Introduction — systematic vs. random errors

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Quantitative nature of analytical chemistry

Modern analytical chemistry is ovenivhelmingly a quantitative science.

A quantitative answer is much more valuable than a qualitative one. it

may be useful for an analyst to claim to have detected some boron in a

distilled water sample, but it is much more useful to be able to say how

much boron is present.

Often it is only a quantitative result that has any value at all. for

example, almost all samples of (human) blood serum contain albumin;

the only question is, how much 7

Even where a qualitative answer is required, quantitative methods are

used t0 obtain it. Quantitative approaches might be used to compare

two soil samples. For example, they might be subjected to a particle

size analysis, in which the proportions of the soil particles falling within

a riurnben say 10, of particle-size ranges are determined. Each sample

would then be characterized by these 10 pieces of data, which could

then be used to provide a quantitative assessment of their similarity

Errors in quantitative analysis

Since quantitative studies playa dominant role in any analytical

laboratory, it must be accepted that the errors that occur in

such studies are of supreme importance. No quantitative

results are of any value unless they are accompanied by some

estimate of the errors inherent in them!

Example 1 — detecting a new analytical reagent

A chemist synthesizes an analytical reagent that is believed to be

entirely new.

The compound is studied using a spectrometric method and gives a

value of 104.

The chemist finds that no compound previously discovered has yielded

a value of more than 100.

Has the chemist really discovered a new compound?

The answer lies in the degree of reliance to experimental value of 104.

lf the result is correct to within 2 (arbitrary) units, i.e. the true value

probably lies in the range 102 2, then a new material has probably

been discovered.

lf, however, investigations show that the error may amount to 10 units

i.e. 104 10, then it is quite likely that the true value is actually less than

100, in which case a new discovery is tar from certain.

a knowledge of the experimental errors is crucial

Example 2 — replicates in a titrimetric experiment

Analysts commonly perform several replicate determinations in the

course of a single experiment.

An analyst performs a titrimetric experiment four times and obtains

values of 24.69,24.73,24.77 and 25.39 ml.

All four values are different, because of the variations inherent in the

measurements

The fourth value (25.39 ml) is substantially different from the other three.

Can it be safely rejected, so that (for example) the mean titre is reported

as 24.73 ml, the average of the other three readings?

Systematic and random errors

Experimental scientists make a fundamental distinction between random, and

systematic errors. To distinguish between random and systematic errors let

us consider a real experiment.

Four students (A-D) each perform an analysis in which exactly 10.00 ml

of exactly 0.1 M sodium hydroxide is titrated with exactly 0.1 NI

hydrochloric acid.

Each student performs five replicate titrations, with the results shown in

Table 1.1.

Table 1.1 mmm. and syscematrc errors

student Results (mi) comment

A 10.0s 10.11 10.09 10.10 10.12 preezse, biased

is ssa 10.14 10.02 mso 10.21 lm recise unbaaseu

C l°-lg 9-79

D 10.04 9.98 10.02 9.97 10.04 Precise, unbiased J

Graphical illustration

The results of experiment represented by dotplots

Correct

result

3 l

b

C

d

•

9,70 10.00 `|0.30

Titrant velume, ml

The true value is 10.00

Systematic error and bias

Systematic error is a deviation of all measurements in one

direction from the true value.

It is well represented by the difference between the

average value ofthe determined values and the true value

of the measured quantity.

This difference is called the bias of measurements.

Random error and precision

Random error is a deviation of a measurement from the

average of measured values.

It is well represented by the standard deviation of

measurements.

This value is often called precision of measurements.

Combined error vs. accuracy

Accuracy is in inverse relation to the total deviation of a

single measurement from the true value.

Correct

result

6 ¢

b

C

d

`

9.70 10.00 10.50

Titrant volume, ml