Question: **How many times repeat the titrations?**

Answer: **Repeat the titrations at least three times, the results of your three repeated trials should agree within 1.0 % relative range of each other.**

How? **Use the following numerical example:**

You are instructed to determine the concentration (in grams/100 mL) of a solution of Ca^{++} by titration with EDTA of given concentration. The titrations are performed on "precisely equal" 25.00 mL volumes of the unknown solution (aliquots delivered by a 25 mL transfer pipet). The instructions state that you should "**report three determinations of the concentration that have a percent deviation less than 1.0 %**." This translates operationally into the statement: "If the percent deviation of the first three determinations is greater than 1%, you should perform a fourth determination." and so on, until the required percent deviation is achieved.

First Titration:

Your first titration requires**19.40** mL of EDTA.

Second Titration:

The second titration requires **19.95** mL.

While the third titration has not yet been performed.

It is useful to examine the results obtained thus far.

Average = (19.40 + **19.95**) / 2 = **19.68** mL

Average deviation = (| **19.40** - **19.68** |+ | **19.95 - 19.68** |) / 2 = (0.28 + 0.0.27) / 2 =**0.275**

(We must take the absolute value of the deviations)

The percent deviation:

% dev = (**0.275** / **19.68)** X 100 = **1.4 %**

(Larger than the wanted percent deviation 1.0 %)

Third Titration:

We now perform our **third titration** with the result that **19.50** mL of EDTA is required.

Average = (19.40 + 19.95 **+ 19.50)** / 3 = **19.62**

Average dev. = $(|19.40 - 19.62| + |19.95 - 19.62| + |19.50 - 19.62|) / 3$

= (0.22 + 0.33 + 0.12) / 3 = **0.22**

Now, the percent deviation is:

% dev = (**0.22** / **19.62)** X 100 = **1.12 %** (still larger than the prescribed 1.0 %)

Fourth Titration:

Suppose the **fourth titration** requires **19.80** mL of EDTA. The instructions suggest reporting 3 values. Is there a basis for selecting three out of the four? If we have an experimental reason for suspecting one of the titrations, e.g., going past the end point in the titration producing the highest result (**19.95**) we might choose to disregard that determination. Such decisions must be documented in the laboratory notebook. I.e., it should **have been noted, before performing the fourth titration** that the end point was passed in the second titration. If there is no reason to view any of the four titrations as unreliable,

Avg = (19.40 + 19.95 + 19.50 **+ 19.80)** / 4 = **19.66**

Ave. dev. = $(|19.40 - 19.66| + |19.95 - 19.66| + |19.50 - 19.66| + |19.80 - 19.66|) / 4$

Avg dev = (0.26 + 0.29 + 0.16 + 0.14) / 4 = **0.21**

% dev = (**0.21** / **19.66)** X 100 = **1. 1 %** (still larger than the prescribed 1.0 %)

Our percent deviation is still 1.1%. If we have no basis for choosing three of the four, the only strategy is to do a fifth determination and hope that it will fall within the range.

Results & Special Consideration:

Case 1:

If, on the other hand, the titration producing the result **19.95** mL was suspect (i.e., we recognized that the end point was passed in that titration), then we can exclude that value and use the three lower values for the calculation of the average and average deviation. Namely,

Avg = (19.40 + 19.50 + 19.80) / 3 = **19.57**
Avg dev = (0.26 + 0.16 + 0.14) / 3 = **0.19**
and the %deviation is:
% dev = (**0.19** / **19.56)** X 100 = **0.95%**

Which is well below the specified limit of 1%?

The process of "throwing out" the result of a determination must be based on more than the desire to meet the required precision. There is an obvious risk in eliminating a result. We must be sure that the result we eliminate is likely to be wrong.

Case 2:

Suppose, for example that we chose instead to exclude the lowest measurement **19.40** mL.

Avg = (19.95 + 19.50 + 19.80) / 3 = **19.75**

Avg dev = (0.29 + 0.16 + 0.14) / 3= **0.20**
and the % deviation is:
% dev = (**0.20** / **19.75)** X 100 = **1.0 %** (which is now lower than the prescribed 1.0 %)

The likelihood that the small value (19.40 mL) was incorrect becomes much less plausible. The results do not suggest a specific problem with that value. The lower values are now just as likely to be incorrect as the larger values. Suppose, in the above example, the "true" value of the volume was 19.65. What is the accuracy of our determination in each of the above instances in percent?

	Average ± Ave. Dev.	%Dev.	Deviation from "True" Value (Ave. - 19.65)	%Deviation from "True Value 100 (Ave. - 19.65) /Ave.
Third Titration	19.62 ± 0.22	1.1	-0.03	-0.15%
Fourth Titration	19.66 ± 0.21	1.1	0.01	+0.05%
Case 1	19.57 ± 0.19	0.95	-0.08	-0.41%
Case 2	19.75 ± 0.20	1.0	0.1	+0.51%

Note that, while the % deviation in the case 2 is within the prescribed precision, the deviation from the true value is comparatively large. **We have sacrificed accuracy by increasing precision.**

Lessons to be learned:

- **It is dangerous to exclude experimental values unless there is a sound experimental reason to do so. Reporting all of your results will generally improve accuracy, even though the precision may be worse.**
- **With small numbers of determinations, the fact that some cluster near one another does not indicate that they are likely to be closer to the true value than an outlying value.**
- **When exercises describe a target precision, it is better to calculate the precision as the experiment progresses rather than to wait until the end to see if the desired precision has been achieved.**