

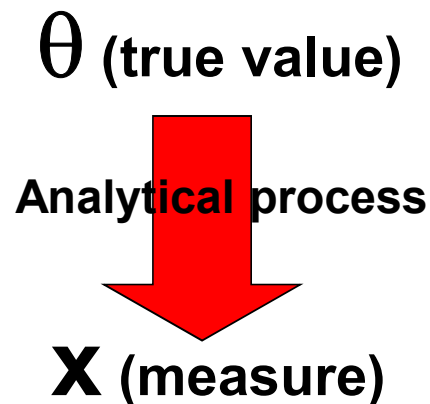
# Measurement process

Systematic and random errors

Accuracy and Precision

# ANALYTICAL MEASURES

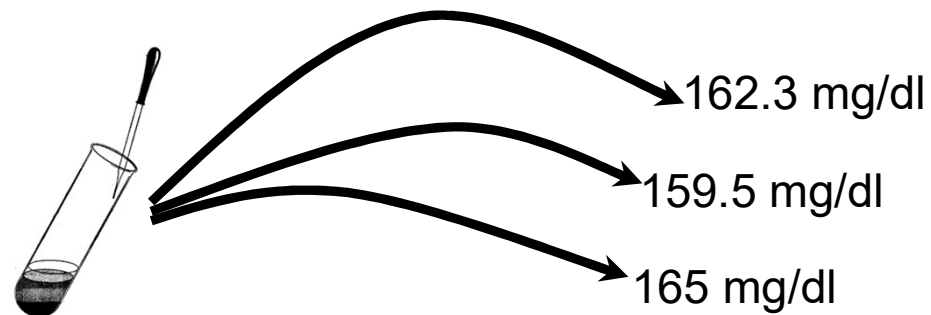
The result of a measurement operation is a real number ( $x$ ), called an analytical measure which expresses the true value ( $\theta$ ).



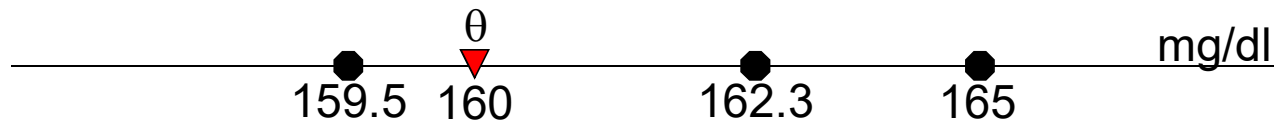
In general,  $\theta$  is not known. Instead, we will refer to situations in which the value of  $\theta$  is known.

# Example

Experience indicates that if you perform multiple measurements of the same quantity the measured values are generally different from the true value of the quantity being measured.

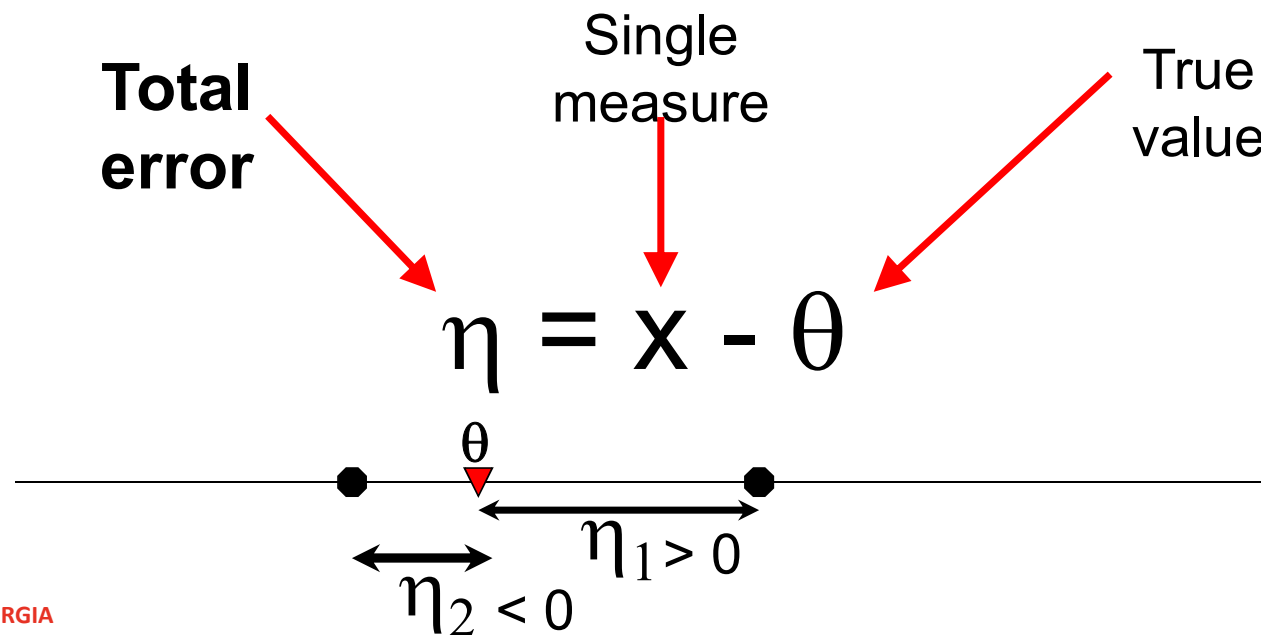


Evaluation of blood glucose:  $\theta = 160$  mg/dl



# Total error

- The difference between the measured value ( $x$ ) and the true value ( $\theta$ ) is called the total error ( $\eta$ ).
- A measure with small total error ( $\eta$ ) has high reliability



# The Nature of Error in Measurement

- **Systematic errors**
- **Random errors**

Assuming the measurement process is appropriately applied, not having gross errors, such as



# Systematic errors

- **systematic errors:** deterministic tendency of a given method to overestimate / underestimate the true value (due to badly calibrated instrument or method of measurement).



# Random errors

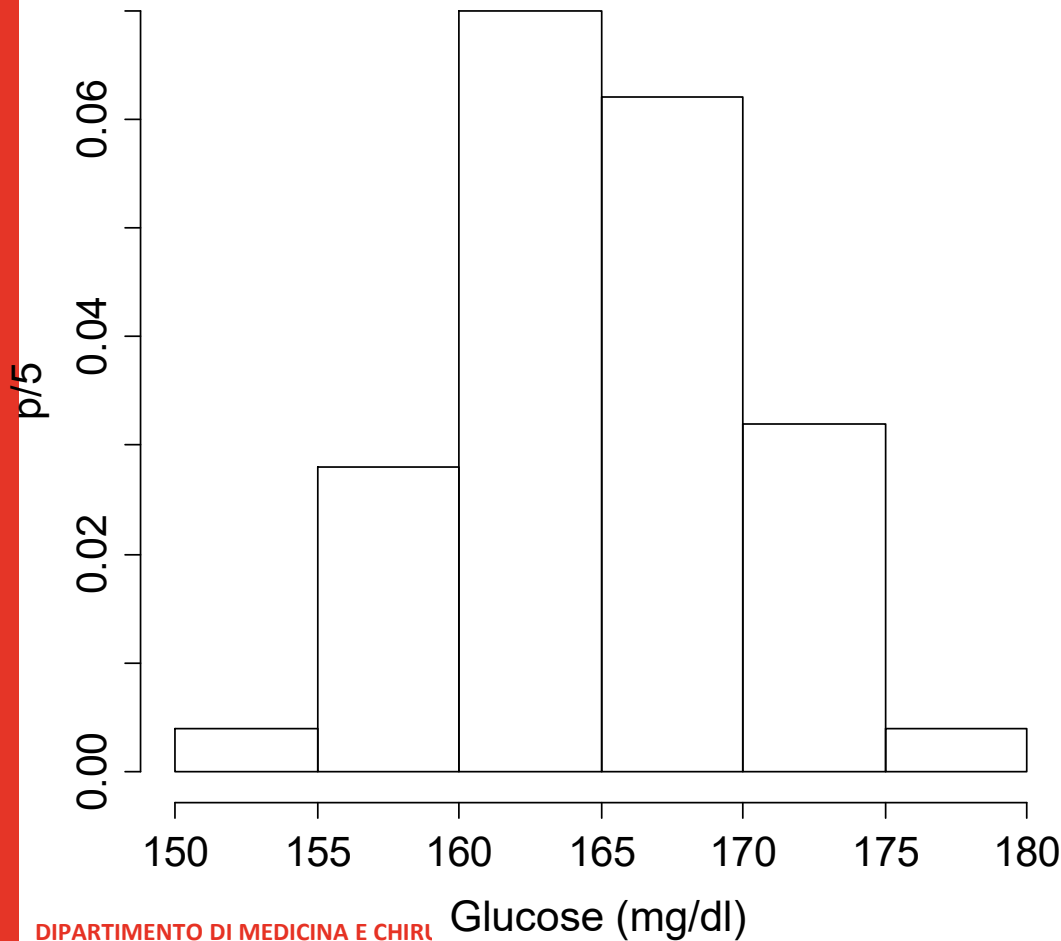
Measurements of the same value, repeated with the same analytical procedure and under conditions as similar as possible, often lead to different measurements.

The sum of all the small and unpredictable variations in the execution of the various analytical operations causes the measurements to fluctuate around a value, which deviates more or less from the true value depending on the systematic error



"No, that doesn't make any difference either, Miss Jones."

A laboratory measures 100 times the blood glucose in the same sample with concentration 160 mg / dl.



The values are concentrated around a value different from the true concentration value.

The measurement operation tends to overestimate the blood sugar value by 5 mg / dl (165-160)!

**The tendency to over / underestimate the true value is called systematic error ( $\delta$ )/bias:**

$$\delta = \mu - \theta$$

$\mu$ : mean of all the infinite measures that could be obtained by measuring  $\theta$

**A measure is more accurate the smaller the extent of the systematic error ( $\delta$ ) from which it is affected.**



## Inaccuracy measure

Difference between sample mean and the true value

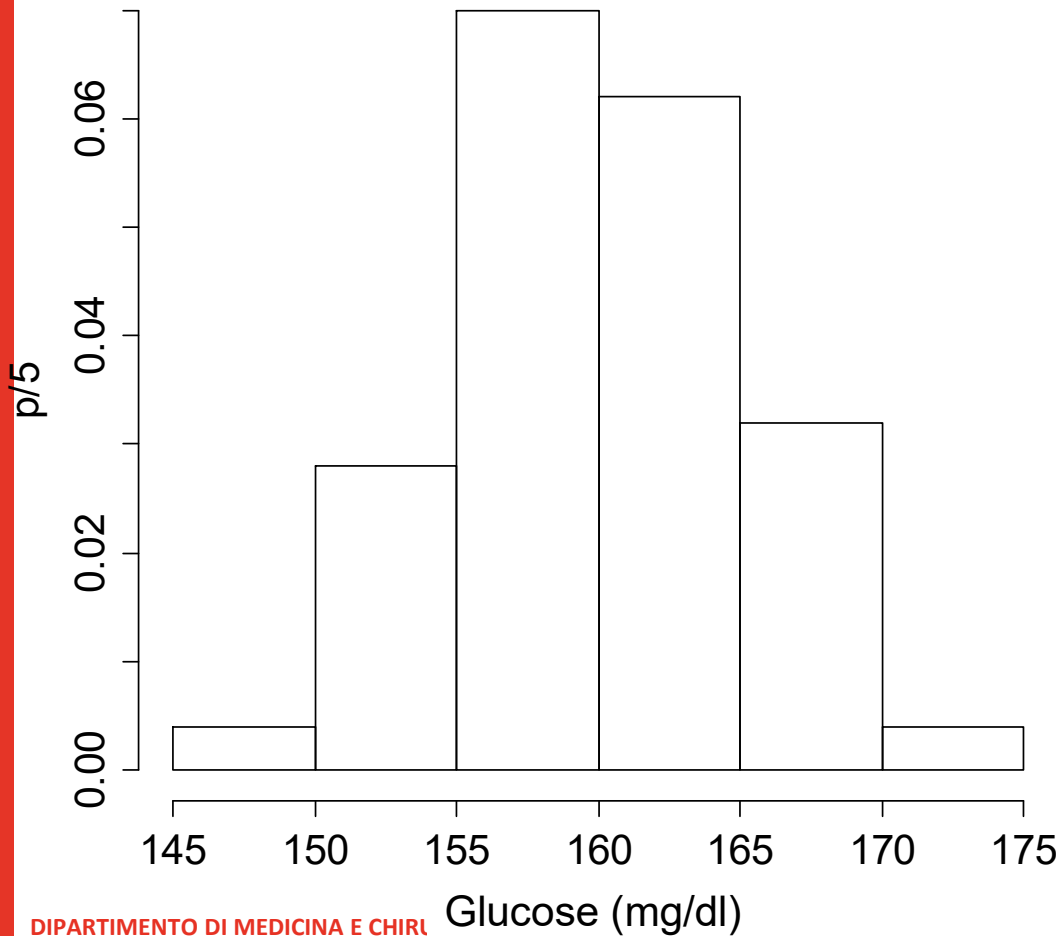
$$\hat{\delta} = \bar{x} - \theta = 165 - 160 = 5 \text{ mg/dl}$$

The measurement operation tends to overestimate the blood sugar value by 5 mg / dl (165-160)!

**The tendency to over / underestimate the true value is called systematic error ( $\delta$ )/bias:**

**A measure is more accurate the smaller the extent of the systematic error ( $\delta$ ) from which it is affected.**

A laboratory measures 100 times the blood glucose in the same sample with concentration 160 mg / dl.



The values obtained fluctuate around the true value of 160 mg / dl BUT they are different from each other (despite being measurements of the same quantity)!

Fluctuations in measurements  $X$  around  $\mu$  are called **random errors ( $\varepsilon$ )**:

$$\varepsilon = X - \mu$$

$\mu$ : mean of all the infinite measures that could be obtained by measuring  $\theta$

**A measure is more precise the smaller the extent of the random error ( $\varepsilon$ ) from which it is affected.**

## Imprecision estimate

Fluctuations in measurements  $X$  around  $\mu$  are called **random errors** ( $\varepsilon$ ):

$$\hat{\sigma} = \sqrt{\frac{(x_i - \bar{x})^2}{n - 1}}$$

**A measure is more precise the smaller the extent of the random error ( $\varepsilon$ ) from which it is affected.**

## Accuracy vs. Precision





### **Accuracy:**

How close measurements results are to the “truth”  
*- a measure of effectiveness/appropriateness*

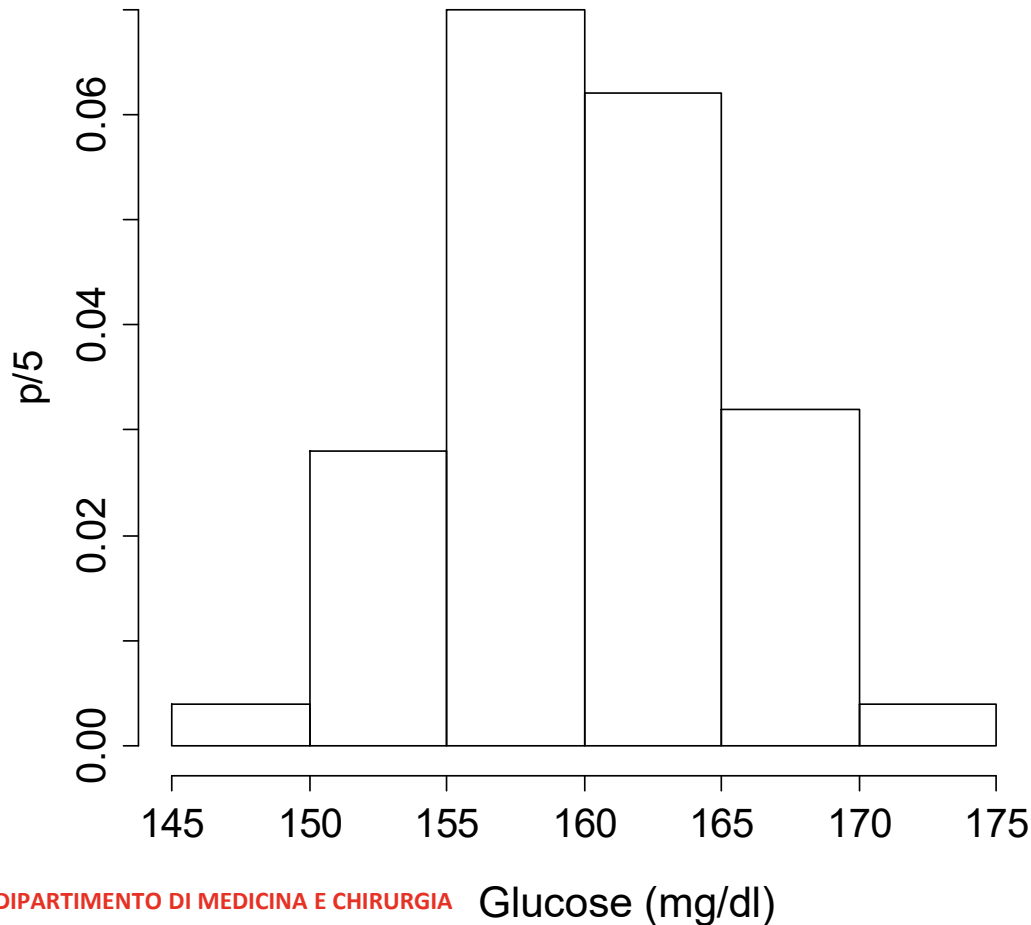
### **Precision:**

How close measurements results are to each other  
*- a measure of technical specification*

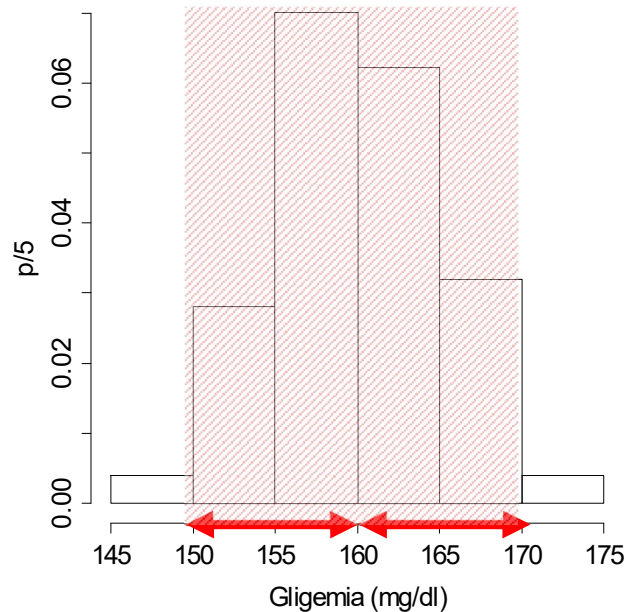
# Accuracy vs. Precision

	Accurate	Inaccurate (systematic error)
Precise		
Imprecise (reproducibility error)		

A laboratory measures 100 times the blood glucose in the same sample with concentration 160 mg / dl.



1. small errors are more frequent than large ones;
2. errors of negative sign tend to occur with the same frequency as those with a positive sign;
3. as the number of measures increases, 2/3 of the values tend to be included in the interval  $\text{mean} \pm 1$  standard deviation & 95% of the values tend to be included in the interval average  $\pm 2$  standard deviations



$$\bar{x} = 160 \text{ mg/dl}$$

$$s = 5.25 \text{ mg/dl}$$

About 95% of all values fall within 150 and 170 mg/dl!

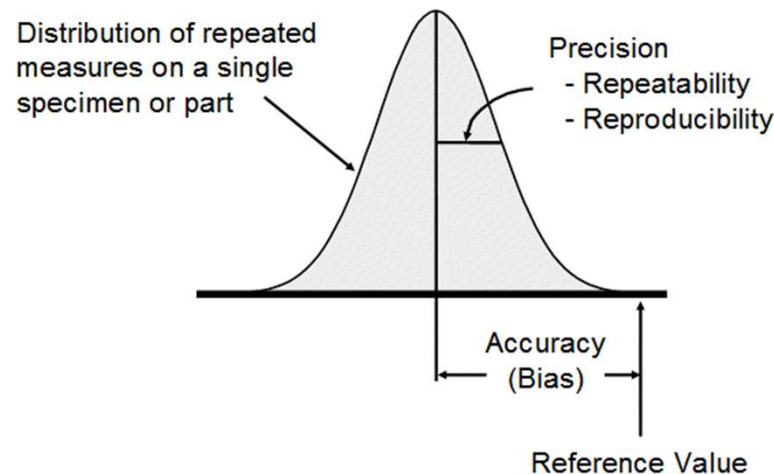
**About 68% of all values fall within 1 standard deviation of the mean.**

**About 95% of all values fall within 2 standard deviations of the mean.**

**About 99.7% of all values fall within 3 standard deviations of the mean.**

# Gaussian distribution & measurement errors

The random measurement errors ( $\varepsilon = x - \mu$ ), taken as a whole, show a typical behavior that can be described as follows:



1. small errors are more frequent than large ones;
2. errors of negative sign tend to occur with the same frequency as those with a positive sign;
3. as the number of measures increases, 2/3 of the values tend to be included in the interval mean  $\pm 1$  standard deviation & 95% of the values tend to be included in the interval average  $\pm 2$  standard deviations



# ESTIMATE OF PRECISION AND ACCURACY

Given  $n$  measures  $\{x_1, x_2, \dots, x_n\}$  obtained with a certain method:

**Inaccuracy estimate**  $\longrightarrow$  **Difference between true value and sample mean**

**Imprecision estimate**  $\longrightarrow$  **Sample standard deviation (s)**

**Example:** let's suppose you have titrated a glucose solution 9 times ( $\theta = 90$  mg/dl – true value)

$\{94, 90, 93, 86, 96, 98, 88, 90, 93\}$

$$H_p: \begin{cases} \theta = 90 \text{ mg/dl} \\ \{94, 90, 93, 86, 96, 98, 88, 90, 93\} \\ n = 9 \end{cases}$$

• Inaccuracy estimate

$$\bar{x} = \left( \frac{94 + 90 + \dots + 93}{9} \right) = \frac{928}{9} = 92 \text{ mg/dl}$$

$$\bar{d} = \bar{x} - \theta = 92 - 90 = 2 \text{ mg/dl}$$

$$\bar{d}\% = \frac{\bar{d}}{\theta} \cdot 100 = \frac{2}{90} \cdot 100 = 2,22\%$$

$$\text{Hp: } \left\{ \begin{array}{l} \theta = 90 \text{ mg/dl} \\ \{94, 90, 93, 86, 96, 98, 88, 90, 93\} \\ \underbrace{\hspace{15em}} \\ n = 9 \end{array} \right.$$

• Imprecision estimate

$$D = (94-92)^2 + (90-92)^2 + \dots + (93-92)^2 = 118 \frac{\text{mg}^2}{\text{dl}^2}$$

$$s^2 = \frac{118}{(9-1)} = 14,75 \frac{\text{mg}^2}{\text{dl}^2} \quad s = \sqrt{14,75} = 3,841 \text{ mg/dl}$$

$$CV\% = \frac{s}{\theta} \cdot 100 = \frac{3,841}{90} \cdot 100 = 4,27\%$$