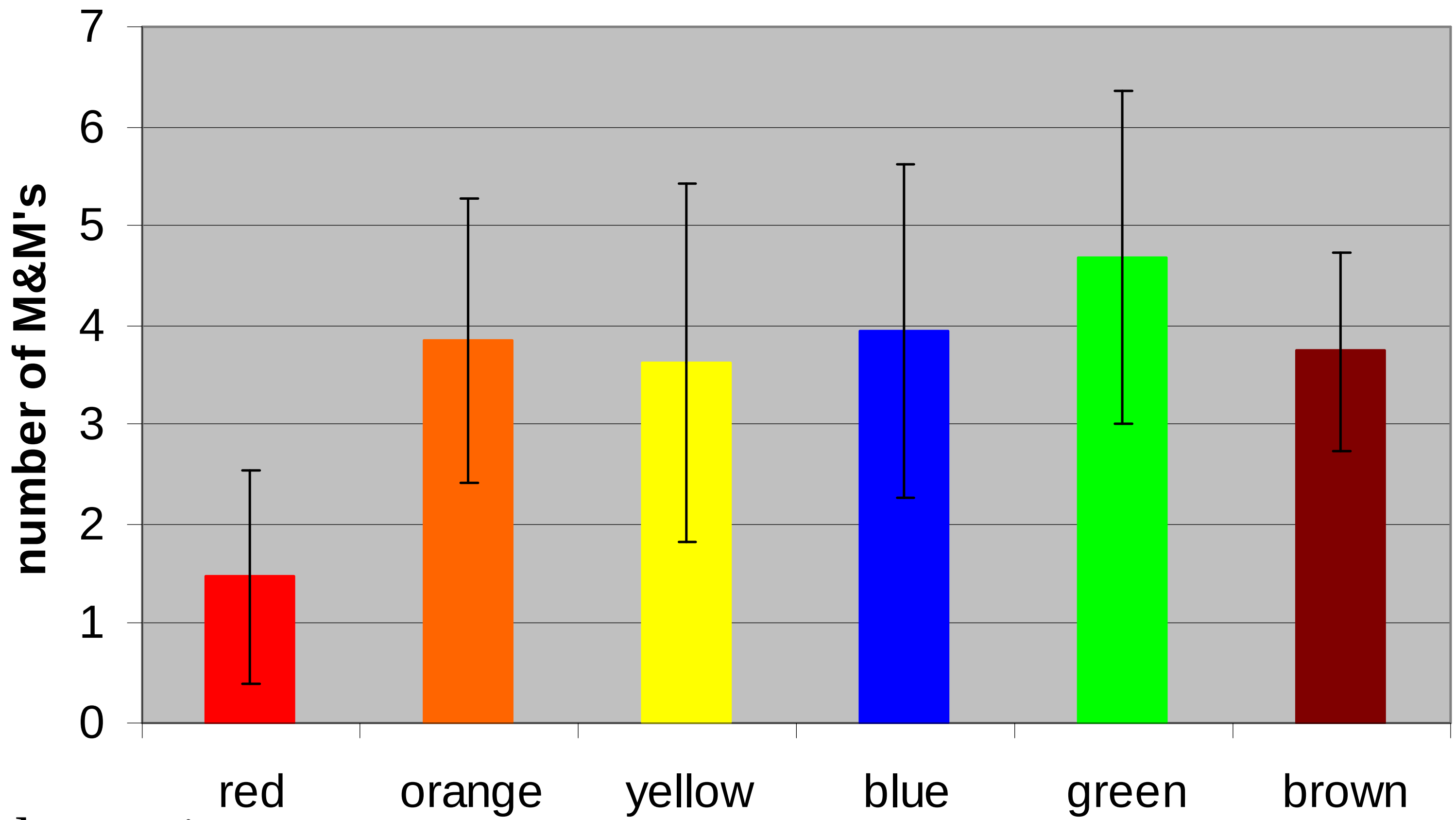
Hypothesis: More brown than other colors, less blue

Conclusion: ~ same of all colors but red, less red – hypothesis incorrect

M&M results Spring 2009

Average Total = 21.3
Std Dev = 1.1

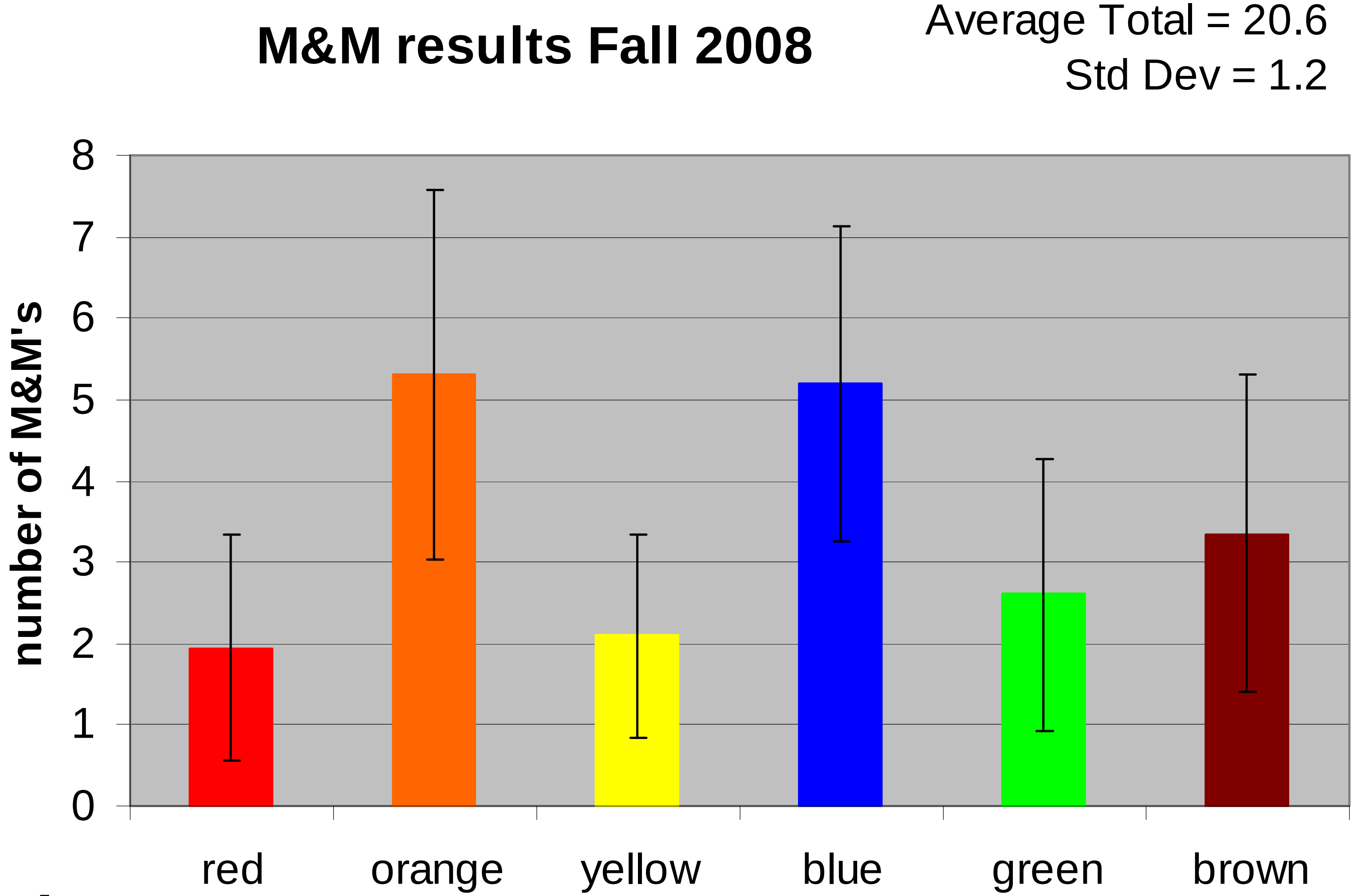


20 data points

Hypothesis: More brown than other colors, less orange/blue

Conclusion: More orange/blue, less red/yellow

– hypothesis incorrect

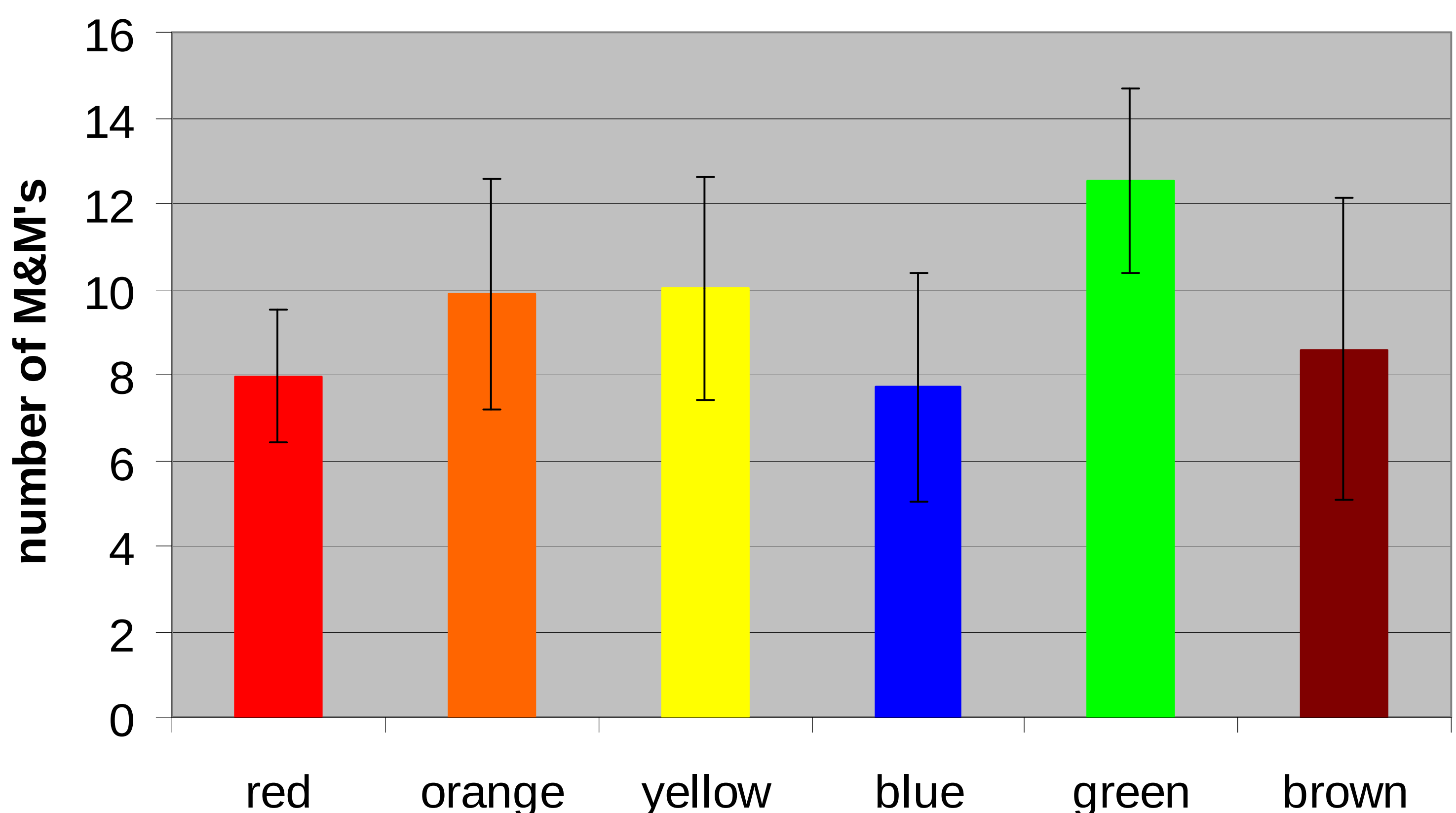


20 data points

Hypothesis: More brown and less orange/yellow than other colors
Conclusion: More green, less others (rest about the same)

ave. total = 57
st. dev. = 1.5

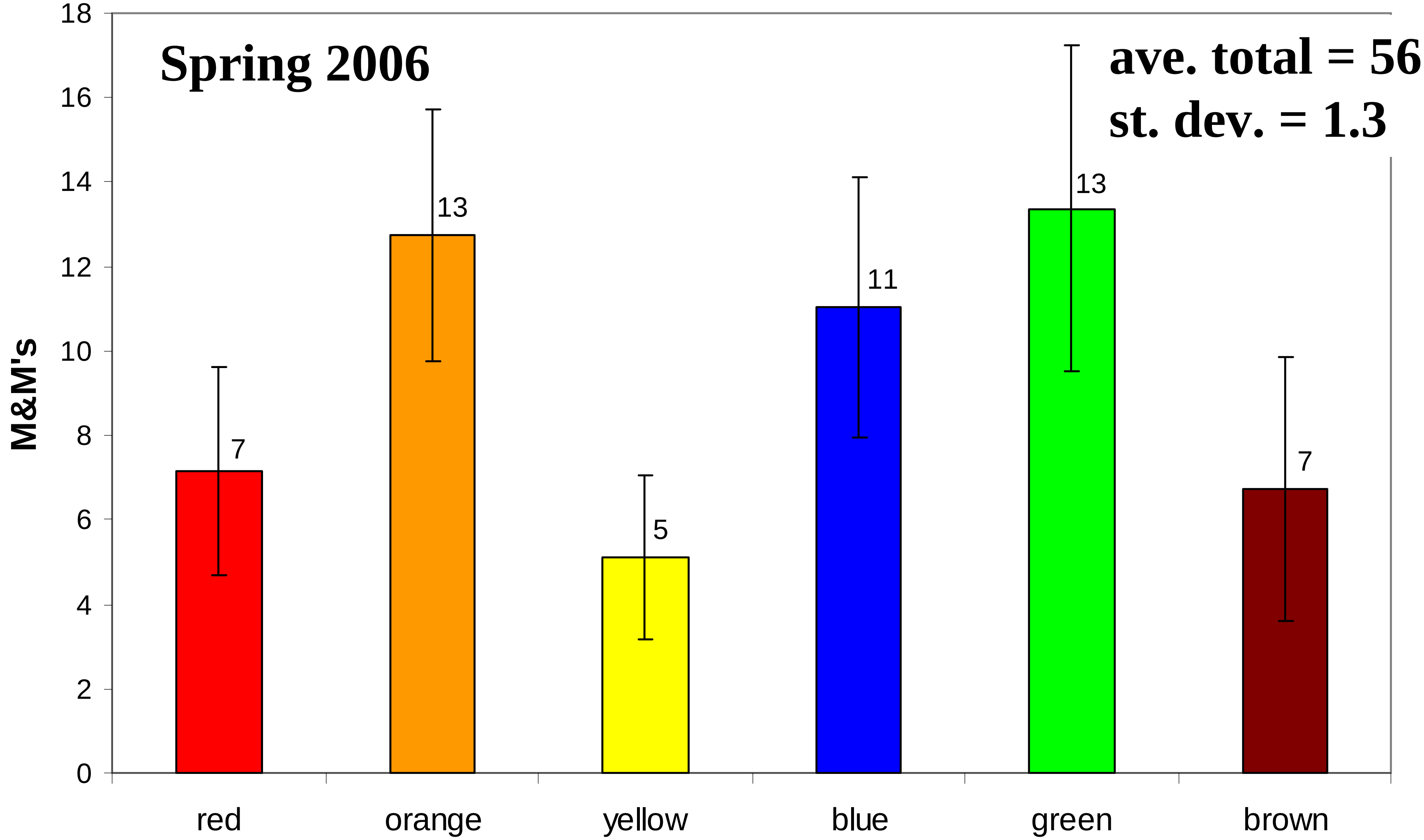
M&M results Fall 2007



38 data points

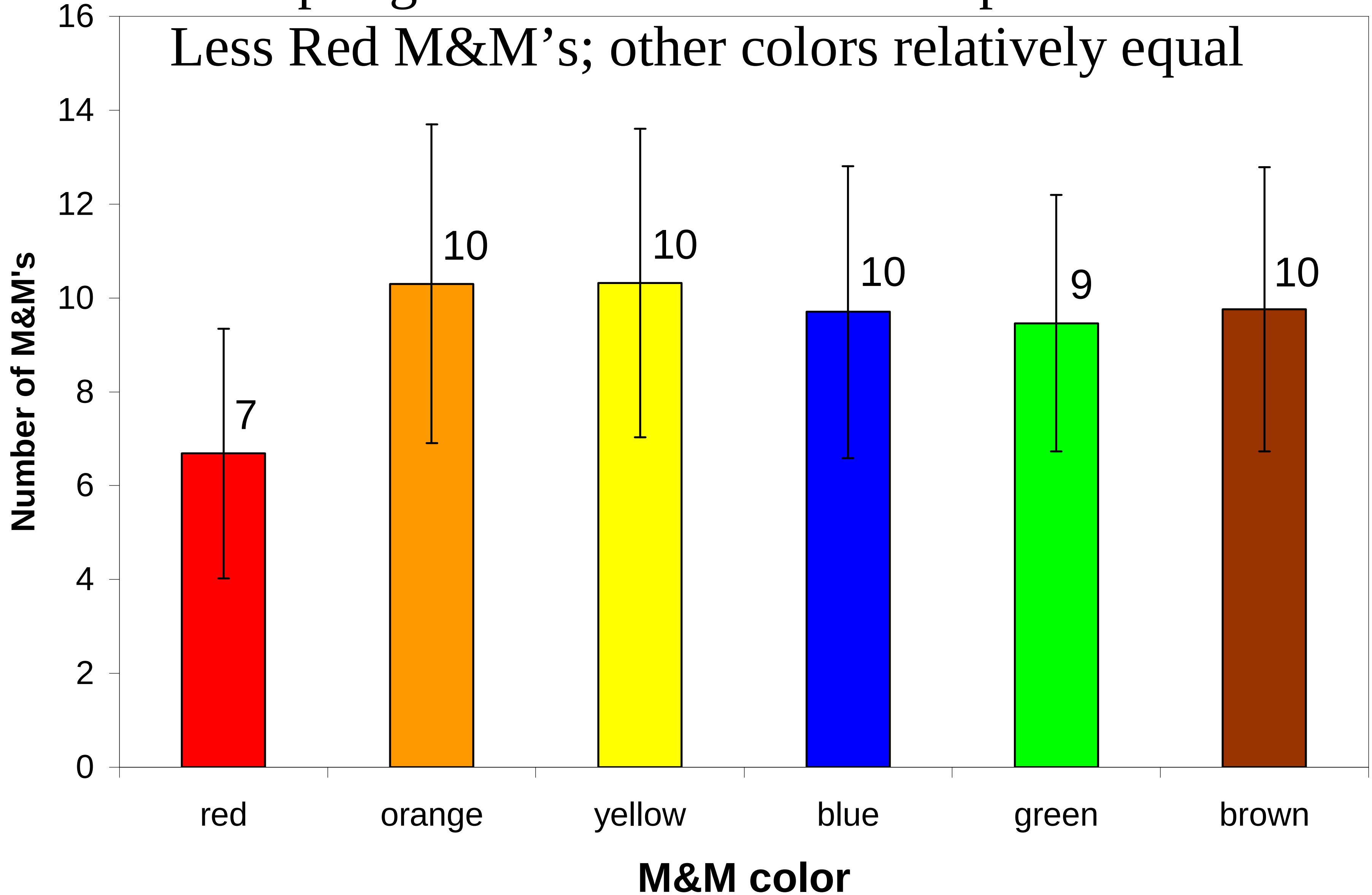
Hypothesis: More brown and less blue than other colors

Conclusion: Less red, yellow, brown than other colors

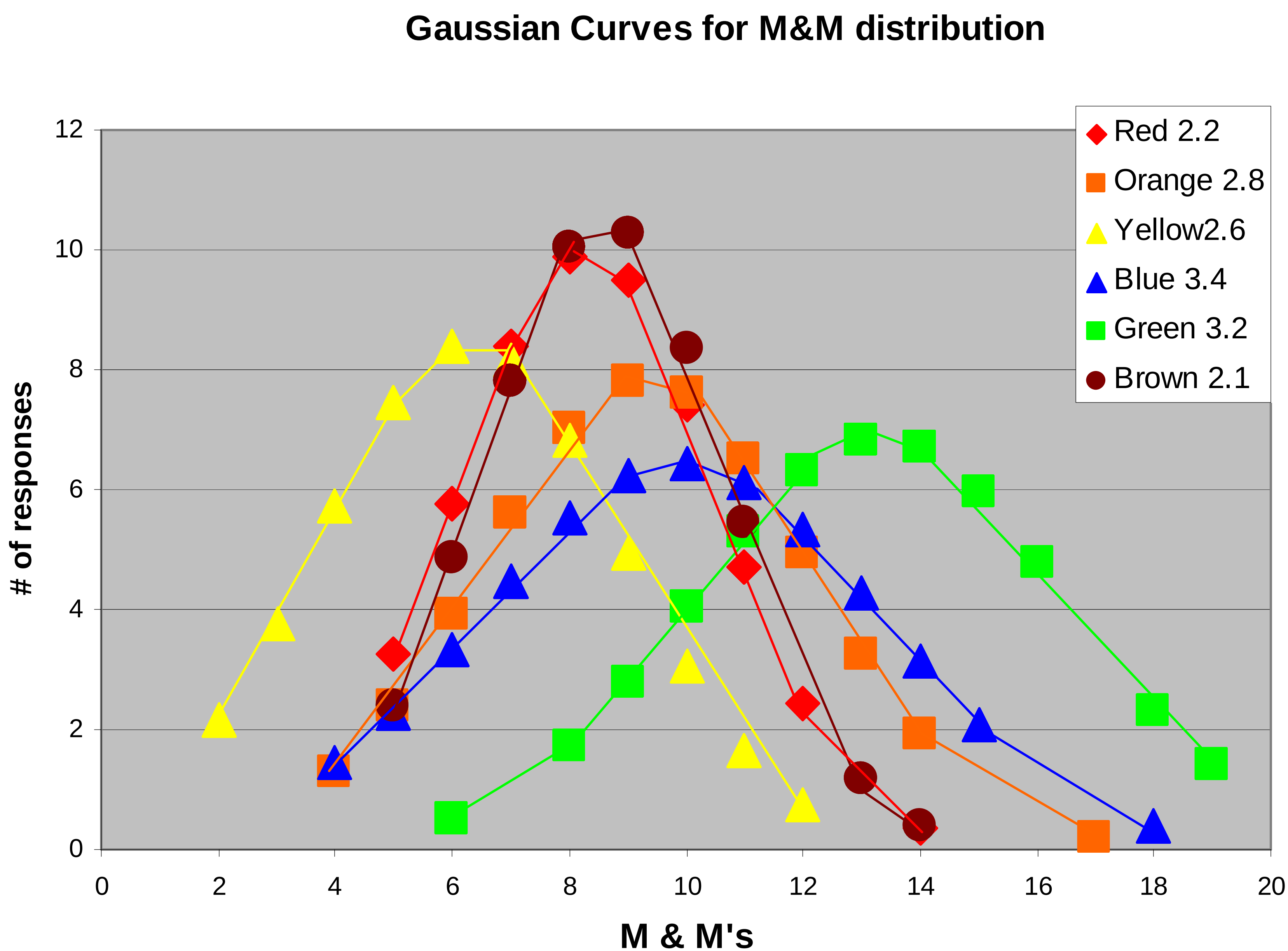


30 data points

Spring ’05 results with 50 data points :
Less Red M&M’s; other colors relatively equal



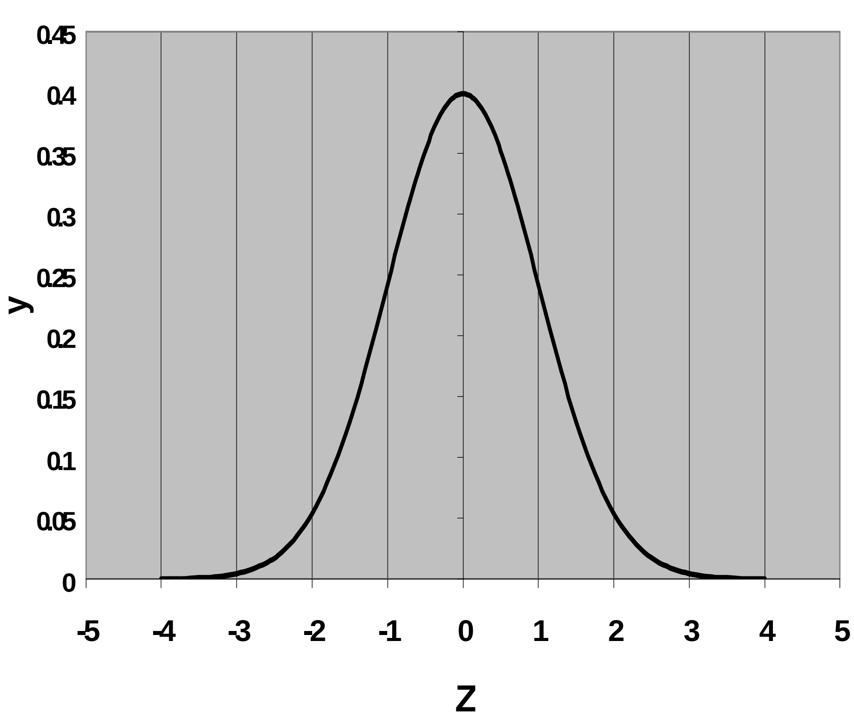
50 data points


Gaussian Curves for M&M distribution
# of responses
M & M's
Red 2.2
Orange 2.8
Yellow2.6
Blue 3.4
Green 3.2
Brown 2.1
0
2
4
6
8
10
12
14
16
18
20

Confidence interval – provides a statistically valid range within which the true value occurs based on a group of measured values

In a population, a Gaussian curve can be used to determine confidence level.

Normal Error Curve



In any Gaussian Curve:

Range	confidence
$\mu \pm 1\sigma$	68.3 %
$\mu \pm 2\sigma$	95.5 %
$\mu \pm 3\sigma$	99.7 %

These % are good when thinking about the **population** as compared to a **sample**.

Confidence Intervals for sample: Student's t

Confidence interval tells you that the true mean, μ, is likely to be within a certain value of the measured mean, x. The confidence interval can be expressed as:

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

where s = measured standard deviation
n = number of measurements
t = value of Student's *t*

t values (Student's *t*) are given in Table 4-2, pg. 58 of Harris. The values are arranged such that you must know the degrees of freedom (n –1), and the confidence level (50%, 90%, 95%, etc.)

Table 4-2 Values of Student's *t*

	Confidence level (%)						
Degrees of freedom	**50**	**90**	**95**	**98**	**99**	**99.5**	**99.9**
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

NOTE: In calculating confidence intervals, σ may be substituted for s in Equation 4-6 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s, the value of t to use in Equation 4-6 comes from the bottom row of Table 4-2.

Statistical Testing for Samples

Common forms of statistical testing encountered by the analytical chemist

- Comparing a result to a group of observations **(the one-sample t-test)**
- Comparing two groups of objects: are the averages different? **(the two-sample t-test)**
- Comparing two standard deviations: **the F-test**
- Testing for outliers: **the Q test**

Example Calculation for Confidence Interval

What is the number of “Green M&M’s” in a bag of M&M’s?

Average = 4.7 St. Dev. = 1.7 # of measurements = 20

What is the 50% and 95% confidence levels for these measurements.

Degrees of freedom = 19 $t_{50\%} = 0.687$ $t_{95\%} = 2.086$
(use an estimate of 20)

$\mu_{50\%} = 4.7 \pm (0.687*1.7)/\sqrt{20} = 4.7 \pm 0.26$ (range 4.44 to 4.96)

$\mu_{95\%} = 4.7 \pm (2.086*1.7)/\sqrt{20} = 4.7 \pm 0.79$ (range 3.91 to 5.49)

Uncertainty can be reduced by increasing the number of measurements

Same example as before, but now you make 5 measurements instead of 20 measurements.

Degrees of freedom = 4 $t_{50\%} = 0.741$ $t_{95\%} = 2.776$
Degrees of freedom = 19 $t_{50\%} = 0.687$ $t_{95\%} = 2.086$

5 measurements: $\mu_{50\%} = 4.7 \pm 0.28$ $\mu_{95\%} = 4.7 \pm 1.05$
20 measurements: $\mu_{50\%} = 4.7 \pm 0.26$ $\mu_{95\%} = 4.7 \pm 0.79$
factor of 1.1 improvement *factor of 1.3 improvement*

SEE THE DIAGRAM AT THE TOP OF PAGE 59 IN HARRIS.

Using the Student's *t* to compare two sets of measurements

We are testing the null hypothesis when comparing the mean values in two sets of data (hypothesis is that the two sets of measurements are statistically the same).

Typically, we are interested in 95% possibility of being correct (1 out of 20 times is wrong).

Cases to Consider:

- Compare our measured values to a known value.
- Compare two different samples measured with the same method (comparing replicate measurements)
- Compare two different methods making measurements on same samples. (comparing methods)

Does my answer agree with the known value at a 95% confidence level?

Calculate a *t* value, and compare to the *t* value from Table 4-2.

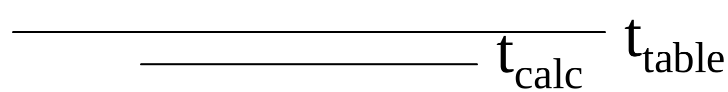
Confidence equation: $\mu = \bar{x} \pm \frac{t\,s}{\sqrt{n}}$

Rearrange: $t_{calc} = (|\bar{x} - \text{known value}| * \sqrt{n}) / s$

Compare t_{calc} to t_{table} .

If $\boldsymbol{t_{calc} > t_{table}}$, your answer does not agree.

If $\boldsymbol{t_{calc} < t_{table}}$, your answer does agree.



Example: How does the measured value of "red M&M's" compare to having a equal distribution of M&M's in bag – i.e. 1/6 of M&M's are red or 3.5 M&M's of the 21 total M&M's?

In order to answer the question, you must determine t_{calc}, and compare it to the t_{table} at 95% confidence.

$$t_{calc} = \left(\left| \bar{x} - \text{known value} \right| * \sqrt{n} \right) / s$$
$$= \left(\left| 3.7 - 3.5 \right| * \sqrt{20} \right) / 1.0$$
$$= 0.89$$
$$t_{table} = 2.086$$

Where:
$\bar{x} = 3.7$
$s = 1.0$
$n = 20$

$$t_{calc} = 0.89 < 2.086 = t_{table}$$

Difference is NOT significant! (statistically same)

Example: Is the chance of getting a brown M&M from a bag of M&M's the same as the chance of getting an orange M&M?

Red M&M: 1.5 ± 1.1 (n = 20)

Orange M&M: 3.8 ± 1.4 (n = 20)

$$t_{calc} = \left(|\bar{x}_r - \bar{x}_o| / s_{pool} \right) * \left(\sqrt{(n_r * n_o)/(n_r + n_o)} \right)$$

$$s_{pool} = \sqrt{[s_r^2 (n_r - 1) + s_o^2 (n_o - 1)]/(n_r + n_o - 2)}$$

$$s_{pool} = \sqrt{[1.1_r^2 (20_r - 1) + 1.4_o^2 (20_o - 1)]/(20_r + 20_o - 2)}$$

$$= 1.585$$

$$t_{calc} = \left(|1.5 - 3.8| / 1.585 \right) * \left(\sqrt{(20 * 20)/(20 + 20)} \right)$$

$$= 4.56$$

$t_{table} = 2.086$

$t_{calc} = 4.56 > t_{table} = 2.086$

DIFFERENCE **IS** SIGNIFICANT (not statistically same)

F-test: Determines if two standard deviations are significantly different from one another.

$$F = \frac{s_1^2}{s_2^2}$$

- **The two samples are arranged so that $S_1 > S_2$**
- **The calculated value of F is compared to the critical value for the sample sizes and confidence level.**

Example:

Yellow M&M – standard deviation = 1.8 (n = 20)

Brown M&M – standard deviation = 1.0 (n = 20)

$F_{calc} = s_Y^2 / s_B^2$ (use s_B in numerator because it is greater than s_Y)

$= (1.8)^2 / (1.0)^2 = 3.24 / 1.00$

$= 3.24$

$F_{table} = 2.16$ *(for degrees of freedom = 19)*

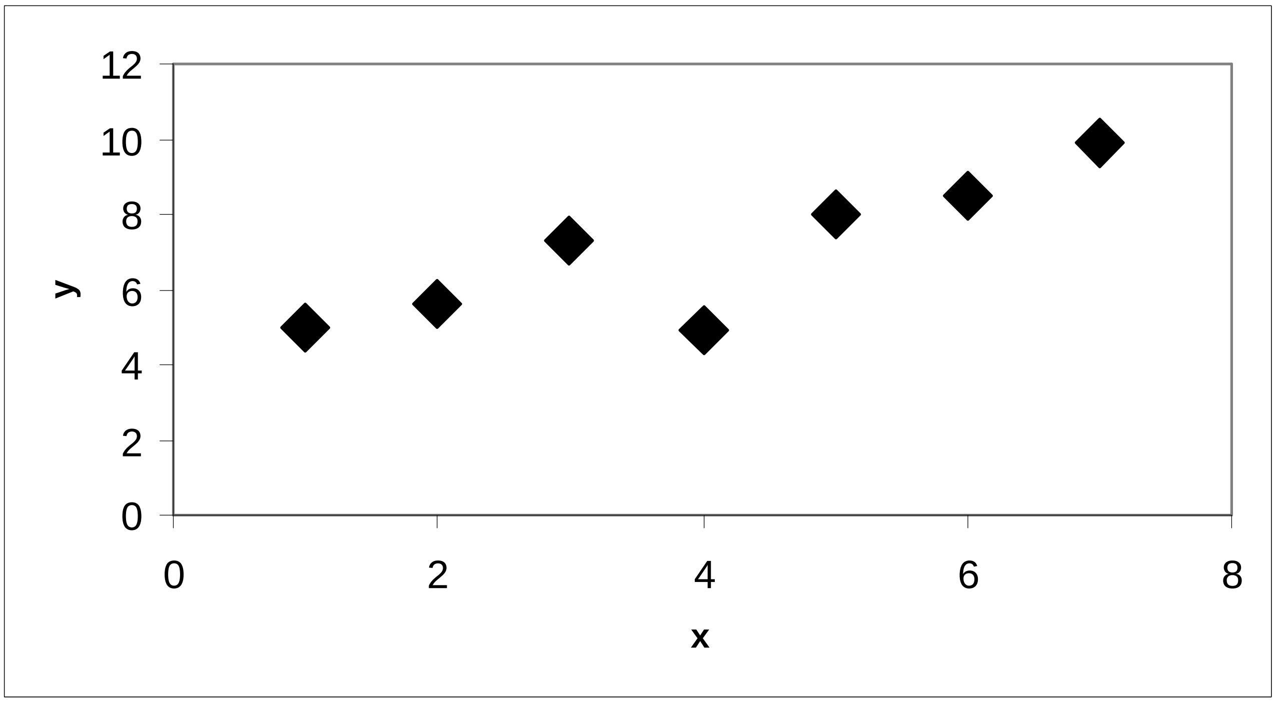
$\mathbf{F_{calc} = 3.24 > 2.16 = F_{table}}$

DIFFERENCE IS SIGNIFICANT

(not statistically same)

Q-test: Determines if a data point is an outlier

- **Used to evaluate the validity of outlying data.**
- **An outlier is a data point that appears unusually different than most.**



Example: Test scores (from last lecture)

90, 89, 68, 95, 100

Steps:

- **List data from low to high: 68, 89, 90, 95, 100**
- **Determine the range: Difference in lowest and highest values (100 - 68 = 32)**
- **Determine the gap: Difference from questionable data point and closest data point (89 – 68 = 21)**
- Q_{calc} **= gap/range = 21 / 32 = 0.66**
- **Compare calculated** Q_{calc} **to** Q_{table} **(from table pg. 75)**

$$Q_{calc} = 0.66 > 0.64 = Q_{table}$$

- $Q_{calc} > Q_{table}$ **the data point *is* considered an outlier and can be removed from the data set.**