

## Uncertainties and limits of quantification

The database Allaska contains quantitative information on the properties of combustion residues in a condensed form. By performing searches in Allaska, the user can retrieve values for the variables of interest, and a reference to the source of the data. In order for the report from a search to be easily readable at a first glance, the results are summarised using statistical parameters such as mean, median, maximum and minimum.

The uncertainties or the errors in the figures are not presented. In the chemical analyses, there are limits of detection or of quantification for a substance. These give rise to questions, first on their representation in Allaska, second on their handling in the report from a search.

### Uncertainty

The values stored in the database are the result from a test or an analysis (e.g. of the chemical composition). The error limits or uncertainties attached to this value are not stored in Allaska, the main reason being that this information is seldom made available to those managing Allaska.

The only way to learn about the uncertainties in a value is therefore, in a first step, to go to the report for the work originating the value. In the best of cases, the desired information will be found there. In most cases, the protocols from the laboratory performing the analysis will not have been reproduced in facsimile in the report. Next step is to take contact with the performer of the research in order to obtain the original protocols.

It may though be useful to know that the uncertainty in most chemical analyses (composition and leaching tests) usually is 20 – 30 % of the value reported. This corresponds to a confidence level of 95 %. For other tests, the user is referred to the original reports.

### Limit of detection or of quantification

The methods of chemical analysis do not have an unlimited sensitivity. There is a concentration in the sample below which a value for the parameter cannot be obtained: the response is so small that one cannot know if this is the actual value of the effect or if it is background noise. In reports from analyses, this is reported as n.d.<sup>1</sup> or with the sign < and a numerical value.

Although the word limit of detection is commonly used, this is actually a limit of quantification (LOQ).

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<sup>1</sup> The letters n.d. mean "not detected", i.e. the substance could not be detected and quantified with the method of analysis that was used

There are different schools of thought regarding how values for single samples should be reported in a collection of data for several samples<sup>2</sup>:

- With the value 0
- With half the value of the limit of detection or of quantification
- With the value of the limit of detection or quantification
- With no value at all (n.d. or blank)

In the initial phases of work with Allaska, it was decided not to ascribe any value to the actual parameter when the report from the analysis stated a value “less than”. It was felt that the value for the user of the database of reporting < 60 mg/kg for all analyses of e.g. tin (Sn) was limited. Furthermore, Access could not manage values with a < or a > sign.

However, the consequence is that in the report from a search, the concentration of chromium can be the mean of 35 values while that for mercury is the mean of 2 values. This could be interpreted as the 33 values not reported for mercury were all below the limit of quantification, but also as follows: for some samples, the value was below the limit of quantification and for some other samples, mercury was not analysed at all.

Consequently, only the highest mercury concentrations enter into the mean reported for a search, which mean is an overestimate of the probable mean value.

Of course, this is not satisfactory. In 2008, the Access interface of Allaska has been modified: a flag has been introduced to signify the sign <, implying that that particular value is a limit of detection or of quantification. Beginning with 2008, new values have been entered using this flag when needed. During 2009, data entered before 2008 are being reviewed and complemented.

The statistics (mean and median) will therefore be computed using the LOQ where the real value is lower than the limit and the real value when this exceeds the LOQ from 2009 onwards.

## **Sum of concentrations**

The question of values below LOQ is important also in another context: when the concentrations of a series of substances are added to a sum of concentrations. This is found for e.g. PAH, PCB and PCDD/F<sup>3</sup>. Such data have not yet been registered in Allaska (per 2009-01-01), but it may be expected that such data will become available in the near future.

In a chemical analysis of a group of substances such as PAH's the concentrations of individual substances are added together and a “Sum EPA 16” is obtained – the sum of the concentration of 16 PAH substances. When the concentration of one or of several substances is below LOQ, one uses LOQ or half the LOQ value as input in the sum.

A consequence of this procedure is that the sum concentration may exceed an environmental limit value even if none of the substances could be detected, if LOQ is rather high in comparison to this limit value. If the method of analysis has a LOQ of 0.2 mg/kg for all

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<sup>2</sup> See t ex Helsel D R; ”Fabricating data: how substituting values for non-detects can ruin results, and what can be done about it”, Chemosphere 65(2006), sid 2434-2439

<sup>3</sup> PAH, Polycyclic Aromatic Hydrocarbons, PCB, PolyChlorinated Biphenyls, and PCDD/F, PolyChlorinated DibenzoDioxins and –Furans (commonly called dioxins and furans)

substances in the EPA 16 PAH, the sum concentration will be 3.2 kmg/kg, which value is then compared with a limit value of 2 mg/kg.

## **Blank samples**

Samples are contaminated when they are taken, when they are transported or stored or handled in the laboratory. The concentration value that is reported may at times reflect the environment in the laboratory more than the sample. In order to show this, it is customary to use a so-called blank sample, i.e. an empty sample vial that will be processed as real samples. This is routine in analyses of PCDD/F or phthalates.

If the result of the analysis of the sample is at the same level as the result of analysis of the blank sample, this is a variant of the LOQ case. One reports the concentration value and adds the words "at the same level as the blank sample" in a parenthesis. These words are usually dispensed with when data for several samples are collected in a larger report for an investigation.

## **Degree of recovery**

Under certain circumstances, the concentration value obtained for a substance may be significantly lower than the real concentration: it was not fully extracted in the treatment of the sample. This happens a.o. for aromatic substances such as PAH's that are strongly bound to unburned carbon in an ash. One may then add an internal standard to the sample, and the ratio between the quantity found in the analysis and the quantity added is stated as a degree of recovery. A low degree of recovery, e.g. 10 %, implies that the actual concentrations of the substances are significantly higher than the concentrations reported.

## **Outliers**

In a collection of values for a parameter, one or several values may deviate strongly from the other values.

One cannot say whether a value is "wrong" or which value is "wrong" only on the basis of data in Allaska. One has to investigate the original data.

The reasons for large deviations are many:

- Deficiencies in sampling – the sample is not representative for the heterogeneous material as sampling did not eliminate the impact of variations between the different components. Strong variations are more common for occasional samples than for samples taken over a long period of time
- Errors in the analyses, transcription errors
- The sample has been contaminated
- The sample is not what one thinks it is

All values are checked before they are entered into Allaska. In spite of this, obviously erroneous values may occur, e.g. 870 % for a concentration. If such is the case, please take contact with Svenska Energiaskor, the value will be checked once more against the original report and corrected.