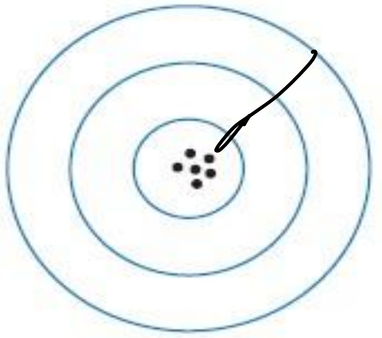
Accuracy and precision

true value نقارن مع

Accuracy is the degree of agreement between the measured value and the true value [Sample]

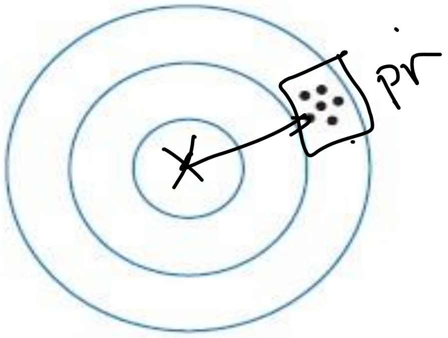
Precision is defined as the degree of agreement between replicate measurements } → Instrum

Accuracy is how close you get to the bullseye

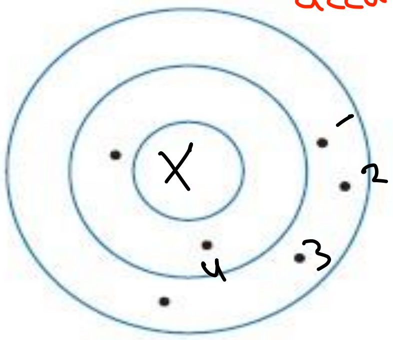


Good precision, good accuracy ✓

Precision is how close the repetitive shots are to one another



Good precision, poor accuracy



Poor precision, poor accuracy

* ليس بالضرورة اذا كانت قياسات precise تكون accurate ولكن اغلب الاوقات ازا كانت accurate تكون precise

* السبب deviation بين duplicate measurment او deviate عن true value

وجود errors

Errors: there are two types of errors that may affect the accuracy or precision of a method

Systematic error → Random

↳ can be determine, fixed, calibration, analyst خطأ / خطأ بالتحضير / storage } → I can fix error.

1. Determinate or systematic errors

- Non-random, determinable & can be either avoided or corrected
- May be constant or variable but can be corrected

Some common determinate or systematic errors:

a. Instrumental Errors: Equipment & uncalibrated glassware
b. Operative Errors: personal errors, corrected by increasing experience
c. Methodical errors: co-precipitation of impurities can be corrected by a blank & the analysis of reference samples also helps against method errors

Errors: there are two types of errors that may affect the accuracy or precision of a method

2. Indeterminate errors [random

- random errors; cannot be avoided, experimental uncertainty that occurs in any measurement

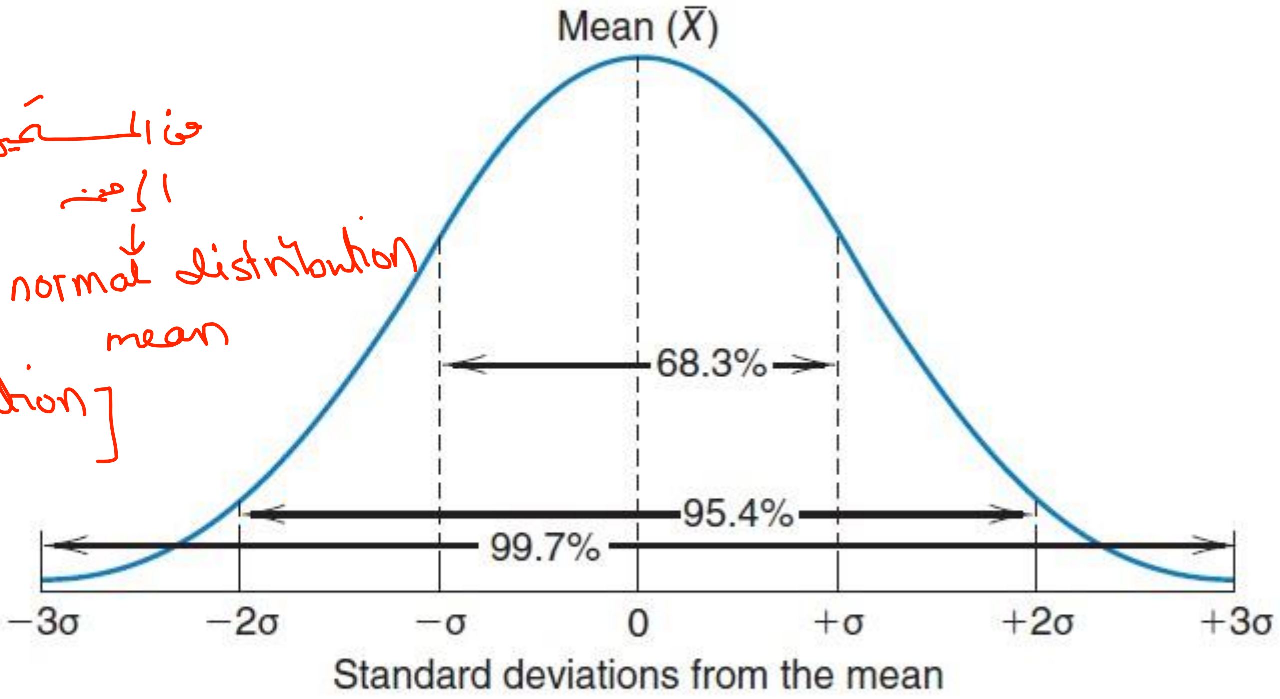
-Often called accidental errors. These errors are revealed by small differences in successive measurements made by the same analyst under virtually identical conditions, and they cannot be predicted or estimated

- These accidental error

فـ المستحيل في التجارب بيعطي نفس
الرقم

normal distribution م لعدد لاساسي يكون قريب من
mean

[Random error distribution]



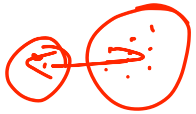
Ways of expressing precision

The estimated standard deviation of a finite set of experimental data (generally $N < 30$)

$$S = \sqrt{\frac{\Sigma(x_i-\bar{x})^2}{N-1}} \rightarrow \frac{\Sigma x_i}{n}$$

Where s: standard deviation
x_i : individual measurement
$\bar{x}$:mean of the measurements
N: number of measurements

Standard deviation of the mean = $s/\sqrt{N}$ = standard error



Relative standard deviation (RSD) = $(s/\bar{x})*100\%$ = $\underbrace{\text{coefficient of variation}}$

Variance= s^2

Example

The following replicate weightings were obtained: 29.8, 30.2, 28.6, and 29.7 mg. Calculate the standard deviation of the individual values and the standard deviation of the mean. Express these as absolute (units of the measurement) and relative (% of the measurement) values

$\left((29.8-\square)^2+(30.2-\square)^2+(28.6$

$+(29.7-\square)^2$

$=\frac{1.41}{3}$

$=\boxed{\square}$

$\sqrt{\ }$ Ans

① Find mean

x_i	X-$\bar{x}$	(X-$\bar{x}$)^2
29.8	0.2	0.04
30.2	0.6	0.36
28.6	1.0	1.00
29.7	0.1	0.01
$\Sigma = \frac{118.3}{4} = \square$		$\Sigma = 1.41$

①

$\bar{x}$ = 118.3/4.0 = 29.6 mg

$s=\sqrt{\frac{1.41}{4-1}} = 0.686\ mg$

RSD $=\frac{0.686}{29.6} * 100.0\% = 2.32\%$

Standard deviation of the mean = s/$\sqrt{N}$ = $\frac{0.686}{2}$ = 0.343

Ways of expressing precision

The precision of any analytical method can be improved by increasing the no. of observation so ($\pm S$) becomes smaller & it approaches 0 if the no. of readings x_i approaches ∞

Mean: arithmetic mean $\bar{X}$ Avg

x ما الفرق بين mean ← average

medium ← القيمة التي بالوسط بعد ترتيبها تنازلي او تصاعدي

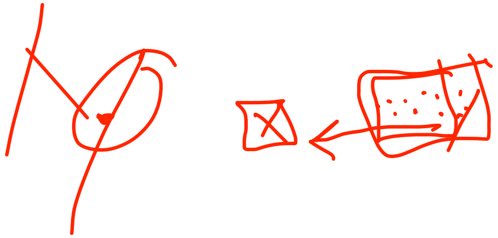
في بعض الاحيان نفضل medium لانه احيانا يكون في قياس عالي جداً او [illegible] وقد يؤثر بشكل كبير على قراءة mean , لكن لا يؤثر على medium

$$\bar{X} = \frac{\overset{\text{مجموعهم}}{\Sigma(x_i)}}{\underset{\text{عددهم}}{N}}$$

, where $\Sigma(x_i)$ = sum of reading
N = No. of reading

Median: is the middle result when replicate data are arranged in order

Range: higher & lower limits (highest – lowest) reading



Ways of expressing precision

Example: The following reading were obtained for the analysis of the main active ingredient of a pharmaceutical preparation: 127.2, 127.1, 128.4, 128.4, 128.8, 127.6, calculate:

a. The mean? Mean = 127.9

$\frac{\Sigma \text{ الجمع}}{6}$

~~128.2~~ ~~128.4~~ $\boxed{\frac{128.4 + 127.6}{2}}$ ~~127.2~~

b. The median? Median = (127.6 + 128.4) / 2 = 128.0

~~127.1~~ ~~127.2~~ 127.6 128.4 ~~128.4~~ ~~128.8~~

take avg.

c. The range? (127.1-128.8)

اقل قيمة . اعلى قيمة

Note: Median:

- ✓For an odd number of data points, the median can be evaluated directly
- ✓For an even number, the mean of the middle pair is used

Precision: repeatability and reproducibility

Repeatability: expresses the precision obtained under the same operating conditions over a short interval of time

- نفس analyst ونفس Instrument ونفس analyte
نغير التجربة اكثر من مرة لاكثر من يوم
repeatability

Reproducibility: expresses the precision between laboratories

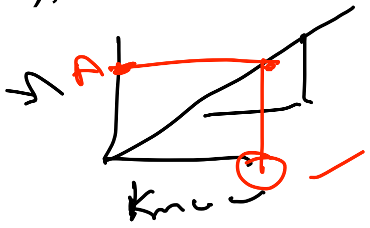
نعطي نفس الطريقة للاب آخر وموظف اخر
اذا كانت نفس القراءات السابقة نوصف
الطريقة انها Reproducibility

Precision	[LPSF/AC04] Added (μg.mL^{-1})	[LPSF/AC04] Found ± S.D. (μg.mL^{-1})
Inter-day		
Same analyst (days 1 and 2)	0.5	0.494 ± 0.02
	1.0	1.011 ± 0.02
	1.5	1.496 ± 0.02
Inter-day		
Analysts 1 and 2 (days 1 and 2)	0.5	0.498 ± 0.02
	1.0	1.008 ± 0.05
	1.5	1.529 ± 0.07
Intra-day		
Different tests (same analyst; day 1)	0.5	0.494 ± 0.02
	1.0	1.019 ± 0.04
	1.5	1.534 ± 0.06

Accuracy

error
Tm

Accuracy of a method is the closeness of the obtained value to the true value for the sample. The accuracy of the method is determined by the recovery of a known amount of analyte samples. Briefly, to determine the accuracy of the proposed method, different levels of drug concentrations should be used: lower concentration (0.5 μM mL^{-1}), intermediate concentration (1.0 μM mL^{-1}) and higher concentration (1.5 μM mL^{-1})



① نحضر ٣ عينات → L, M, h

② نعمل Calibration curve

③ نجيب Absorbance

④ من معادلة نحسب unknown conc

Added	Found (±S.D.)[a]	Mean recovery % (±S.D.)[a]
0.5 Low	0.505 ± 0.010	101.06 ± 2.09
1.0 medium	1.012 ± 0.028	101.26 ± 2.87
1.5 high	1.510 ± 0.020	100.71 ± 1.35

$\frac{\text{Found}}{\text{expected}} \times 100\% =$ Recovary نقيس ⑤

100% → actual = expected
>100 → actual > expected
<100 → " < "

Ways of expressing accuracy

$\square - x_t$

Absolute Error: $E = \boxed{x_i} - \boxed{x_t}$

The difference between the true value and the measured value, with regard to the sign. Where x_i is the measurement of a quantity, x_t is the true value or

accepted value of the quantity

Trial	Value
Trial1	2.51 g – 2.62
Trial2	2.58 g – 2.62
Trial3	2.65 g – 2.62

3

If the true value for copper mass in an experiment was 2.62 g Absolute error in trial1 = $\boxed{2.51} - \boxed{2.62} = -0.11$ g

Ar.

Mean Error: The mean error can also be calculated by taking the average difference, with regard to sign, of the *individual* test results from the true value

$$= \left(\frac{\text{(absolute error of trial 1 + absolute error of trial 2 + absolute error of trial 3)}}{\boxed{3}}\right) =$$

value	absolut
2.51	2.51 - 2.62
2.58	2.58 - 2.62
2.65	

Σ

(– 0.11+ – 0.04 +0.03)/3.0 = – 0.040 g

Ways of expressing accuracy

Relative error: the absolute or mean error expressed as a percentage of the true value

The relative error in trial 1 = (– 0.11/2.62)*100.0% = – 4.2%

$$E_r = \frac{\overbrace{x_i - x_t}^{\text{absolute error}}}{x_t} \times 100\%$$

$\cancel{4.2} + x = 100$ 95.8 ✓

-4.2

95.2

Relative accuracy

Relative Accuracy: is the measured value or mean expressed as a percentage of the true value

$$\text{Relative accuracy} = \frac{\text{Measured value}}{\text{True value}} \times 100\%$$

Trial	Value
Trial1	2.51 g
Trial2	2.58 g
Trial3	2.65 g

The relative accuracy of trial2 = (2.58/2.62)*100.0% = 98.5%

$$\text{Relative error trial 2} = \frac{2.58 - 2.62}{2.62} \times 100\%$$

$$= -1.5\%$$

$$\frac{2.58}{2.62} \times 100\%$$

98.5%

Correlation
Linear
يهمنا عند عمله تجربه يكون لدينا
حتى استطيع استخدام الخط المستقيم ومعادلة
لايجاد التركيز.

Linearity

× لا يمكننا استخدام معادلة الخط
المستقيم اذا لم تكن العلاقة
Linear.

A linearity study verifies that the response is linearly proportional to the analyte concentration in the concentration range of sample solutions. The study should be performed using standard solutions at five concentration levels, in the range of 50 to 150% of the target analyte concentration. Five concentration levels should allow detection of curvature on the calibration curve. Each standard should be measured at least three times

لازم يكون التركيز اقل او اعلى من التركيز المحتمل

$r^2 \geq$ ٠.٩٩٨

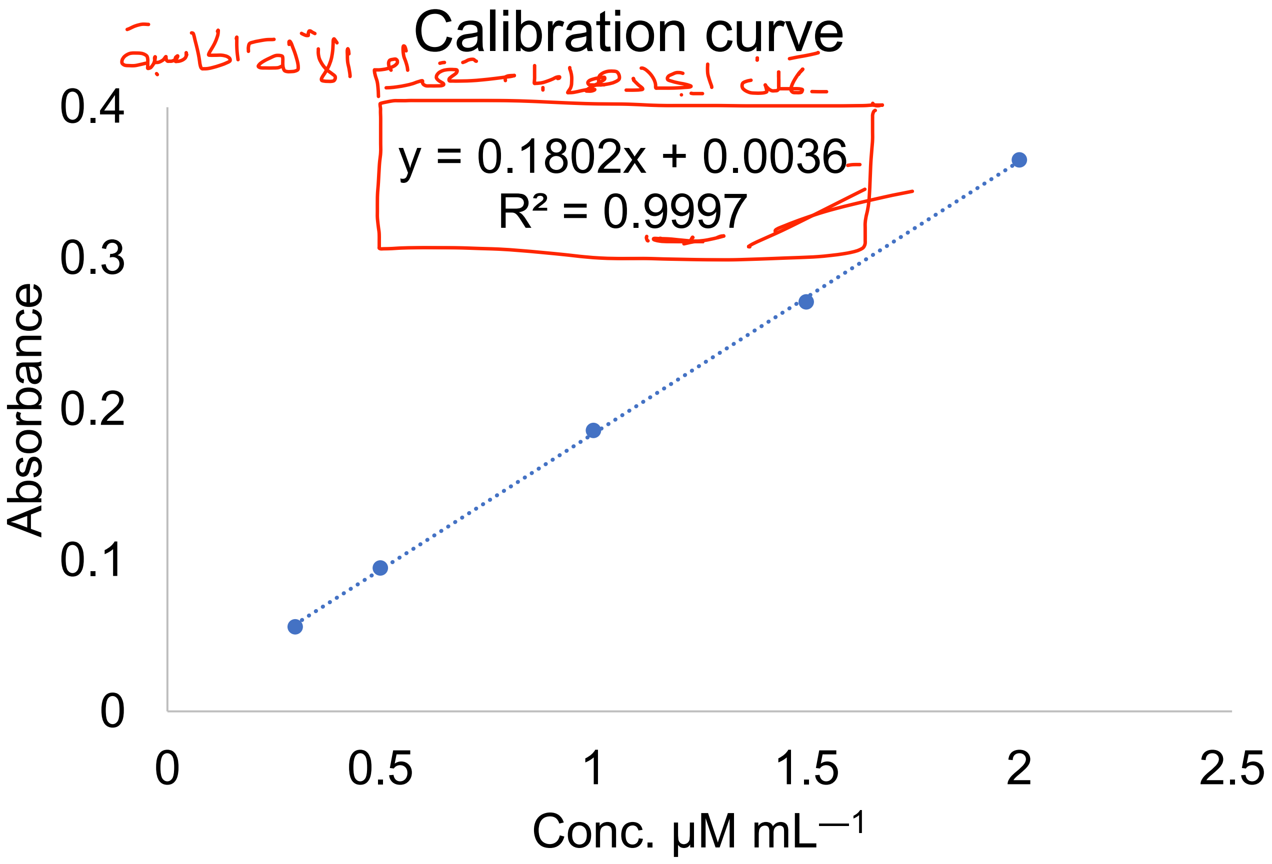
[تعلم ايجاد regression على الآلة الحاسبة] (*)

Linearity data are often judged from the coefficient of determination (r^2). An r^2 value of > 0.998 is considered as evidence of acceptable fit of the data to the regression line. You should always do a visual inspection of the calibration curve. The linearity will often deviate somewhat at high and low values

Linearity

Conc. (μg/mL)	Mean absorbance (±SD)
0.3 x	y 0.056 ± 0.002
0.5	0.095 ± 0.004
1	0.186 ± 0.007
1.5	0.271 ± 0.004
2	0.365 ± 0.007

لازم يكون عنا
at least 5 points
you get the point (x,y)

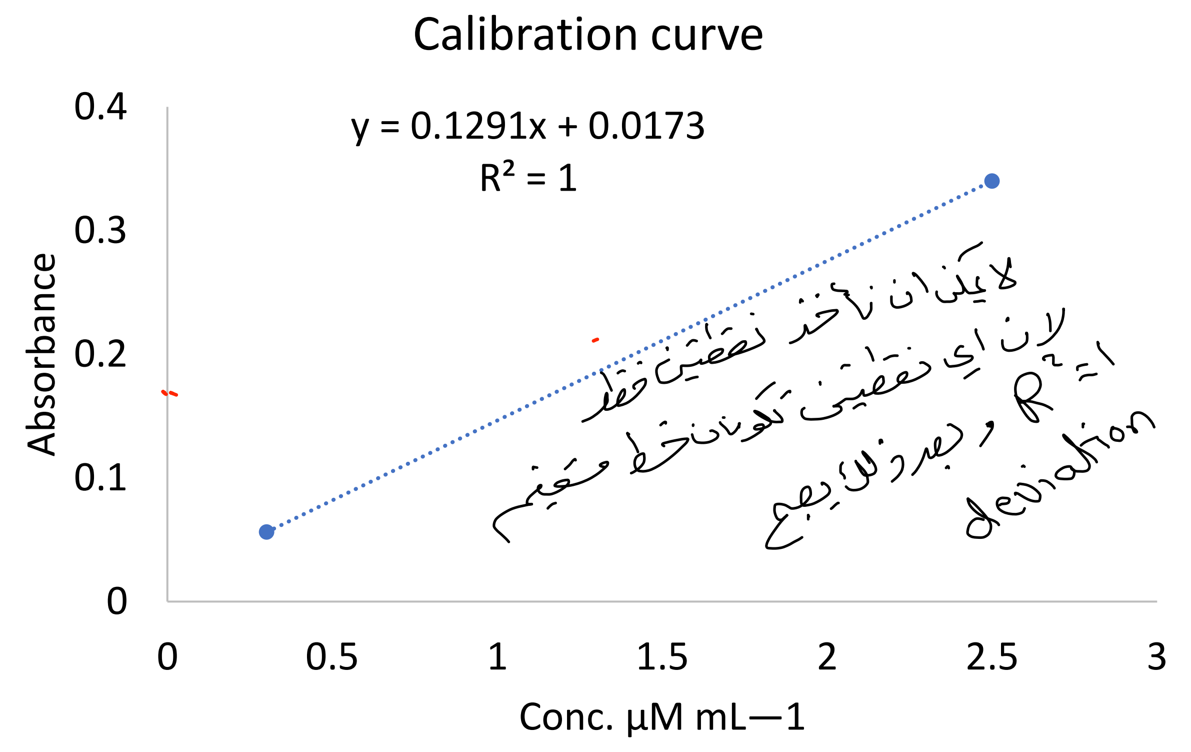


ممكن ايجادهما باستخدام الآلة الحاسبة

* ملاحظة إذا لم تتمكن من إيجاد الفيديو المقترح لتعلم إيجاد المعادلة الخطية و r^2 ، راسلني → @safaaalsalman Telegram

ابحث Youtub or + Regression and Correlation - Casio/fx 991ms/fx 100ms → Clear Explanation

Linearity

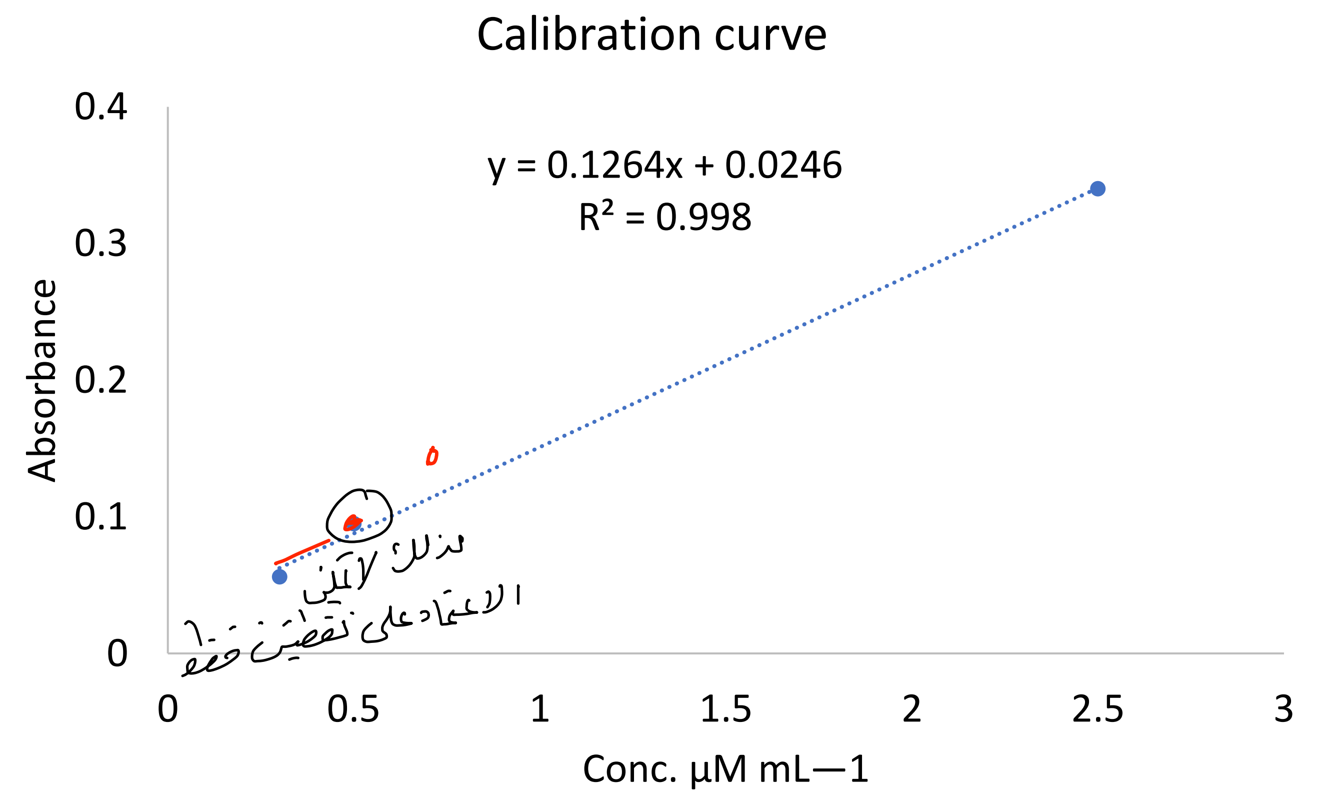


لا يمكن ان نأخذ نقطتين فقط

لان اي نقطتين تكونان خط مستقيم $R^2 = 1$

و بعد ذلك يصبح

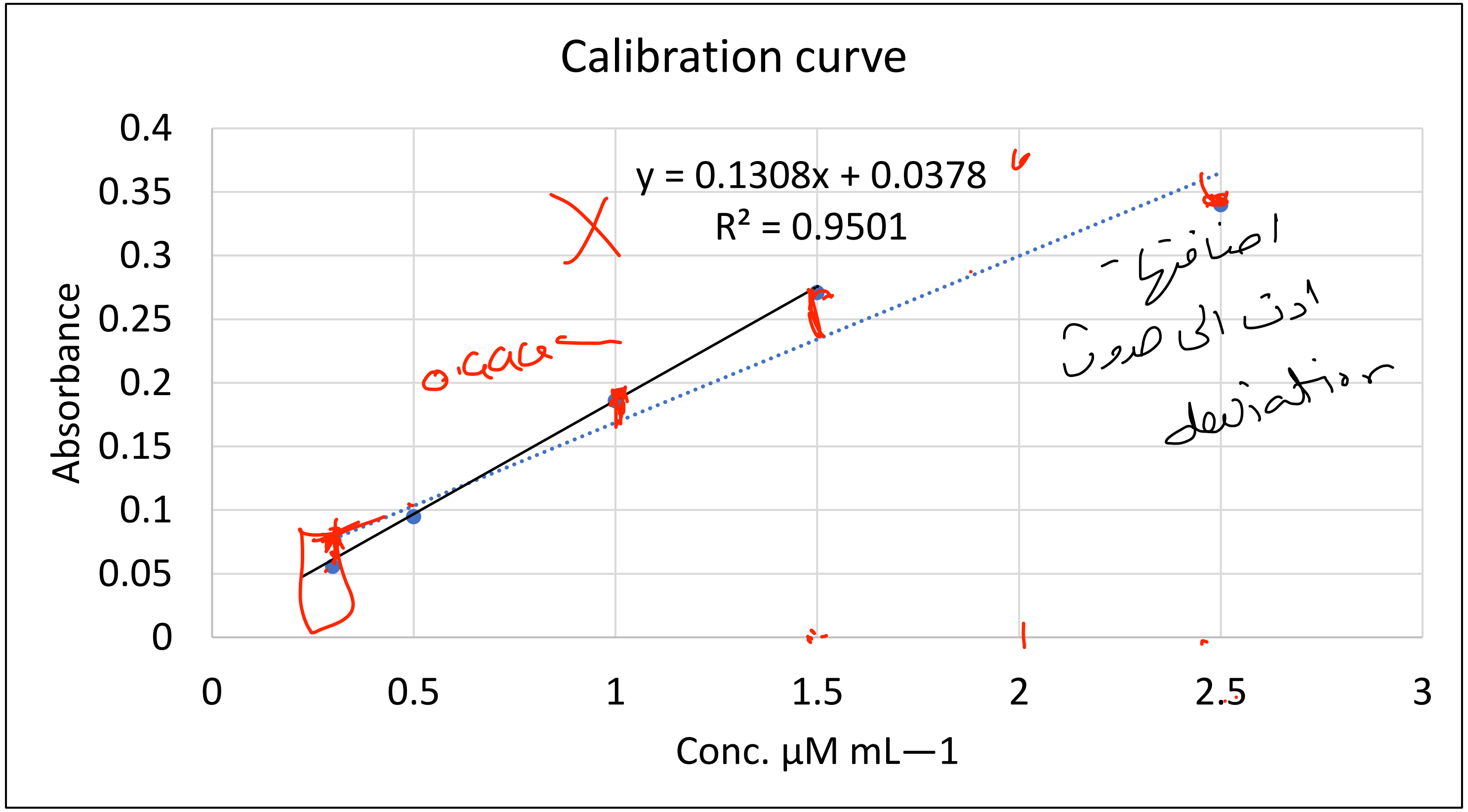
deviation



لذلك لا يمكن

الاعتماد على نقطتين فقط

Linearity



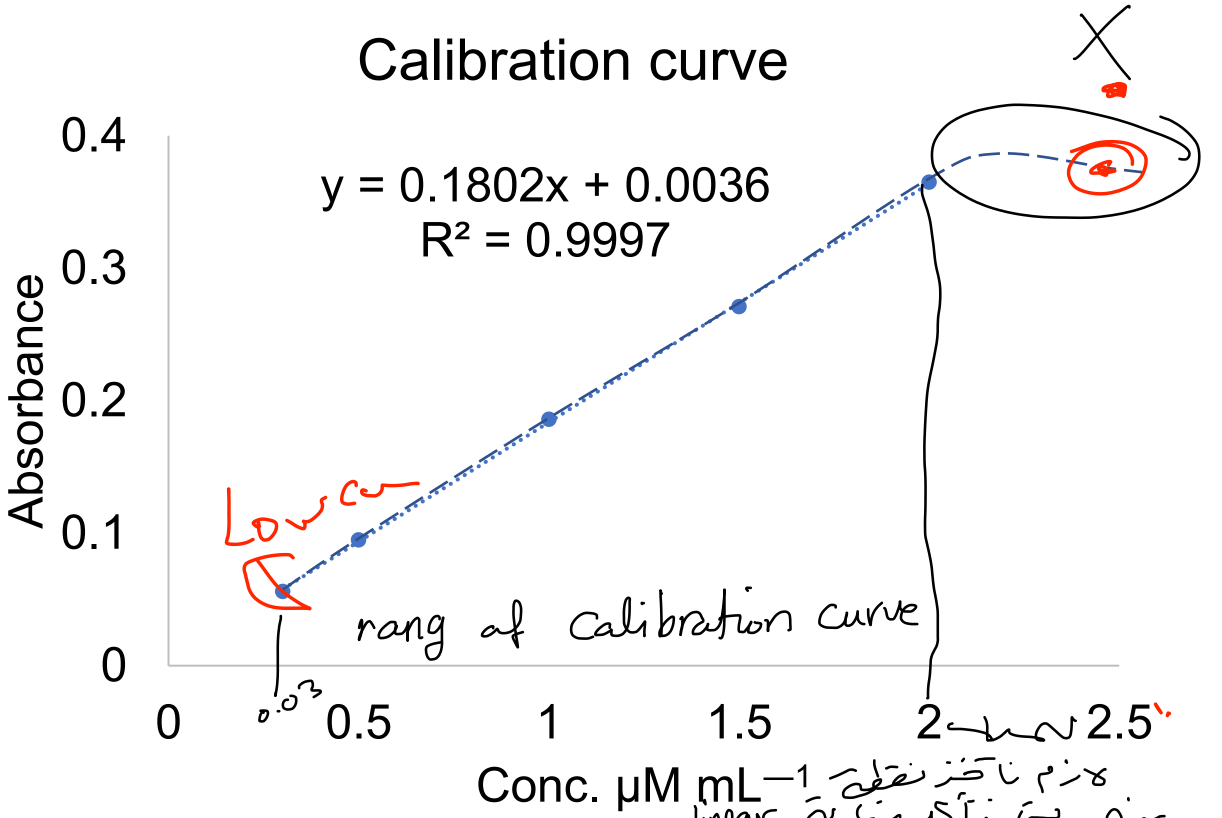
كل ما اخذنا
Rang standard
اعلى كل ما تحرف
في deviation
يصير وما linear
line يحدث

طالطلاقة Calibration curve بنفس نستخدم

Linear.

Range

The working range of a method is the concentration range over which acceptable accuracy and precision are obtained. Usually, it also includes linearity



LOQ

لازم ناخذ نقطة

linear عشان نتأكد منها انه

Line.

Sensitivity

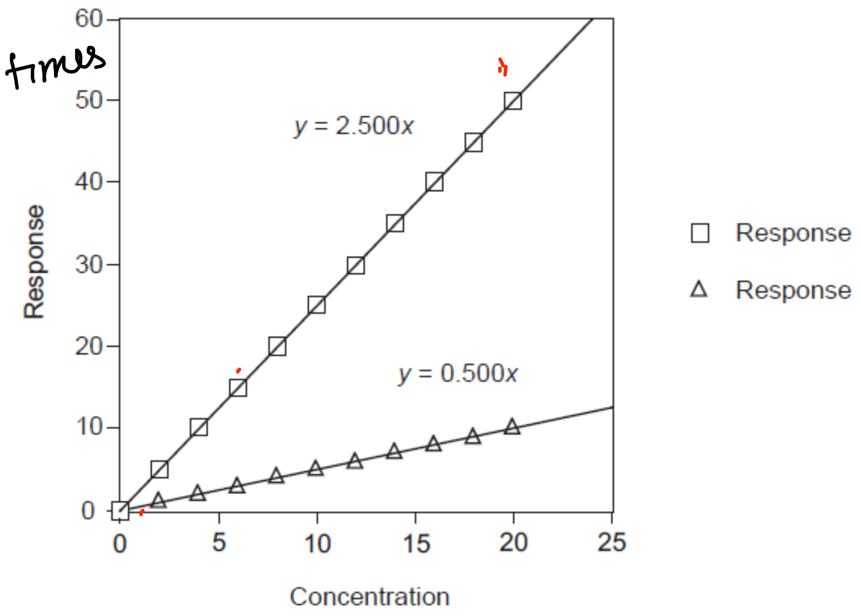
The sensitivity is determined by the slope of the calibration curve and generally reflects the ability to distinguish two different concentrations

← يساعدنا لمعرفة هل method is sensitive enogh. لحتى نتقدم بعملية التحليل.

$\frac{2.5}{0.5} = 5$ times

The method having a linear response y = 2.5x is five times more sensitive than the method exhibiting a linear response y = 0.5x

??



$\underset{sen}{\gamma} = \frac{slop}{SD}$

slope & sens. يوجد علاقة طردية ما بين

sensitivity لا تعتمد على conc. *لاحظ ذلك.

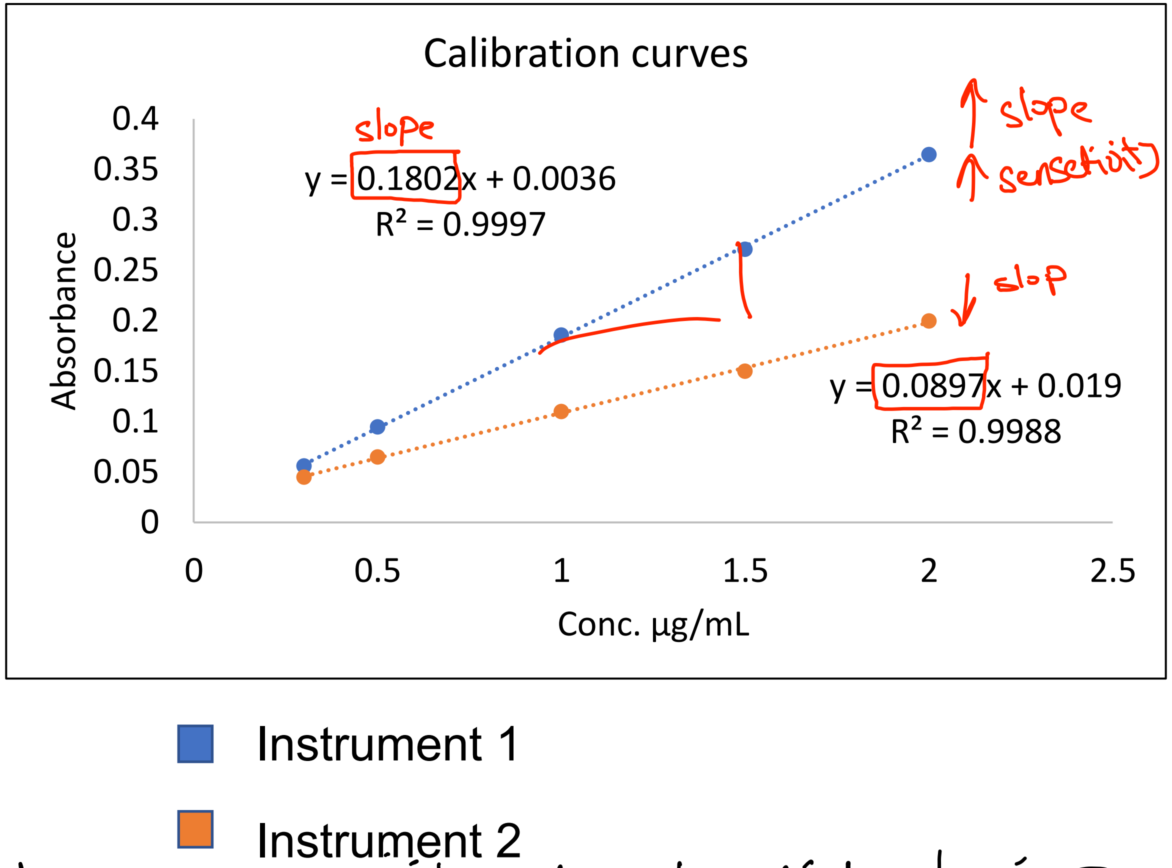
sensitivity لها علاقة مباشرة مع slope & percision (re producibility)

Sensitivity

Conc. (µg/mL)	Absorbance (instrument 1)	Absorbance (instrument 2)
0.3	0.056	0.045
0.5	0.095	0.065
1	0.186	0.11
1.5	0.271	0.15
2	0.365	0.2

0.2 µg/mL 0.039 0.02

بما ان فرق القراءات اكبر
يعني جهاز بحس ب absorption
بطريقة اعلى
more sensetivity



نستطيع التمييز بين التراكيز افضل باستخدام Instrument 1

Instrument can sense smaller conc. / وتكون respose اعلى ما يمكن.

ادني تركيز ممكن اوصل بـ measurment:

Limit of detection

Limit of detection (LOD): is the lowest concentration level that can be determined to be statistically different from a blank

detect

There are numerous ways that detection limits have been defined, the ICH definition:

سؤال:- ماهو اقل تركيز ممكن الجهاز

يقرأه ← LOD.

$$LOD = 3.3\frac{SD}{S}$$

SD.

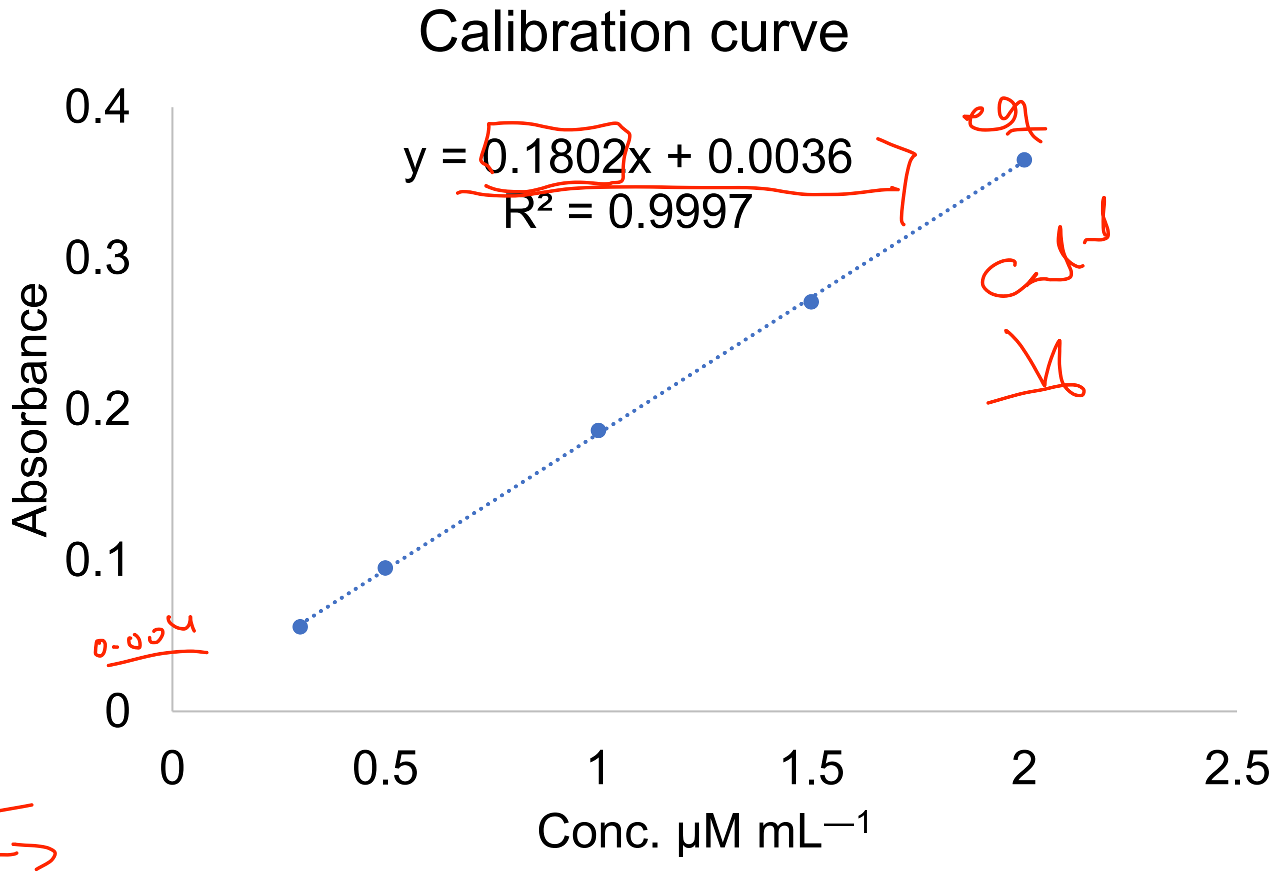
slope

Where SD: standard deviation of the response from the blank

S: slope or sensitivity of the calibration

Limit of detection

Conc. (µg/mL)	Mean absorbance (±SD)
0.3	0.056 ± 0.002
0.5	0.095 ± 0.004
1	0.186 ± 0.007
1.5	0.271 ± 0.004
2	0.365 ± 0.007



blank absorbance readings were 0.002, 0.000, 0.008, 0.006, and 0.003

لا يمكن ان نحدد انه zero بالفعل وانما بناءا على LOD نحدد اذا كانت zero

SD of the blank signals: 3.19×10^{-3}

$$LOD = \frac{3.3SD}{S} = \frac{3.3 * 3.19 * 10^{-3}}{0.1802} = 0.058$$

$$LOQ = \frac{10SD}{S}$$

N+

$\sqrt{Av}$

Lowest conc. يستطيع جهاز رؤيته

اقل من ذلك لا يمكنه

S

UV

quantitative qualitative

Limit of quantitation

LOD اعلى من

This is the lowest concentration of analyte that can be measured in the sample matrix at an acceptable level of precision and accuracy.

سؤال بالامتحان .

determine Conc that lowar

can use this method measure this Conc.

يكون مقصود بالسؤال احسب

LOD
LOQ

علاقة

range.

LOL
LOQ

$$LOQ = 10\frac{SD}{S}$$

LOD
LOQ

Where SD: standard deviation of the response from the blank

S: slope or sensitivity of the calibration

ما العلاقة بين sensitivity

LOQ LOD

كلما زادت sensitivity قل LOD↓

يعني كان جهاز حساس بزيادة انه كان قادر على كشف تراكيز قليلة من المادة

LOD < LOQ

Lowest.

LOD → 1. $\frac{\mu g}{L}$

لا اتأكد من القيمة

LOQ → 3 $\frac{\mu g}{L}$

qualit

quan

Level

واثق بوجود القيمة بحين صحيحها

① → ④ $\frac{\mu g}{L}$

② 2 $\frac{\mu g}{L}$

100% → Conc.

Robustness

→ not effect in small chang

كم الطريقة تتحمل التغيرات سواء بالحرارة او environment

Robustness: refers to the effect of deliberate small changes to the method on its performance

It refers to how sensitive the method is to deliberate or uncontrolled small changes in parameters, such as the size of the sample, the temperature, pH of the solution, reagent concentration, time of reaction, and so forth

1 2 3 4 5

← نختبر اذا ← detect method

Pattern → vibrational

The end of First exam. / Thank you, / your teacher Safaa