

CHEM 370 Week 3 Activity

Name: Key

Introduction

This assignment covers Chapters 3 and 4 of *Analytical Chemistry 2.1* by Harvey involving basic analytical chemistry terms, statistical analysis, and confidence intervals.

You should work in groups to complete this activity. Remember to maintain physical distance even when working in groups!

Types of Error

1. An analyst is diluting samples using a micropipette and mistakenly sets it to deliver 100.0 ml of solution instead of 10.00 ml of solution. Is this a determinate or indeterminate error? What affect will this have on \bar{x} when the samples are analyzed? What about s ?

↳ constant offset

↳ no effect

Characterizing Data

Chemists usually use the **mean** as a measure of spread. When a mean represents a set of measurements we call it the *sample mean*, \bar{x} ; when it represents every possible measurement, we call it the *population mean*, μ . All chemical measurements determine \bar{x} :

$$\bar{x} = \frac{\sum_{i=1}^N x_i}{N}$$

where N is the number of data points, x_i .

Chemists usually use the **standard deviation** (SD) as a measure of spread. It has the same units as the mean. When a SD represents a set of measurements we call it the *sample SD*, s ; when it represents every possible measurement, we call it the *population SD*, σ . All chemical measurements determine s :

$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$$

The population is described by a *normal distribution*, a smooth function, governed by μ and σ . Real data are shown as a *histogram*, or bins of real data that approximate a normal distribution and represent the sample statistics.

1. The normal distribution in Figure 1 represents the theoretical daily high temperatures for the month of August in Altamont. The population mean is $\mu = 26^\circ\text{C}$ and the population standard deviation $\sigma = 2^\circ\text{C}$.

1. What percentage of days would you expect to have a high between 24°C and 28°C?

$$+/- 1SD = \boxed{68\%}$$

2. What percentage of days would you expect to have a high between 28°C and 32°C?

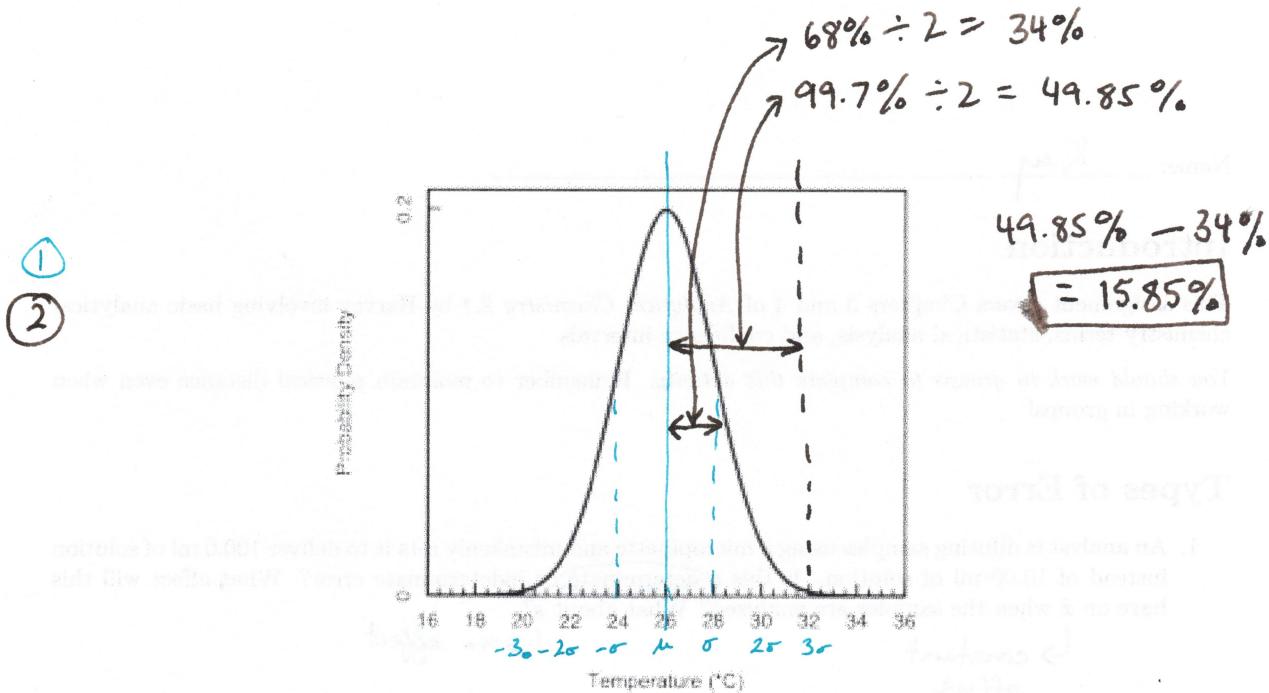


Figure 1: Normal distribution of daily high August temperature in Altamont.

Confidence Intervals

When comparing data, we must be certain the differences are *significant*. Chemists use *confidence intervals* to determine significance. If the confidence intervals do not overlap, the measurements are significantly different.

A confidence interval is calculated at a predetermined level of certainty, for example 95% (or $\alpha = 0.05$). A measurement is always reported with the confidence interval:

$$\text{value} = \bar{x} \pm \text{CI} = \bar{x} \pm t \frac{s}{\sqrt{n}}$$

where t comes from a *t*-table.

1. The *histogram* in Figure 2 shows the measured daily high temperatures for the month of August in Altamont for the year 2020. For this data, $\bar{x} = 25.6^\circ\text{C}$ and $s = 2.23^\circ\text{C}$. An observation was made on every day of August. What range of temperatures can you be 95% certain encompass μ ?

$$\mu = \bar{x} \pm t \frac{s}{\sqrt{n}}$$

$N = 31$
 $S = 2.23^\circ\text{C}$
 $\bar{x} = 25.6^\circ\text{C}$

$t = 2.042 \rightarrow$ from *t*-table, 30 DOF
 $\text{CI} = (2.042) \frac{(2.23^\circ\text{C})}{\sqrt{31}} = 0.818^\circ\text{C}$

$\mu = 25.6^\circ\text{C} \pm 0.818^\circ\text{C} \Rightarrow \boxed{24.78^\circ\text{C} \rightarrow 26.42^\circ\text{C}}$

Statistical Methods

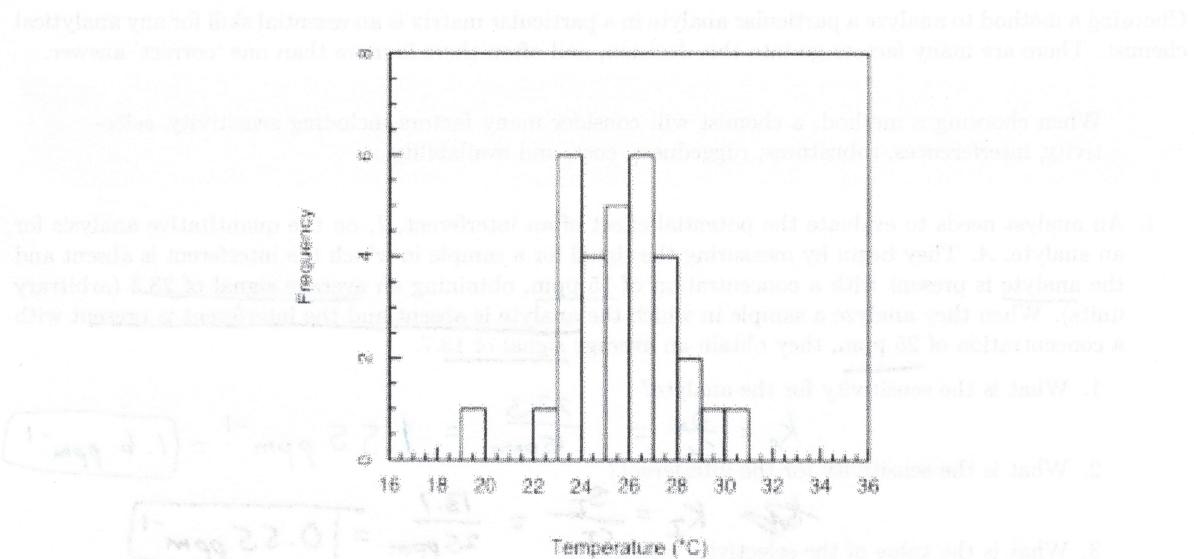


Figure 2: Histogram of measured daily high August temperatures in Altamont. (n = 31)

2. Gacs and Ferraroli reported a new method for monitoring the concentration of SO_2 in air. They compared their method to the standard method by analyzing urban air samples collected from a single location. Samples were collected by drawing air through a collection solution for 6 min. Shown here is a summary of their results with SO_2 concentrations reported in $\mu\text{L m}^{-3}$. Using an appropriate statistical test, determine whether there is any significant difference between the standard method and the new method at $\alpha = 0.05$.

Standard Method	New Method
21.62	21.54
22.20	20.51
24.27	22.31
23.54	21.30
24.25	24.62
23.09	25.72
21.02	21.54
$\bar{x} = 22.86$	22.51
$s = 1.278$	1.921

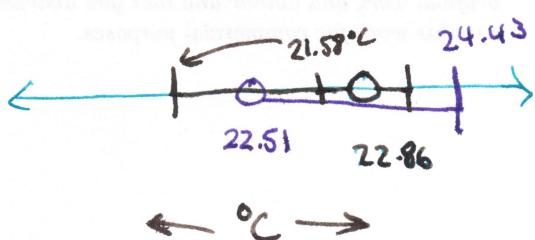
The data in this problem are from Gacs, I.; Ferraroli, R. Anal. Chim. Acta 1992, 269, 177–185.

If CIs ~~overlap~~ overlap there is no significant diff!

$$22.86 - 1.278 = 21.58^\circ\text{C}$$

$$22.51 + 1.921 = 24.43^\circ\text{C}$$

} overlapping = no diff



Choosing a Method

Choosing a method to analyze a particular analyte in a particular matrix is an essential skill for any analytical chemist. There are many factors go into this decision, and often there is more than one 'correct' answer.

When choosing a method, a chemist will consider many factors including sensitivity, selectivity, interferences, robustness, ruggedness, cost, and availability.

1. An analyst needs to evaluate the potential effect of an interferent, I , on the quantitative analysis for an analyte, A . They begin by measuring the signal for a sample in which the interferent is absent and the analyte is present with a concentration of 15 ppm, obtaining an average signal of 23.3 (arbitrary units). When they analyze a sample in which the analyte is absent and the interferent is present with a concentration of 25 ppm, they obtain an average signal of 13.7.

1. What is the sensitivity for the analyte?

$$K_A = \frac{S_A}{C_A} = \frac{23.3}{15 \text{ ppm}} = 1.55 \text{ ppm}^{-1} = 1.6 \text{ ppm}^{-1}$$

2. What is the sensitivity for the interferent?

~~$$K_I = \frac{S_I}{C_I} = \frac{13.7}{25 \text{ ppm}} = 0.55 \text{ ppm}^{-1}$$~~

3. What is the value of the selectivity coefficient?

$$K_{A,I} = \frac{K_I}{K_A} = \frac{0.55}{1.6} = 0.35$$

4. Is the method more selective for the analyte or the interferent?

If $K_{A,I} < 1$, technique is more selective for analyte

2. Refer to NIOSH (National Institute for Occupational Safety and Health) Method 3500 to complete the following questions.

1. What is the analyte?

Formaldehyde

2. What is the technique used?

UV-Vis Absorption Spectroscopy

3. What is one interferent?

Ethanol, alcohols, olefins, aromatic HCs, cyclohexanone, dust

4. What is one step/precaution described that will help avoid interferences?

Use PTFE filter to remove dust

5. How was the method verified?

3 analysts in 3 separate labs

6. Is this a method, procedure, or protocol?

*

7. What is the stimulus used in this experiment?

580 nm light

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