Subject: chapter 3 ANALYTICAL

* analytical chemistry :- measurment science deals with فصل seperating and تحديد quantifying relative تقريب amount of substance

* sample
  - → Analyte : thing to be Analyze
  - → sample Matrix : All constiunt in the sample containing an analyte.

* analytical chemistry
  - نوعي معرفه نوع العنصر → qualitatie analysis :- Reveals the idenstity of the element or compound
  - كمي معرفة كمية العنصر → quantitative Analysis indicated the amount of each substance in the sample.

دور Role on Analytical chemistry ⟹ مركز central of science

Instrumental Analysis : Analyte quantity respond to Analytical signal

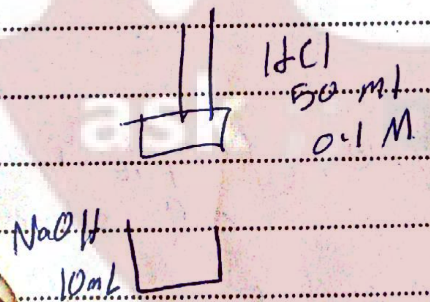
3. processing the sample : samples تجهيز كل عينة
$CaCO_3 \xrightarrow[HCl]{\Delta} CaO + CO_{2(g)}$ decompision (تفكك) solvent

a. Dissolution of sample or digestion (هضم) ⇒ using solvent and avoid decompostion (تحلل).

b. prepartion of solid sample ⇒ drauding to a certain particle size.

Define Replicate sample of same size, weight, and analyte and procedure at the same time under the same condition.

4. Eliminating of Interferences : Are species that cause an error in Analysis



$V_{HCl} = 10.3\ mL$

$V_B = 0.4\ mL$

$V_{real}\ HCl = 10.3 - 0.4 = 9.9\ mL$

* specific method : work for one analyte.
* selective method : work for few Analyte.

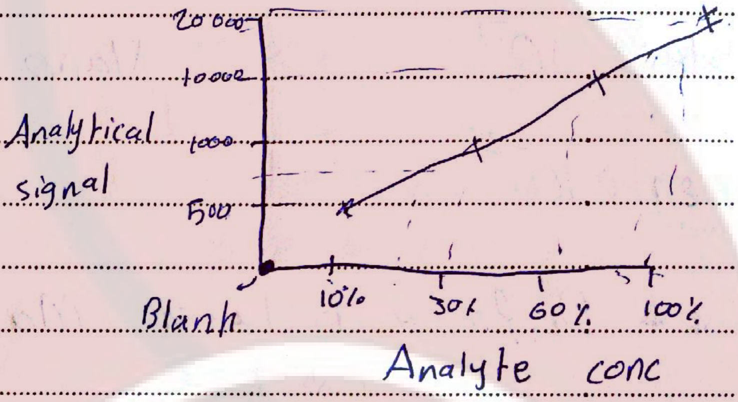
Subject: chapter 3+4

مقرر

5 calibration and Measurment :-

calibration :- is the process of determing the ~~proportion~~ proportionality between the Analyte conc. and a measured quantity

$C_A = kX$



Real sample = 700 → 12%
Si

6 calculating of Result

Si
12.3 ± 0.4

7 Evaluating results by estimating their reliability

→ statistic

ch 4 calculation Used in Analytical chemistry:

Units of measurments

SI units ⇒ International standards of units.

Mass → kg
Length → m
Time → S
Temprature K
Amount of substance mole
Electric curent A

Subject: chapter 4 / /

prefix of units :-

Giga 10^{9} Mega 10^{6} milli "mL" 10^{-3} pico 10^{-12}

kilo 10^{3} micro (μ) 10^{-6} femto 10^{-15}

deci 10^{-1} Nano "n" 10^{-9}

centi 10^{-2}

** Diffrence between Mass and weight.

Mass :- invariant measure of the amount of matter in an object → constant so we used it in chmestry

weight :- the force of gravitational attraction between that matters

* The mole : number of atoms of C^{12} in exactly 12 g of C^{12} (12 amu) = Avogadro's NO.
= $6.022 * 10^{23}$ atom molecule ion particles.

Molar mass : is the mass in g of one mole of the substance = $\sum$ atomic mass of the element.

$$mol\ (m)_x = \frac{mass\ of\ x}{MM\ x}$$

Molar mass $\overset{12}{C}\overset{1.008}{H_2}O^{\to 16}$ = $mm = 12 + 1.008 * 2 + 16 = 30.0$ g/mol

$C_6H_{12}O_6$ = $12 * 6 + 1.008 * 12 + 16.00 * 6 = 180.0$ g/mol

Ex 1 How many moles and millimoles of benzine acid (mm = 122.1 g/mol) are contained in 2.00 g of the pare acid ?

$$mol\ BA = \frac{2.00\,g}{122.1\,g/mol} = 0.0164\ mol$$

m mol BA = 16.4 mm Ba.

bl atomic ma
mnstahhdem
$\boxed{\text{significant figure}}$

بال significant لذا رقم حالو Exact Mo منحط أي خانات بزيادة

Ex 2 How many grams of Na^+ (22.99 g/mol) are contained in 25.00 g of Na_2SO_4 (142.0 g/mol) ?

$$g\ Na^+ = \frac{25.00\,g}{142.0\,g/mol} \times \frac{2 \times mol\ Na^+}{mol\ Na_2SO_4} * \frac{22.99\,g}{mol\ Na^+}$$

$= 8.10\ g\ Na^+$

** concentration ~~of~~ solution (C)

Molar concentration } (M)
molarity

$$M = \frac{no\ of\ mol\ of\ solute}{Volume\ in\ solution\ (L)}$$

$$\frac{solute\ مذاب}{(L)\ vol\ solution} = \frac{no\ of\ m\,mole\ of\ solute}{Volume\ solution\ (mL)}$$

Ex 1 calculate the molar conc. of ethanol in an aquace sol that contains 2.30 g of C_2H_5OH (46.07 g/mol) in 3.50 L solution?

$$M_{ethanol} = \frac{\frac{2.30\ g\ ethanol}{46.07\ g/mol}}{3.50\ L} = \underline{0.0143\ M}$$

concentration in solution

- Molar conc.
- [Analytical Molarity : total num. of ~~mol~~ solute in 1 L solution]
- Equilibrum Molarity

Ex 1.0 M HCl → 1 mol HCl in 1 L solution
37 g HCl " " "

→ Equilibrium Molarity : the molar conc. of particular spacies in a solution of eq.

1.0 M HCl → $H^+ + Cl^-$
0.0 at equili ماكو إنتزان

بعد ما نطلع ال M منحتاج بالمسألة.

Ex calculate the Analytical and equibrum molar conc. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ of solute species in an aquaus solution that contains 285 mg of CH_3COOH (163.4 g/mL) in 100 mL (the acid is 73% inized inwater)

→

$$C = \frac{\frac{280 \times 10^{-3}}{163.4\ g/mol}}{10.04 \times 10^{-3} L} = 0.174\ M$$

$$HA \rightleftharpoons H^+ + A^-$$

27% 73% 73%

$$[HA]_{eq} = 0.17414 \times \frac{27}{100} = 0.047\ M$$

$$[A]_{eq} \quad 0.174\ M \times \frac{73}{100} = 0.127\ M$$

Ex Descripe the proporation of 2.00L of 0.108M $BaCl_2$ from $BaCl_2$ from $BaCl_2 . 2H_2O$ (244 g/mol)??

g $BaCl_2 . 2H_2O$ = $(2.00\ L \times 0.108 M) \times \frac{244 g}{mol\ BaCl_2 . 2H_2O}$

✓ = 52.8 g

1 to 1

Ex Describe the proporation of 500 ml of 0.074 M Cl^- $BaCl_2 . 2H_2O$ (244 g/mol)??

g $BaCl_2 . 2H_2O$ $= 500 \times 10^{-3} L \times 0.074\ M \times \frac{1}{2} \times 244 g/mol$

✓ = 4.52 g

** concentration in solution :-

- percent concentration = part per hundred (High conc.)

weight % (w/w) = $\frac{\text{weight of solute}}{\text{weight solution}} \times 100$ 37 (w/w) HCl

37 g HCl
100 g solution

Volume % (V/V) = $\frac{\text{Volume solute}}{\text{Volume solution}} \times 100$

7% ml (V/V)
7 ml CH_3OH
100 ml solution

weight/volume % (w/V) = $\frac{\text{weight of solute}}{\text{Volume solution}} \times 100$ 5 $AgNO_3$

5 g $AgNO_3$
100 mL solution

إذا قال mass ماله vol/weight منه weight/vol مستخدم

- part per million (ppm) , part per Billion (ppb)
→ low concentration

$C_{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$ ppm = mg/L

$C_{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9$ ppb = μg/L

Ex what is the molarity of K^+ in an aqueous solution that contain 63.3 ppm of $K_3Fe(CN)_6$ 329.2 g/mol ??

$$C_{K^+} = \frac{63.3 \frac{mg}{L} \times 10^{-3} \frac{g}{mg} \times 3}{329.2 \text{ g/mol}} = 5.77 \times 10^{-4} \text{ mol/L}$$

Subject: chapter 4

* Solution - Diluent volume Ratio :-

1:4 → solution   ratio:- Dilute one volume
solute   with three volume

P - function or P - value
For chemical species X : $Px = -\log[X]$
$pH = -\log[H^+]$

Ex $200 * 10^{-3}$ M NaCl and $54 * 10^{-4}$ M HCl solution :-

$pH = -\log[H^+] = -\log[54 * 10^{-4}] = 2.27$

$pNa = -\log[Na^+] = -\log[200 * 10^{-3}] = 0.699$

$pCl = -\log[Cl^-] = -\log[200 * 10^{-3} + 54 * 10^{-4}] = 2.595$

* Density and specific gravity :-

mass per unit volume
kg/m³ , kg/L , g/mL

↳ the ratio of the mass of a substance to the mass of an equal volume of water (4 °C) → kg/L

Ex calculate the molar conc. of HNO_3 (63.0 g/mol) in a solution that has a sp.g of 1.42 and is 70 % HNO_3 (w/w).

$$C_{HNO_3} = \frac{1.42\ kg/L * 10^3 \frac{g}{kg} * 70}{63.0\ g/mol} = 16.0\ M \quad ??$$

$$M = \frac{d * \% * 10}{mw}$$ القانون

Subject: Chapter 4   /   /

* Describe the preperation of 100 mL of 6.0 M HCl from a conc, reagent that has a sp.g of 1.18 and is 37% (w/w) HCl (36.5 g/mol)?

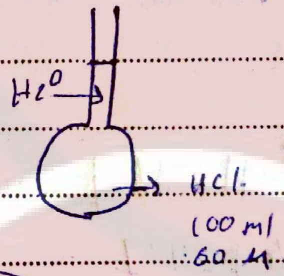
$$C_{HCl} = \frac{1.18 * 37 * 10}{36.5} = 12.0\,M$$

$$\boxed{M = \frac{d * \% * 10}{mm}}$$

$(MV)_{conc.} = (MV)_{diluted}$

$120\,M * V = (100\,ml * 6.0\,M)$

$\boxed{V = 50\,ml}$



* Chemical stiochiometry :- mass relationship among reacting chemical species.

صيغة بدائية

Emperical formula
simplest whole-number between the atoms
CH_2O

Molecular formula } صيغة جزيئية
the no. of the atom in the molecular

structural formula
extra information about ______ of the atom in the molecule
HCOH   H—C(=O)—H

CH_2O
$C_2H_4O_2$
$C_6H_{12}O_6$
C_2H_6O

Ex [a] what mass of $AgNO_3$ (169.9 g/mol) is needed to convert 2.33 g Na_2CO_3 (106.0 g/mol) to Ag_2CO_3 ??

[b] what mass of Ag_2CO_3 (275.7 g/mol) will be formed?

$Na_2CO_3 + 2AgNO_3 \longrightarrow Ag_2CO_3 + 2NaNO_3$

[a] $g\ AgNO_3 = \frac{2.33g}{106.0 g/mol} * 2 * 169.9 g/mol = 7.47 g$

[b] $g\ Ag_2CO_3 = \frac{2.33g}{106.0 g/mol} * 1 * 275.7 g/mol = 6.06 g$

Ex what mass of Ag_2CO_3 (275.7 g/mol) is formed when 25.0 mL of .200 M $AgNO_3$ mixed with 50.0 mL of 0.08 M Na_2CO_3 ??

$Na_2CO_3 + AgNO_3 \longrightarrow Ag_2CO_3 + 2NaNO_3$

$n\ Na_2CO_3 = 50.0 * 10^{-3} L \times 0.03\ M = 4.00 * 10^{-3}$ mol

$n\ Ag_2NO_3 = 25.0 * 10^{-3} L * 0.200 M * \frac{1}{2} = 2.50 * 10^{-3}$ mol L.R

$g\ Ag_2CO_3 = 2.5 * 10^{-3} mol * 275.7 g/mol = 0.689 g$.

[b] what will be the molar analytical conc. of Na_2CO_3 will be produced in solution :-

$C_{Na_2CO_3} = \frac{(4.00 * 10^{-3} - 2.5 * 10^{-3})}{(25 + 50) * 10^{-3}} = 0.02 M$

Chapter 5 : Errors in Chemical Analysis :-

- Measurments invorrably involve errors and uncertinity can never be uliminated and measurment give good estimate of the true value (central value)

– Reliability can be assessed in several ways :-

1. Experimental design
2. compound with known composition
3. consult to the chemical literature.
4. Equipment Calibration
5. statistical test.

* chemist usually carry (2–5) portion of sample Analysis ⟹ (Replicates are samples of about the same size that are carried at it exactly the same way.

– The Best estimate of the central value (true value) are the mean and median.

ال median و mean قريبين من بعض

$$Mean = \bar{x} = \frac{\sum x_i}{N}$$

مجموع القراءات على عددهم

"كل ما زادوا عدد القراءات صاروا ال Mean و median نفس الاشي تقريبا"

Ex calculate the mean and median for the following measurment of the conc. of Fe in blood sample.

19.4 , 19.6 , 19.8 , 20.1 , 19.5 ppm

$$\bar{X} = \frac{\text{مجموع}}{6} = \boxed{19.78}\ ppm$$

قريبين

$$Median = \frac{19.6 + 19.8}{2} = \boxed{19.7}\ ppm$$

Subject: Chapter 5

8-10 Date
8-10 mohadra آخر ميعاد / /

precetion ⇒ Describe the repsodciblty of measurment.

⇒ closses of result that have been obtained in exactly the same way.

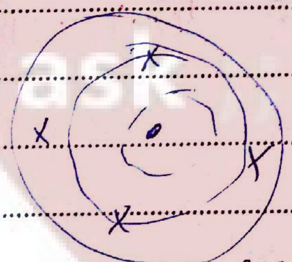
⇒ Terms used to describe the precision.

1. standered deviation (S) ✓
2. Variance (S^2) ✓
3. cufficiant of variation ✓
4.

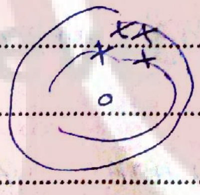
- Devtion from the mean $d = |x_i - \bar{x}|$

Accuracy : the clossnes of measurments to the value central acceptable.

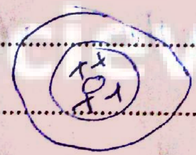
- Expressed in terms of : measured value
1. Absolute error $E = x_i - x_t$ → true vale or $\bar{x}$
2. Relative error $E_r = \frac{x_i - x_t}{x_t}$ → $\frac{\text{Abs. Error}}{\text{True Value}}$



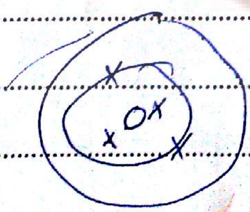
low accuracy
low precetion



high presition
low accuracy



High
High



High accuracy
low P

Subject: chapter 5

/ / measured − true value

Ex To lernence of A class pipet 20 mL ± 0.03 :-

Absolute error :- ± 0.03

Relative error :- $\frac{\quad}{\text{true value}} = \frac{\pm 0.03}{20} = \pm 0.0015$

percent error% = ± 0.15 %

Ex Result from six piplicates determination of iron in aq sample is 19.8 ppm where the standard solution containing 20.0 ppm iron determine [1] Error [2] R.R.E

E = 19.8 − 20.0 = −0.2

R.E = $\frac{-0.2}{20} * 100 = -1\%$

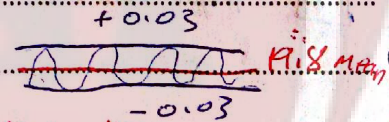
precison → بالقايا آكي

قراءات قريبة بطلع صفر

قراءات بعيدة بطلع عالي

Types of error :-

presion
a- Random error (indetermine error)
- affect measurment presision
- cause the data to be scattered more or less
- symetrically around the mean



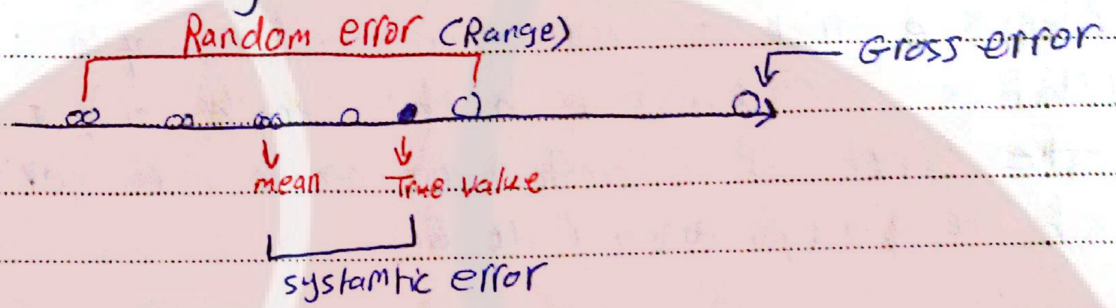
كل القيم الي بطلع precision

accuracy أخطاء محددة، ثابتة محددة وثابتة

b- systematic error (determane error)
- affect the accuracy of measurments
- cause the mean of a data set to differ from the accepted value.

c Gross error (outlier) خطأ بشري كبير

- often the Product of human error.
- occur occasionally and one often large.



systematic errors :- lead to bias in measurments results
+ve
-ve

* Three types :-

[1] **Instrumental errors** :- are caused by non ideal instrument behavior, by faulty calibration or by use under inappropriate condition c all electronic are subjected to this type of error.

→ calibration aliminates most instrument systemitic error (detectable and collectable) Graduated cylinder - volumetric flask - burette - pipet

التي بيحدث الحرارة يؤدي إلى تغير في الماء ... systematic error

[2] **method error**, arrise from nonideal chemical or Physical behavior of Analytical system.
titration
عدم إستقرار بعض الجزيئات

Ex slowness of some reaction, incompleteness or instability of analyte in reagents and possible occurrence of side rxn
- difficult to detect.
سبب تحديده صعب

[3] **personal error** : result from carelessness, inattention or personal limitating of experimentor (result from judgment)

Effect of systematic errors on Analytical results systematic (method, Personal, 'wl') → constant / → proportional

a. constant

يزداد تأثير هذه الأخطاء بنقصان حجم العينة

- independent of the sample size been Analysed
- Absolute error is constant with sample size but the relative error varies with the sample size change
- The effect of a constant error because more serious as the size of the quality measured decrease

لتفادي الخطأ يتم زيادة حجم العينة

b. proportional

- Decrease or increase in proprtino to the size to sample
- Absolute error is varies with size of sample but the relative error
- a common cause of proportional error is the presense of interfail continimnse in the sample:

لـ وجود الشوائب الملوثة بالعينة (interfering) ← تكون نسبة الخطأ ثابتة مع تغير الحجم

systematic method erro detection :-

1. analysis of standard sample : Best way of estemating the bias is using the standard refrence material (SRMS)

(SRMS): materials that contains one or more analyte at known conc. level

can be prepared by synthesis.

can be pirchsed Ex sigma chemical , NIST

اشترى

2. Independent Analysis

second indipendent and reliable analytical method can be used in parallel with the method been evalued → statistical test

S T A R S Notebook

[3] variation in sample size, as the size of measurement increase, the effect of a constant error decrease.

[4] Blank determenation

- Blank contains the reagent and solvents used in a determination but No Analyte.
- sample constituant are added to simulate the sample matrix of Analyte.

chapter 7 : statistical Data treatment and Evaluation.

13.3 ± 0.2 — under the curve. مسحة ضيقة : confidence و uncerthinty الفرق بين

confidenc limit

كل ما عدد القراءات زادوا ~~بتزيد~~ بقل CI

13.1 → 13.5 ⇒ confidence intervals.

The possibility that your lies in a range where the true value "μ" lies, This range is called (confedence Intervals) CI and limits for this range are called (confidence limit) CL

confidnselim. قيمتها الحد

confidnce Intervals Range ال

CI ↓ N ↑

-8 confedence بحسب ال

population standerd diviation

[1] Finding the confuidence intervals when σ is known or s is good estimate of σ

standerd

$$CI \text{ of } \mu = \bar{X} \pm \frac{z\sigma}{\sqrt{N}}$$

z score — population s.d

No. of implict (عدد القراءات) — $\sqrt{N}$ تبين

z قيمة بتعين CI's

area under the curve

Subject: (area under the curve) / /

لما يزيد Z يزيد

CL%	50	68	80	90	95	99
Z	0.87	1.00	1.28	1.64	1.96	2.58

Ex calculate the 80% and 90% confidence limits for
[a] The first entry (1108 in glucusa) in Ex 6.2
[b] The mean value for month 1 in the example
Assume that in each part $s = 19$ is a good estemate of σ

Month 1
1108
1122
1075
1099
1115
1083
1100
Avg. 1100.3 ppm

sol: [a]

CI at 80% $= \frac{1108 \pm 1.28 \times 19}{\sqrt{1}} = 1108 \pm 24.3$ ppm confidence limit

confidence intervals = 1083.7 — 1132.3 ppm

CI at 90% $= 1108 \pm 1.64 \times 19 = 1108 \pm 31.2$ ppm

confidence intervals = 1076.8 − 1145.2

عند 80 أفضل لأنو ال limit كل ما قلت أفضل

[b] 80% $= \frac{1100.3 \pm 1.28 \times 19}{\sqrt{7}} = 1100.3 \pm 9.2$ ppm

CI 90% $= \frac{1100.3 \pm 1.64 \times 19}{\sqrt{7}} = 1100.3 \pm 14.1$

كل ما زدنا N ال confedence limit

Ex How many replicates measurments (No of measurment) in month 1 ex 6.2 are needed to decreas the 95% confidence intervals to 1100.3 ± 10.0 ppm glucose

at 95% $\pm 10 = \pm \frac{z\sigma}{\sqrt{N}}$

$10 = \frac{1.96 \times 19}{\sqrt{N}} \Rightarrow N = \left(\frac{1.96 \times 19}{10}\right)^2 = 13.9$

$\simeq 14$

chapter 7 ← dots

Subject: ch $\boxed{1, 4, 5, 6, 7}$ 9-10 اثنين 31-10 ملاحظة / /

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{5.7\times10^{-10}} = 1.75\times10^{-5}$ M

$[OH^-] = \sqrt{K_b\, C_B} = \sqrt{1.75\times10^{-5} \times 0.075\,M} = 1.15\times10^{-3}$ M

Ex calculate the $[OH^-]$ in 0.01 M sodium hypoclorde sol

NaOCl → $Na^+ + OCl^-$

$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$ base $K_a = 3.0\times10^{-8}$ M

$[OH^-] = \sqrt{\frac{1\times10^{-14}}{3.0\times10^{-8}} \times 0.01} = 5.8\times10^{-5}$

← chapter 7 مهم

$\boxed{1}$ Finding confidence limit when σ unknown

CI of $\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$ t: student statics
s: sample standered deviation

Degree of freedom	80% t-statistics	90%
1	3.08	6.31
10	1.37	1.81
20	1.32	1.73
60	1.30	1.67
∞	1.28	1.64

Ex A chemist obtained the following data for the alcohol ~~content~~ content in a blood sample C_2H_5OH%: 0.084, 0.089, 0.079 calculate the 95% confidence intervals for the mean assuming

Subject:.................... / /

[a] the 3 results obtained are the only indication of the precison of the method [b] from the previous experince of 100 of measurments, we know that the standered diviation of measurments, we know that the standered diviation of the method $S = 0.005\%$ C_2H_5OH and is a good estimate of σ ??

Sol CI at $95\% = \bar{X} \pm \frac{tS}{\sqrt{N}}$

$$\frac{0.84 \pm 4.304 \; 0.005\%}{\sqrt{3}} = 0.084 \pm 0.012\%$$

a منهم في b
في limit بس

* Detection of Gross error
* Q-test
* $Q_{exp} = \frac{|X_{suspected} - X_{nearest\ value}|}{(X_{max} - X_{min})}$ range speed

$Q_{critical} = 0.64$ 90% if $Q_{exp} > Q_{critical}$ rejected
$Q_{exp} < Q_{critical}$ accepted

Ex The analysis of CaO% : 55.95, 56.00, 56.04, 56.08, 56.23. The last value appear anoialous, should it be retained or rejected (Q critical at 90% = 0.64)

$Q_{exp} = \frac{|55.23 - 56.08|}{65.23 - 55.95} = 0.54$ $Q_{exp} < Q_{critical}$

** The median is used when a set of data contains outlier

Scanned by CamScanner