

Analysis of variance

Citation: *Anal. Methods*, 2013, 5, 5373

Analytical Methods Committee, AMCTB No 57

Received: 4 September 2013

DOI: 10.1039/C3AN90070

View Article Online

Non-parametric statistical methods, which make few assumptions about the underlying distribution, have often been neglected in the analytical sciences. A major advantage is that methods are often simpler to use than the more complex parametric methods.

Parametric vs. non-parametric?

Analytical scientists generally make replicate measurements and treat them as a random sample, from which estimates are made of the properties of the (hypothetical) infinite population of measurements. The population mean, confidence limits, etc. are usually calculated using the assumption that the underlying distribution is normal (Gaussian), with mean μ and variance σ^2 , etc. It can be summarised as $N(\mu, \sigma^2)$. The terms μ and σ are the parameters of the distribution. Similarly a binomial distribution is described as $B(n, p)$, where the parameters n and p are respectively the total number of measurements and the probability of one of the two possible outcomes.

This parameter-based approach to data handling is not essential, and may not always be appropriate. Some times it is known that a population distribution is not normal or even close to it, so deductions made on the assumption of normality might be unreliable. This is particularly true in cases where the same measurements are made on similar but non-identical sample materials of natural origin. The antibody levels in blood plasma samples from different human subjects are roughly log-normal distributed, with the addition of some subjects with exceptionally high levels in various diseases, etc. Methods that do not make assumptions about the form of the population distribution are called non-parametric or distribution-free methods. In applying them the familiar approach of

significance testing is still used. We set up a null hypothesis H_0 and find the probability of obtaining the actual or more extreme results if H_0 is true: if this probability is smaller than H_0 is rejected. But their simplicity makes non-parametric methods attractive even in situations where more familiar tests such as the t -test might otherwise be applied, as the examples below will show.

Some simple examples

Suppose that an analytical reagent is suspected to have a purity of 99.5%, and that successive batches are found to have purities of 99.2%, 99.8%, 98.9%, 99.4%, 99.1%, 99.3%, and 99.0%. Is there evidence that the purity of the material is lower than it should be? Such results are unlikely to come from a normal population (after all, the maximum possible purity is 100%) so a non-parametric approach could well be safer. A key statistic here is the median: the null hypothesis is that the data come from a population with a median purity level of 99.5%. To carry out the test simply subtract the median from each of the experimental results, and note the sign of the result. This gives six minus signs and one positive sign, i.e. six of the seven results lie below the median. (An result that is equal to the hypothetical median is ignored completely). The probability of getting six (or more) minus signs out of seven is provided by the binomial theorem, but the values are provided in statistical tables, and can be memorised if the analyst makes the same number of measurements. Here the probability of getting 6 or more minus signs is 0.0625, a little higher than the probability level commonly used in significance testing ($\alpha = 0.05$), so we retain the null hypothesis that the results could come from a population with a median purity of 99.5%. As always we have to be prepared that they do come from such a population: we have

failed to disprove it. Note that this is a one-tailed test, as the question is whether the proportion is lower than it should be. With a significance level of 0.05, the null hypothesis would only be rejected if all seven results give minus signs when compared with the median value: this outcome has a probability of only $(1/2)^7 = 1/128$. This method is called the sign test, and it can be extended to other situations, such as comparing two sets of paired results, or studying a possible trend in a sequence of results.