APPLIED CHEMICAL AND ISOTOPIC GROUNDWATER HYDROLOGY

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:tection for Li is 0.015 mg/l, then a value of 0.07 mg/l is analytically gnificant (this point is further discussed in section 5.8).

.8 Errors and significant figures

ıs seen in the previous section, measured values are not absolute, but are btained with a certain degree of uncertainty. The uncertainty is caused by he combined effect of several error sources. Four major sources for data ıncertainty have been described in the previous section: *reproducibility*, *ccuracy*, *resolution* and *limit of detection*. To these may be added other actors, e.g. instability of instrumentation, contaminations, accuracy of ıreparation of standard solutions, etc. The sum of all uncertainties is called he *analytical error*. The analytical error is a cumulative outcome of all :rrors involved in a measurement. Data included in a laboratory report ihould always be accompanied by the relevant analytical error, written with ı ± sign, to the right of the result, e.g. 25.62 ± 0.50 mg/l. The analytical :rror is computed by the various laboratories in slightly different ways, but ɔasically is means that if the same water is analysed 100 times, 67 times the data will be in the given range. Thus, to use the last example, 67% of repeated measurements will fall in the range of 25.62 ± 0.50 mg/l, i.e. 25.12 to 26.12 mg/l.

The analytical error is occasionally expressed as a percentage of the obtained value. Thus 25.62 ± 0.50 mg/l, may also be stated as 25.62 mg/l ± 2%.

In certain cases the analytical error is not computed for each value, but given in a general mode, e.g. in the bottom line of a table. For example: Analytical errors: Na: ± 0.50 mg/l, Ca: ± 0.70 mg/l, etc., or: Na: ± 2%, Ca: ± 2.5%, and so on.

The analytical error is needed to decide which data differ from each other with analytical significance: only data that differ by more than the relevant analytical error should be regarded as different for purposes of data processing. Accordingly, data should be reported only in *significant figures*. SO_4^{2-} concentrations of 16.273 mg/l or 106.16 mg/l are meaningless if the analytical error is, for example, ± 0.7 mg/l. In such a case the data should be reported using only significant figures, namely 16.3 mg/l and 106.2 mg/l.

Reaction error. The sum of cations equals the sum of anions in each solution. Hence, the same should be true for reported laboratory data and the deviation from such an equality provides another way to assess data quality. The equation used is:

$$\text{Reaction error} = \frac{\Sigma_{\text{cations}} - \Sigma_{\text{anions}}}{\Sigma_{\text{ions}}} \times 100$$

The reaction error is thus expressed as a percentage of the total ion concentration. Positive reaction errors indicate cation excess and negative errors indicate anion excess. Reaction errors are caused by:

- The analytical errors of the individual parameters.
- The fact that not all possible ions are commonly measured.

In certain cases it is worthwhile to enlarge the list of ions analysed in order to lower the reaction error: for example, to include No_3^-, Fe^{3+}, or PO_4^{4-}.

At the beginning of each study a decision has to be made which reaction errors will be acceptable. The cut-off at 2% or 5% is common. Analysis with high reaction errors are omitted in the data processing and, if possible, they are discussed with the laboratory personnel.

5.9 Checking the laboratory

Only in rare cases do field hydrochemists themselves measure all the parameters. In most cases samples are sent to laboratories for part, or all, of the measurements. It is the hydrochemist's duty to discuss with the laboratories their data quality, and obtain, at least, the analytical error and limit of detection for each parameter measured. In addition, laboratories should be checked by their clients. There are several kinds of laboratory checks. The most important are:

Duplicate samples. Each batch of samples sent to the lab should include duplicates of one sample, sent with different names and sample numbers. The results for the duplicate sample give a fair picture of the quality of the data. If the duplicates fall in the range of the quoted analytical error, the data for the whole batch of samples is acceptable. If, however, the duplicate values differ by more than the stated analytical error, the results should be discussed with the laboratory personnel and the data of the whole sample batch should be regarded questionable. The differences observed between duplicate samples of several sample batches establish, eventually, the analytical error, of the specific laboratory for each parameter.

Dilution of a sample with measured amounts of distilled water. The results of the diluted sample are acceptable if they agree with the calculated diluted value, within the stated analytical error.

Example: a water sample has been diluted with 1 volume of distilled water. The laboratory results for Mg were 105 mg/l for the non-diluted sample, and 52,9 mg/l for the diluted sample and the analytical error was 0.8 mg/l. Thus, the reported diluted value, 52.9 ± 0.8 mg/l, included in its range the calculated value for 1:1 diluted sample, 52.5 mg/l, and the Mg data of the laboratory may be accepted for the whole batch.

Standard water sample. A highly recommended procedure is to collect a large sample of groundwater, keep it in a cold dark place (to avoid bacterial