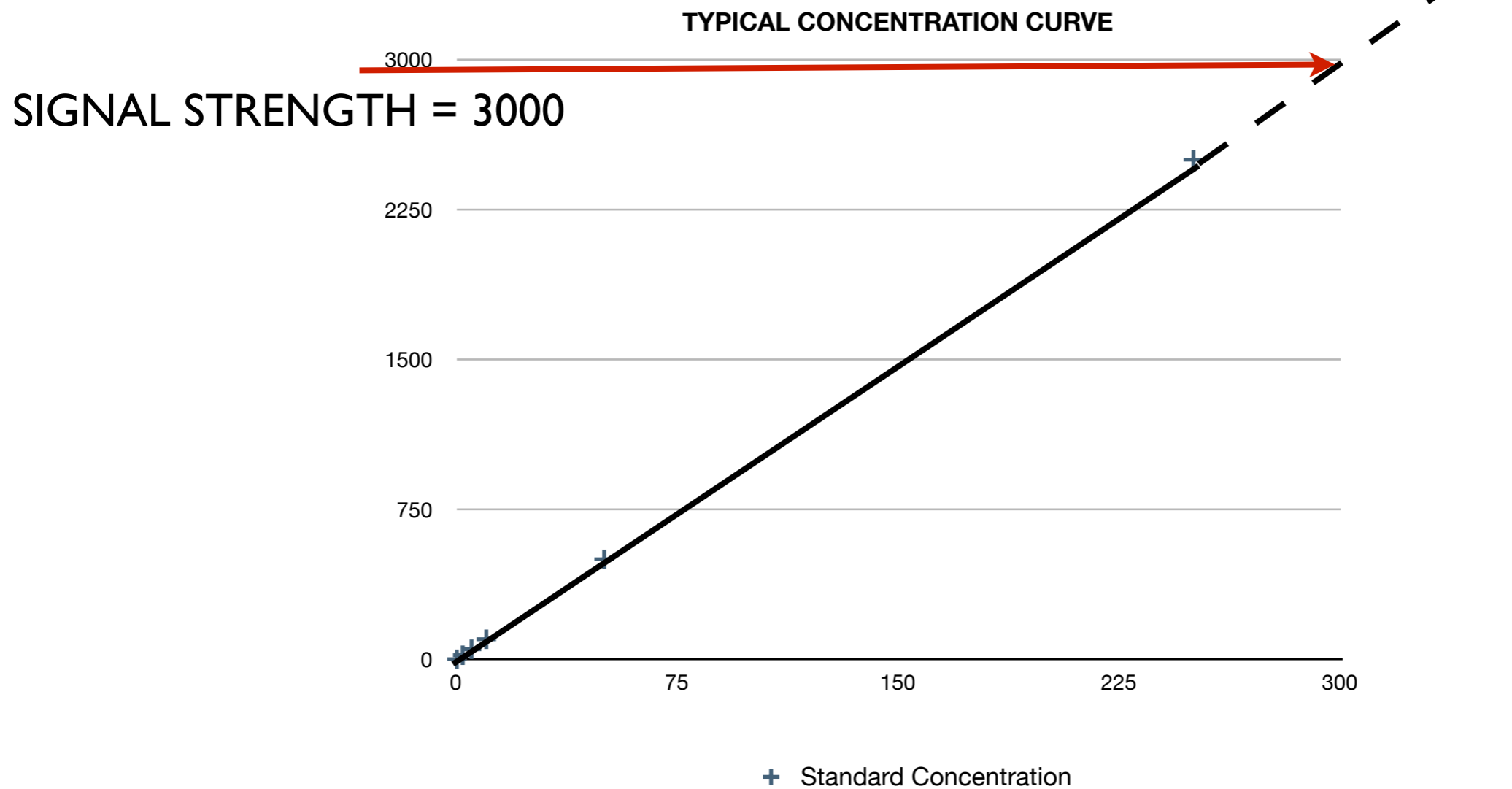
+ Standard Concentration

CALIBRATION / DILUTION

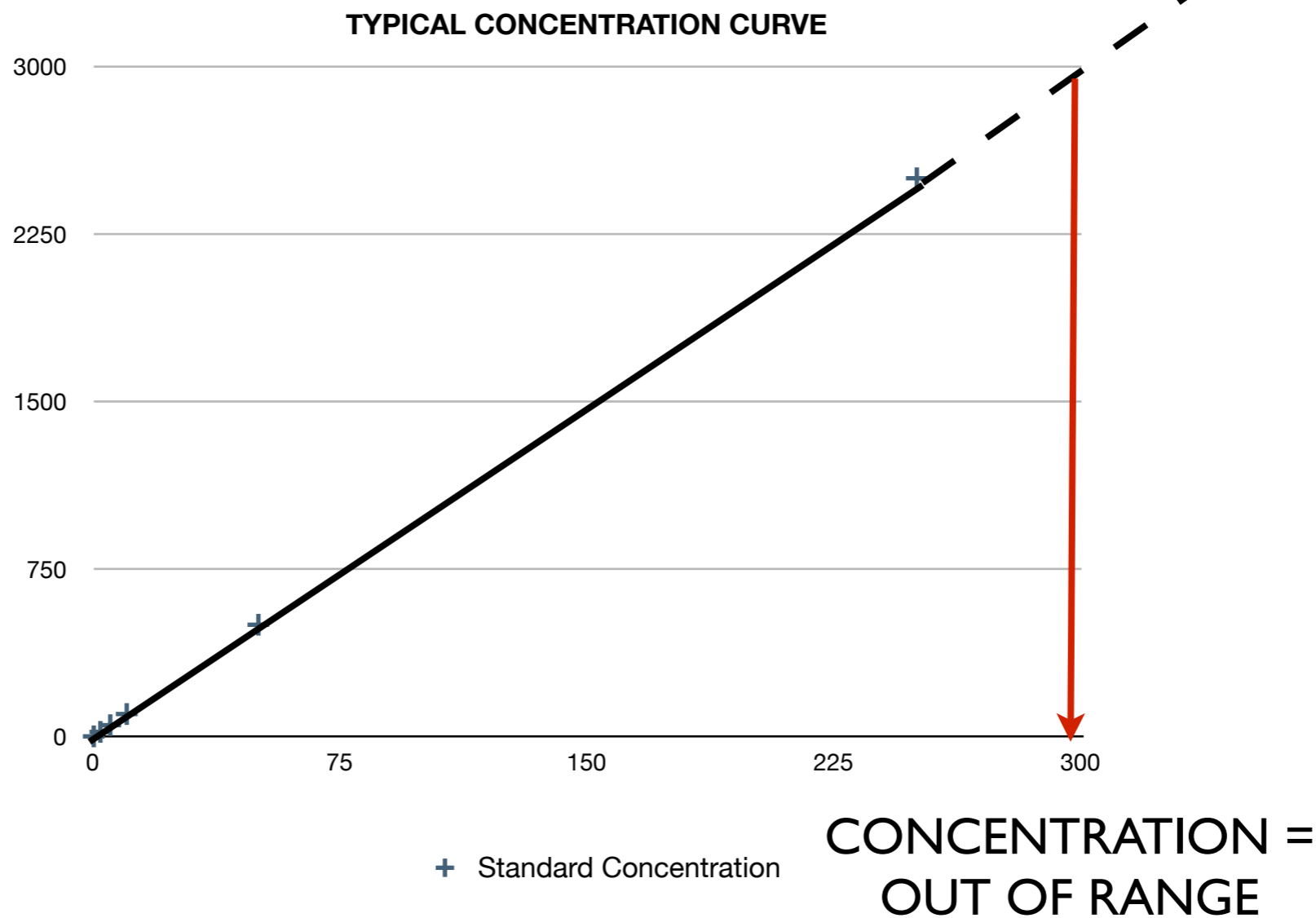




CALIBRATION / DILUTION



CALIBRATION / DILUTION



SAMPLE REQUIRES DILUTION



SAMPLE DILUTION PROTOCOL

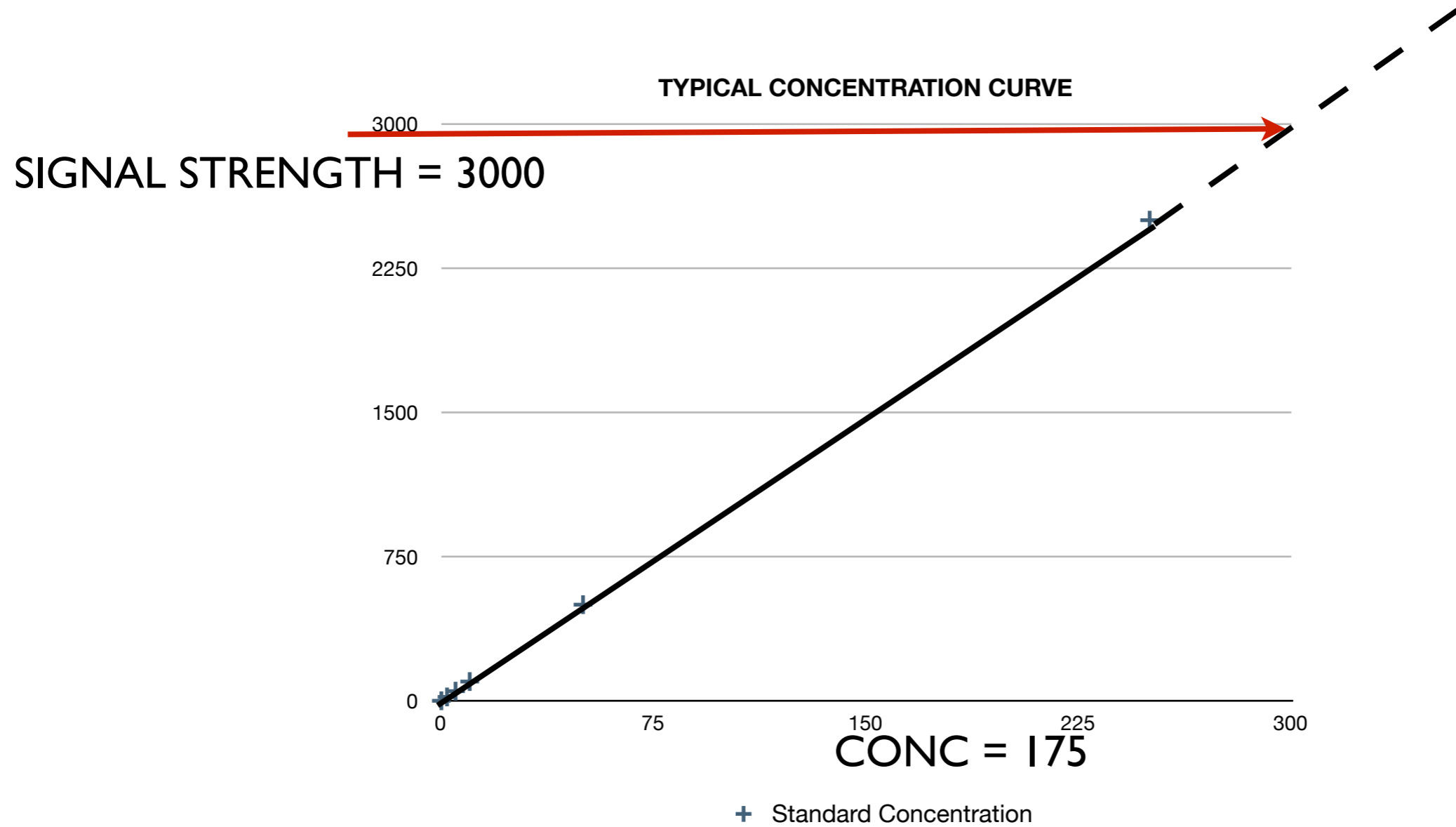
SITUATIONS MAY ARISE (PARTICULARLY WITH VOCs) WHERE DILUTION CAUSES RESULTANT RDLs TO BE ABOVE REGULATORY REPORTING LIMITS

THIS IS OK, SO LONG AS THE RDL IS STILL BELOW STANDARD

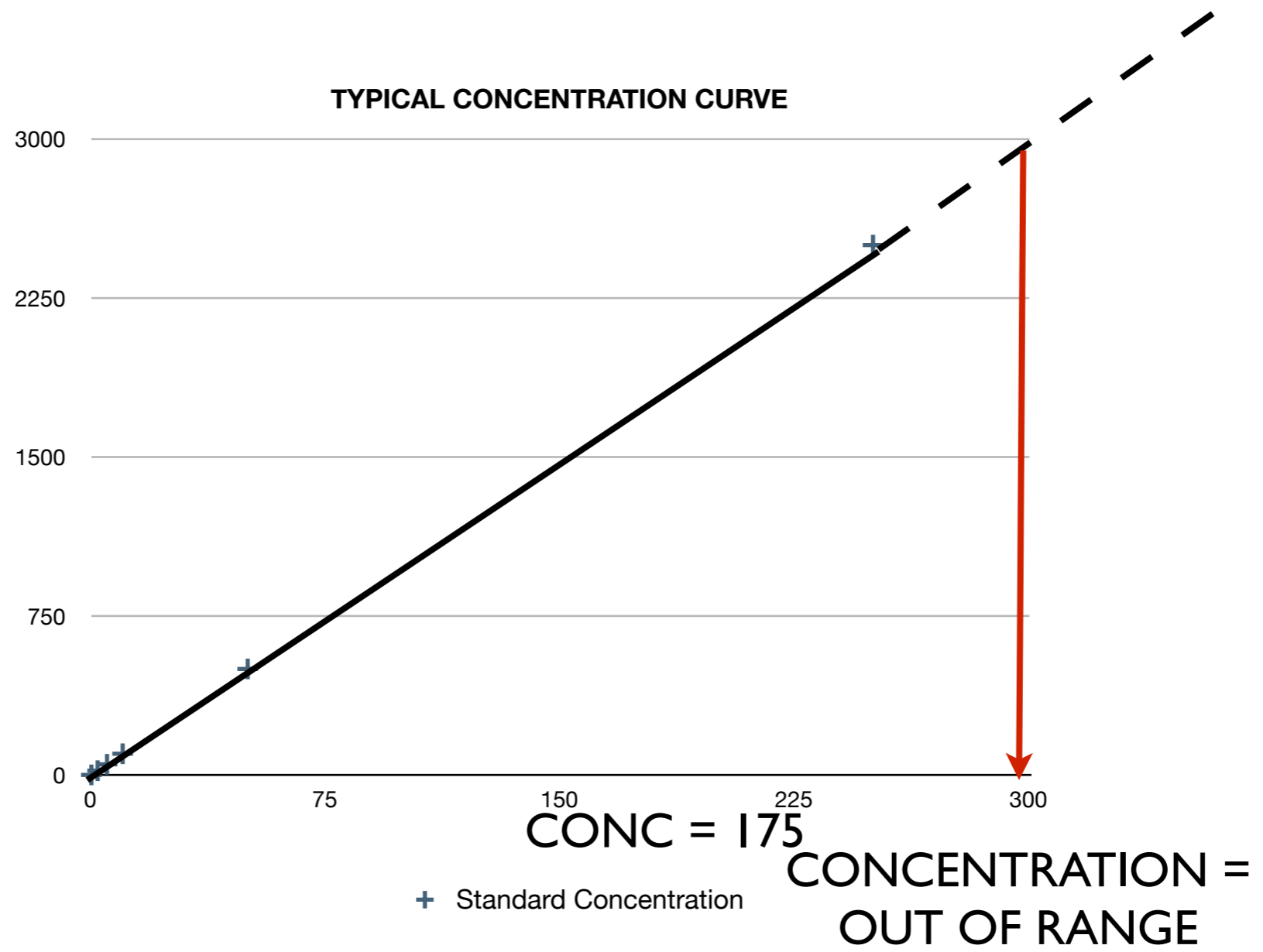
THE POST DILUTION CONCENTRATION OF THE HIGHEST REPORTED PARAMETER MUST BE ABOVE 20% OF THE HIGHEST CALIBRATION STANDARD



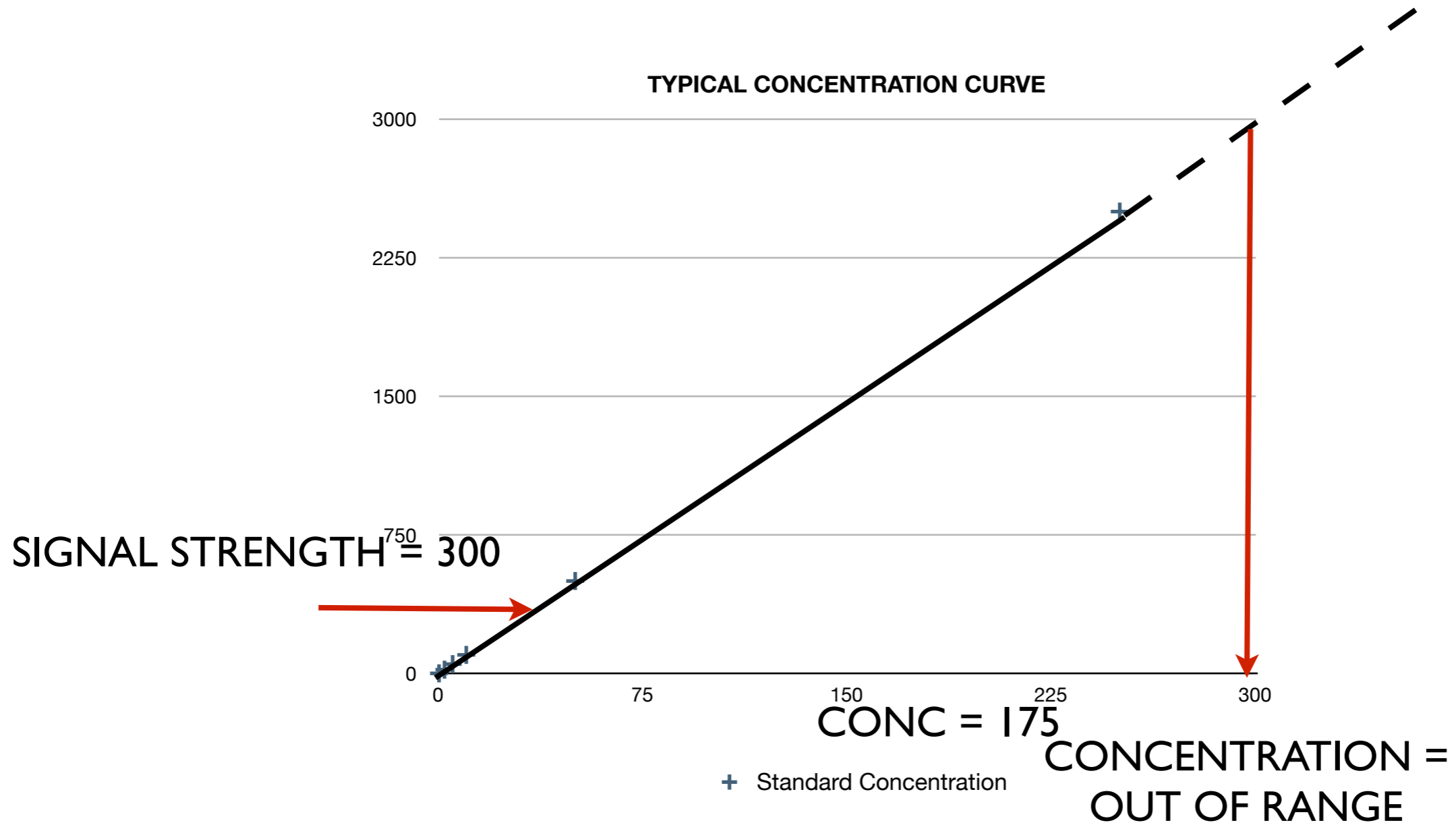
DILUTION PROTOCOL - NOT ALLOWED



DILUTION PROTOCOL - NOT ALLOWED



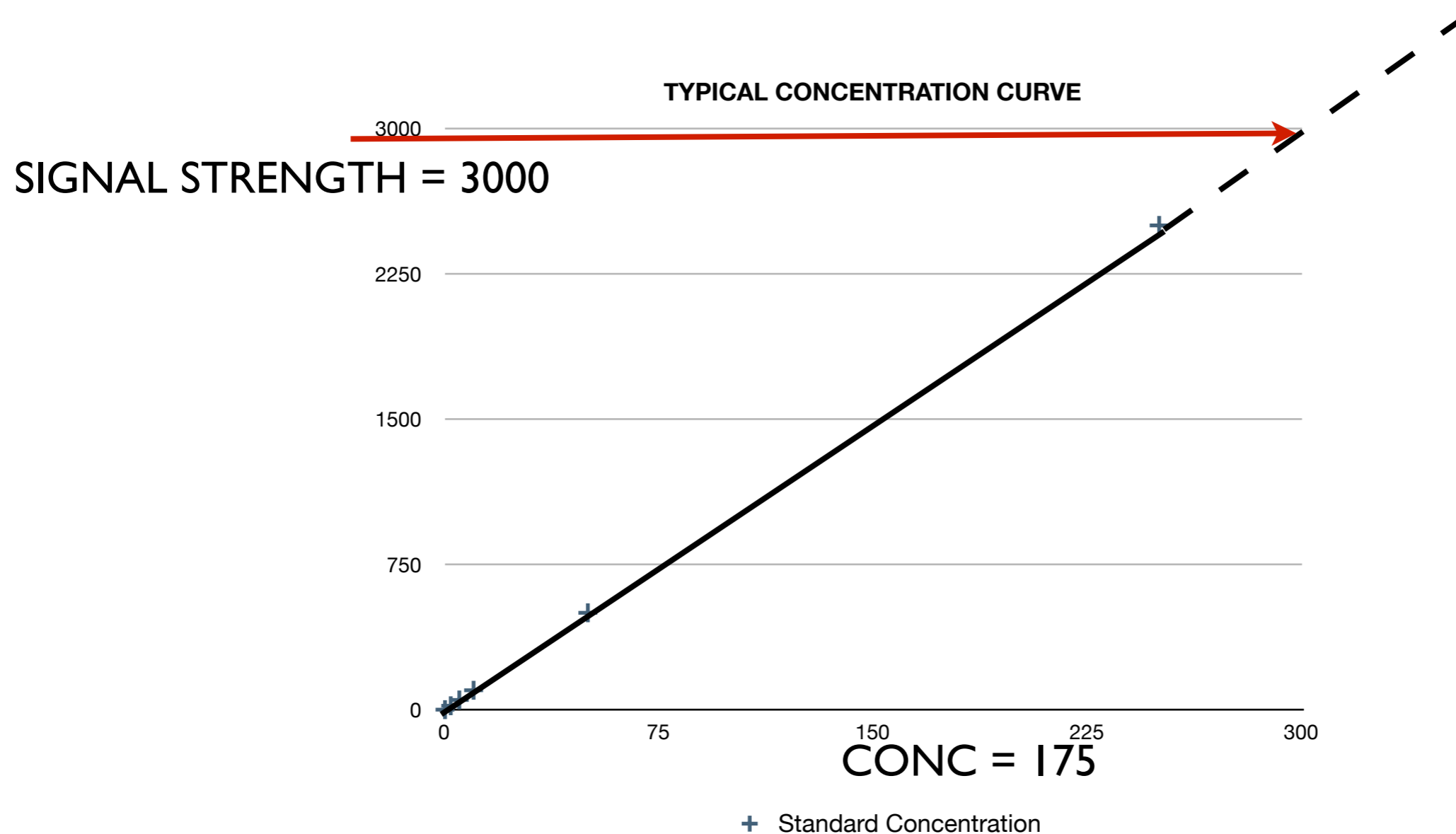
DILUTION PROTOCOL - NOT ALLOWED



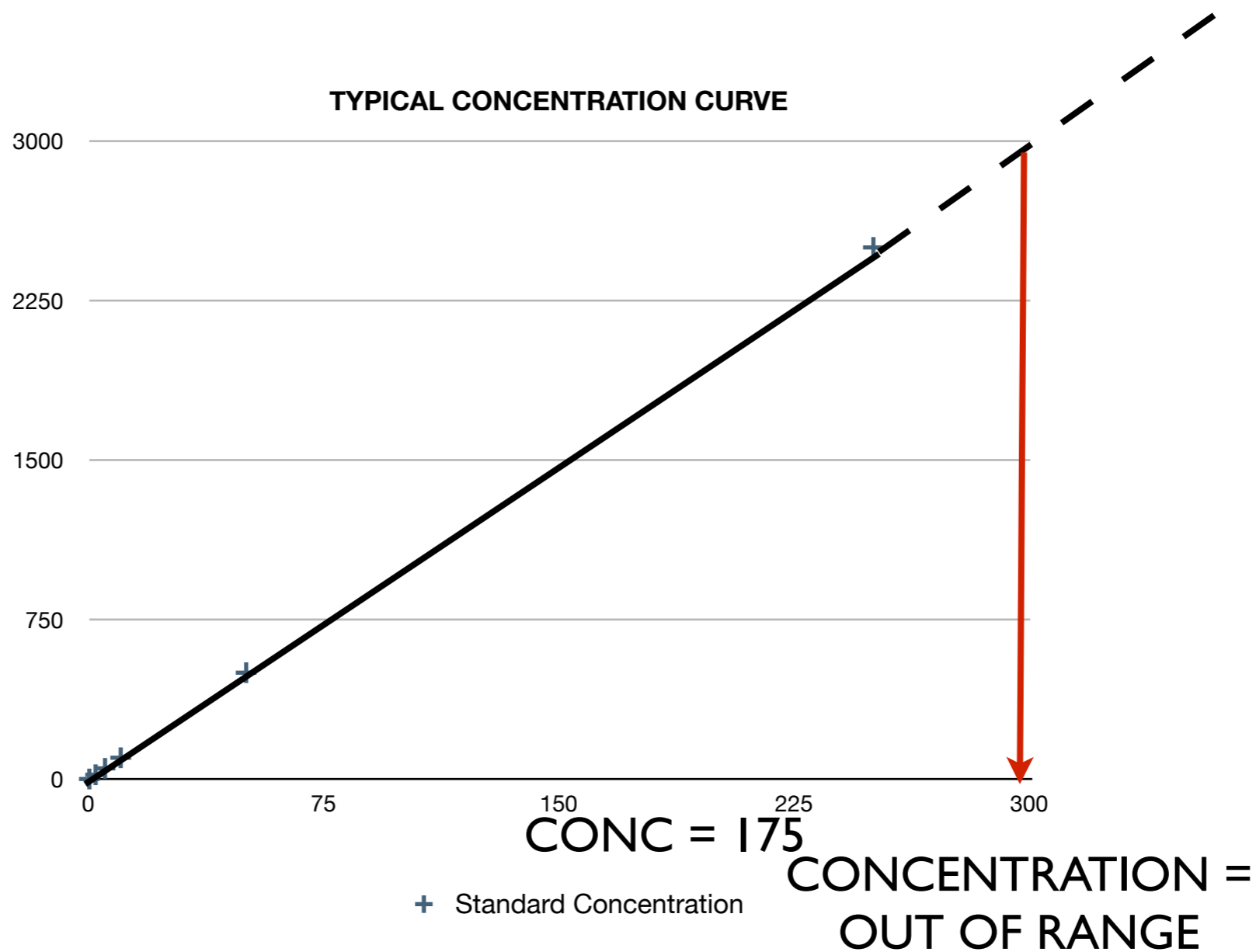
DILUTION AT 10X

300 < 20% OF 2500 - NOT ALLOWED!

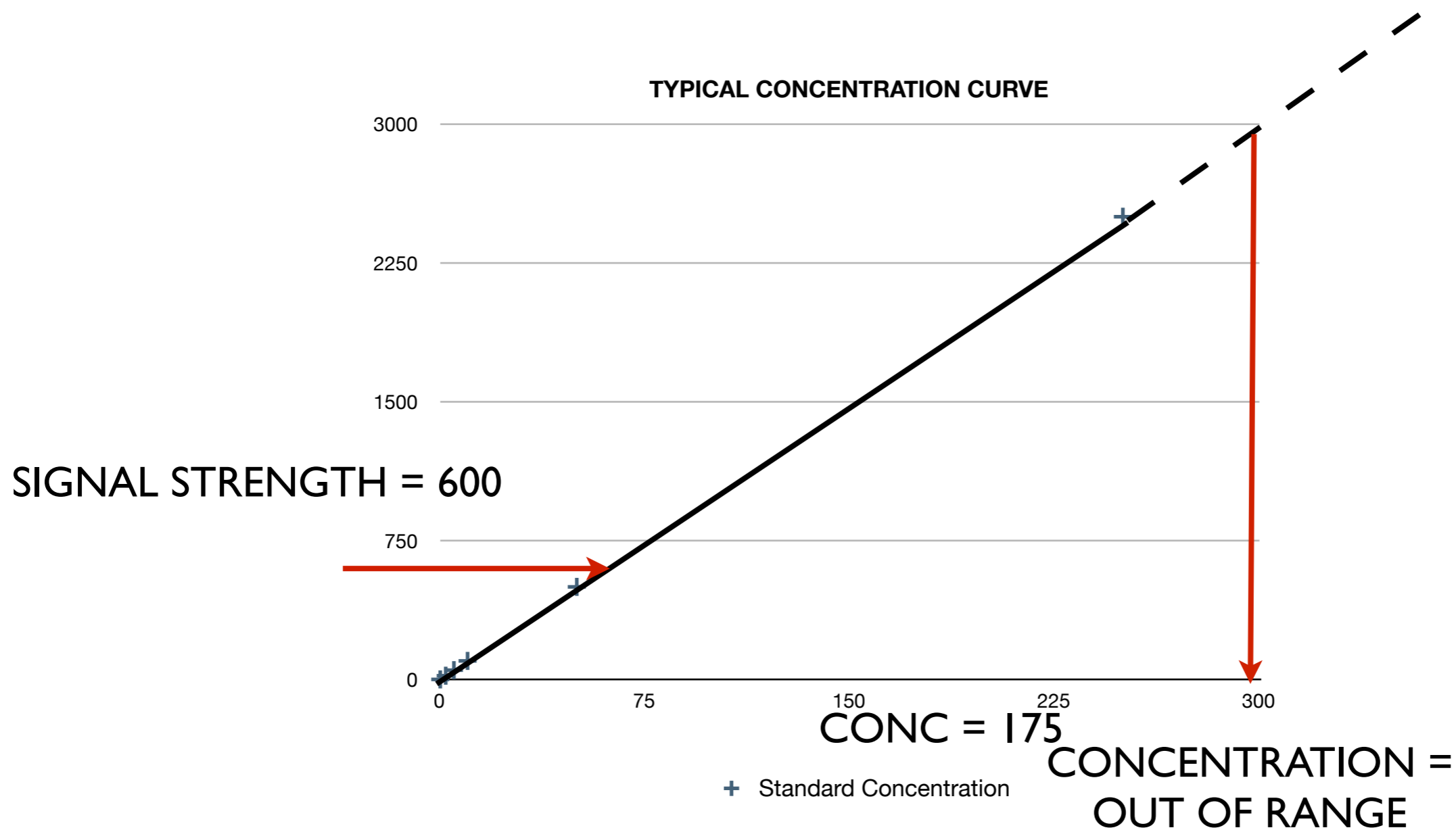
DILUTION PROTOCOL - ALLOWED



DILUTION PROTOCOL - ALLOWED



DILUTION PROTOCOL - ALLOWED



DILUTION AT 5X
600 > 20% OF 2500
DILUTION IS ALLOWED



SAMPLE DILUTION PROTOCOL

WHAT IF MY RDLs ARE NOW ABOVE STANDARD?

THE PROPOSED ANALYTICAL PROTOCOL TELLS US THAT IF IT ISN'T A CONTAMINANT OF CONCERN IDENTIFIED IN THE PHASE I SITE ASSESSMENT - DON'T WORRY ABOUT IT.

IF THE RAISED RDL AFFECTS CONTAMINANTS OF CONCERN IDENTIFIED IN THE PHASE I - BACK TO WORK IN THE LAB

DEPENDING ON THE SEVERITY OF THE CONTAMINATION, THIS MAY INVOLVE ADDITIONAL COSTS FOR AN ANALYTICAL SOLUTION TO REACH THE REQUIRED REPORTING LIMIT

IT MAY ALSO NOT BE POSSIBLE



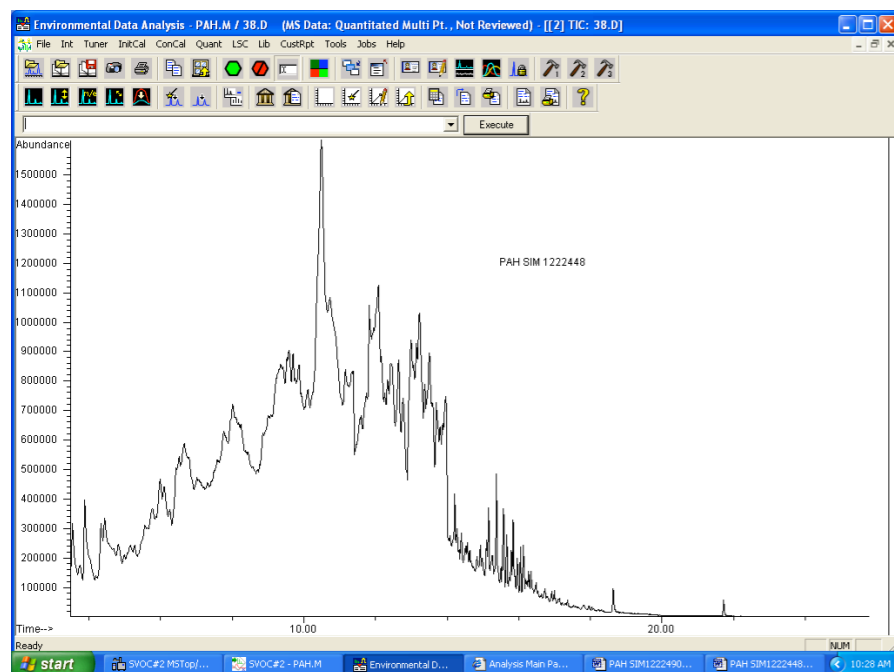


MATRIX INTERFERENCE PROTOCOL

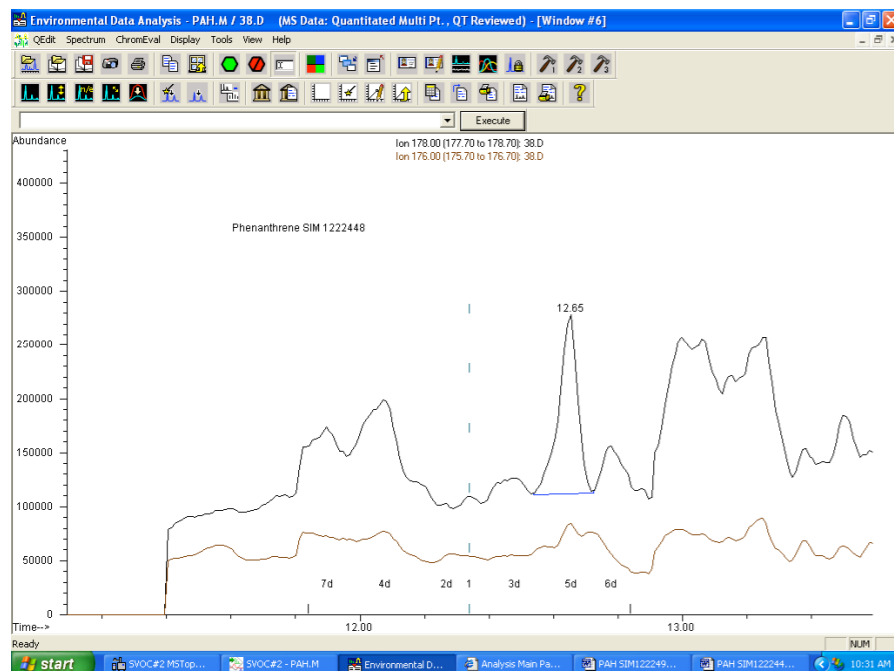
- NOT YET BUILT INTO THE ANALYTICAL PROTOCOL - BUT HAS BEEN PROPOSED
- SOMETIMES IT MAY NOT BE POSSIBLE TO REACH RLs IN THE CASE OF HIGH MATRIX INTERFERENCE
- EXAMPLES MAY BE VERY HIGH DISSOLVED SOLIDS FOR INORGANICS
- HIGH GASOLINE (LIGHT PETROLEUM HYDROCARBONS) CONTAMINATION FOR VOCS
- HIGH DIESEL CONTAMINATION FOR PAHS
- APPROXIMATELY 10,000 PPB REPRESENTS A PROBLEM



MATRIX INTERFERENCE PROTOCOL



TOTAL ION CHROMATOGRAPH
FOR A DIESEL CONTAMINATED
SAMPLE - LOOKING FOR PAHs

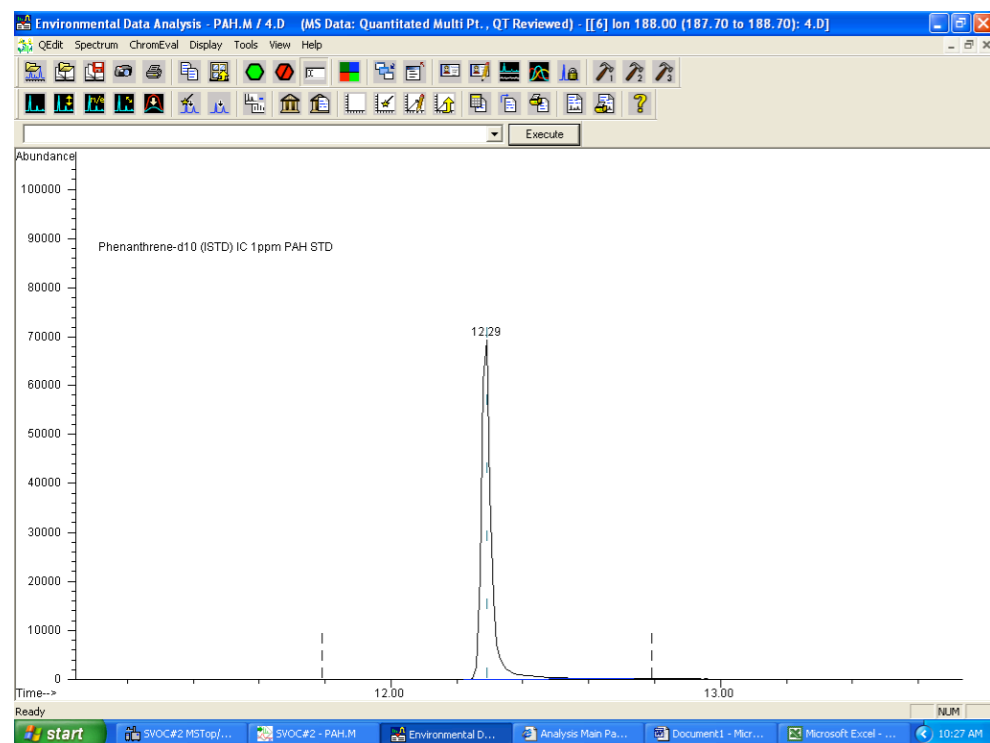


SELECTIVE ION MONITORING
“SIM” IN THE SAME SAMPLE





MATRIX INTERFERENCE PROTOCOL



SELECTIVE ION MONITORING IN
A "CLEAN" SAMPLE FOR THE
SAME SURROGATE



MINISTRY SET REPORTING LIMITS

BASED ON LABORATORY CONSENSUS - ALL LABORATORIES THAT PARTICIPATE IN THE “TAG” AGREE THAT WE CAN MEET THESE

THE REPORTING LIMITS, BY AND LARGE REPRESENT REPORTING DETECTION LIMITS, BUT CAN ALSO REPRESENT METHOD DETECTION LIMITS IN SOME CASES

REPORTING LIMITS AT THE METHOD DETECTION LIMIT REPRESENT A “COMPROMISED” VALUE THAT REFLECTS INPUT FROM THE STANDARDS BRANCH AND THE TECHNICAL ADVISORY GROUP

OVERALL, A VERY GOOD STEP FORWARD





THE SAMPLING PROTOCOL

- VOLATILE ORGANIC COMPOUNDS IN SOIL
- POLYAROMATIC HYDROCARBONS IN WATER
- OTHER CONSIDERATIONS



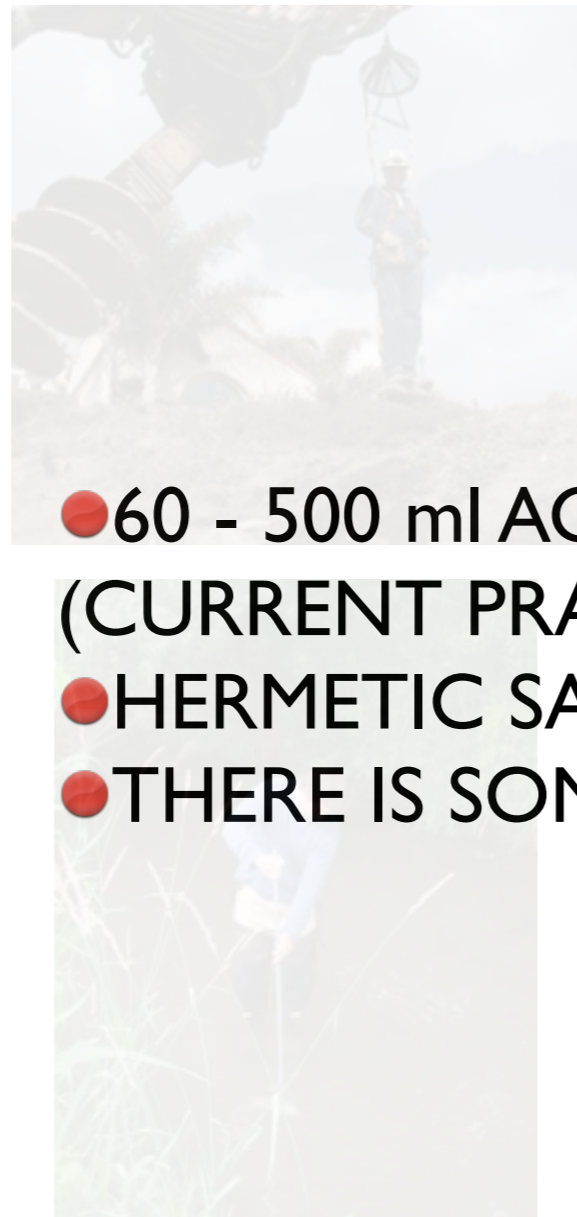
SAMPLING PROTOCOL



- OVERALL A LARGER EMPHASIS ON SAMPLE INTEGRITY
- VIOLATIONS MAY RESULT IN “QUALIFIED” DATA
- QUALIFIED DATA MAY OR MAY NOT BE ACCEPTED



ENVIRONMENTAL SAMPLING ORGANIC SOILS - PROPOSED VOCs



- 60 - 500 ml AGJ WITH TEFLON LIDS / NO VOIDS (CURRENT PRACTICE)
- HERMETIC SAMPLING DEVICES (ENCORE, EPA 5035)
- THERE IS SOME DANGER WITH THIS APPROACH



ENVIRONMENTAL SAMPLING OTHER PROPOSED (SIGNIFICANT) CHANGES



Parameter (Organic)	Sample Matrix	Type of Container and Minimum Sample Quantity	Preservative and / or Storage Conditions	Maximum Holding Time	AGAT or TAG Comments (where applicable)
Petroleum Hydrocarbons C6-C10	Groundwater	43ml VOA vials with teflon lined septum cap; (Minimum 2, recommend 3) NO HEADSPACE	Adjust to pH <2.0 by addition of HCl or NaHSO ₄ to container before sampling. Chlorinated water samples require vials containing Na ₂ S ₂ O ₃ for dechlorination	7 Days unpreserved; 14 days preserved	AGAT Comment: Slight difference between the current protocol where the hold time is listed at 7 days solid.
Petroleum Hydrocarbons C10-C50	Groundwater	1L Amber Glass bottles with teflon lined screw caps	Refrigerate at 4 ± 2 C and store in the dark	14 days to extraction, 40 days from extraction to analysis	TAG Comment: The lack of preservative may bias results low if significant microbial populations exist within the sample. Recommend HCl



ENVIRONMENTAL SAMPLING OTHER PROPOSED (SIGNIFICANT) CHANGES



PAHS IN GROUNDWATER

- 2 X 1L AMBER GLASS BOTTLES
- ONE FILTERED FOR “DRINKING WATER” PAHs
- ONE UNFILTERED FOR OTHER PAHs
- NOT APPLICABLE TO PAHs DESTINED FOR NON-TABLE I ANALYSIS



ENVIRONMENTAL SAMPLING OTHER PROPOSED (SIGNIFICANT) CHANGES

METALS IN GROUNDWATER



- GREATER EMPHASIS ON FIELD FILTRATION
- NON-FIELD FILTERED SAMPLES MAY REQUIRE QUALIFIED RESULTS



ENVIRONMENTAL SAMPLING THE ROLE OF TEMPERATURE

- GENERALLY A GREATER CONCERN FOR ORGANICS THAN INORGANICS
- OF VERY GREAT CONCERN FOR VOC SAMPLES
- INORGANIC SOILS TO BE DRIED ANYWAY
- TEMPERATURE TRUMPS TIME TO THE LABORATORY??