§2.3.2 The test of the accuracy of the analytical methods-----the judgment of the systematic error

We usually face the following problems when we analyze certain samples:

(1) Is a new analytical method reliable or not?

- (2) Which result is more accurate when the same sample is analyzed by two labs or two persons by using the same analytical method?

For the first problem, we usually compare the new analytical method with the standard method by means of two sets of data.

The difference between two sets of data exists inevitably because of the random error. But the judgment of the systematic error is dependent on the significant difference between two sets of data. And it's also the key point to judge the reliability of the new analytical method and the accuracy of the results. The difference is significant if the systematic error exists. And the difference isn't significant when the result is introduced by random error. We usually use the t test and F test to compare one set of data with another to decide whether they are "the same" or "different" from each other Ⅰ.The comparison between the mean($\bar{X}$) and the standard value($\mu$)--- t test 1.Calculating tc value $t_{计算} = \frac{\bar{X} - \mu}{S/\sqrt{n}}$ 2. Finding the critical t value according to the number of results and confidence level 3. Comparing the tc and the critical t value If $t$c exceeds the critical t value, it represents existence of the significant difference, and the systematic error exists. So the analytical method should be improved. If $t$c isles than the critical t value, the analytical method can be adopted because there is no significant difference. The point at which the titrant added just completely reacts with the analyte. Ⅱ.The comparison between the means of two sets of data ( for the same sample and no standard value) .

The kind of test is usually used to (1) the comparison between the two sets of data by means of new method and standard method (2) the comparison between two sets of data determined by two labs or two analysts 1. t test

The material used to indicate the end point because of the color change near the stoichiometric point.The procedure is as follows:

1) Calculating the pooled standard deviation making use of two sets of data $S_{合} = \sqrt{\frac{(n_1-1)S_1^2 \cdot (n_2-1)S_2^2}{n_1+n_2-2}}$ 2) Calculating the tc ' value: 公式 $t_{合} = \frac{|\bar{X}_1 - \bar{X}_2|}{S_{合}} \sqrt{\frac{n_1 \cdot n_2}{n_1+n_2}}$

3) Finding the critical t value ( the freedom $f = f1 + f2 = n1+n2-2$) 4) Comparing the tc ‘ and the critical value t

2. F test

It’s a comparison between $S21$ and $S22$ of the two sets data.

The F test indicates that the difference between variances or precisions of two sets of data is significant or not. The procedure is as follows:

1) Calculating the Fc value

$$F_{计算} = \frac{S^2_{大}}{S^2_{小}}$$

.

2) Finding the critical F value

3) Comparing the Fc and the critical F value

If Fc exceeds the critical F value, then the difference in variance or precision is significant.

If Fc is less than the critical F value, then there is no significant difference.