

Elemental Analysis Manual

for Food and Related Products

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3.2 Analytical Figures of Merit

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GLOSSARY

Establishment and monitoring of several analytical figures of merit are performed to ensure data quality and reliability. Before routine analytical operations, these figures of merit are characterized for a chemical measurement system and specific to a particular instrument and laboratory. The information is generated using operating conditions and standardization routines that will be used for routine sample analysis. The figures of merit are determined initially and then re-determined or verified at least once a year or when there are significant changes to the analysis (*e.g.*, instrument hardware, instrument operating conditions, reagent quality, personnel). The established figures of merit are applied to routine analyses performed by the laboratory.

Not all of the figures of merit given below apply to all methods.

3.2.1 INSTRUMENT

- (1) Instrumental detection limit (IDL)—an estimate of the lowest analyte concentration that an instrument can detect in a standard blank according to the statistics of hypothesis testing, with a 95% confidence such that the probabilities of false positives (α) and false negatives (β) are both 0.05.

IDL is based on at least 5 concentration measurements (to at least 3 significant digits) of a standard blank. IDL is calculated as follows and the result is rounded up to the next greatest two significant-digit number.

$$IDL = 2 \times t_{0.95} \times \sqrt{1 + \frac{1}{n}} \times s$$

where

$t_{0.95}$ = one-sided Student's t at 95% confidence level

s = standard deviation of the standard blank measurements

The value of $t_{0.95}$ is dependent on the number (n) of measurements and a table of $t_{0.95}$ values is provided in 3.2 Table 1. Units of IDL are usually the same as the standard solutions.

- (2) Characteristic mass (m_o)—mass of analyte that produces an integrated absorbance signal of 0.0044 A-sec (or 0.0044 absorbance if peak signal).

Characteristic mass is associated with graphite furnace atomic absorption spectrometry and is a function of instrument design, operating conditions and analyte-matrix-graphite interactions. Characteristic mass is calculated from the volume and concentration of solution injected into the graphite furnace. The concentration of analyte in the solution used to calculate m_o should be chosen to result in an instrument response in the middle of the working range (*i.e.*, approximately 0.050 A-sec). A mean m_o is calculated over time from daily values for a given set of operating conditions to represent an instrument-method combination. Several weeks of data should be used for calculating the m_o . If operating conditions are new and thus no historical mean value exist then the m_o is the manufacturer's stated m_o for the instrument. Units of m_o are usually pg.

- (3) Linear dynamic range (LDR)—portion of the response range of the analytical instrument having a linear relationship between response and analyte concentration.

Establish the upper limit of the LDR for each analyte and set of instrument conditions by measuring response of at least 6 standards, with the concentration of the two highest standards near the estimated upper limit. LDR upper limit is that point at which response for a given standard is 5% below the level linearly extrapolated from the 4 lower standards. However, if the LDR extends upward beyond the useful range for analysis, the LDR range needs to be verified only as high as will be useful for analysis. LDR lower limit is the analytical solution detection limit (ASDL). Knowing the upper limit is especially important when using method of standard additions for quantification. The combined signal from the native level plus additions must be within the LDR.

- (4) Sensitivity (\hat{A})—ratio of instrument response to solution concentration. Instrument sensitivity is compared to manufacturer specifications to verify that the instrument is optimized.

The sensitivity is calculated using the response of a standard solution in the middle of the analyte's LDR as follows.

$$\text{Sensitivity, } \hat{A} = (R_s - R_b) / C_s$$

where

R_s = response of standard solution

R_b = response of standard blank

C_s = concentration of analyte in standard solution (*e.g.*, $\mu\text{g/L}$)

Instrument sensitivity may also be represented by the slope of the least squares regression obtained from the standards used for standardization. Units of \hat{A} are the response units/standard solution concentration units.

3.2 Table 1. Student's t-Distribution for 1 to 20 Degrees of Freedom at the 95% Confidence Level, one-sided

n	Degrees of freedom	$t_{0.95}$
2	1	6.314
3	2	2.920
4	3	2.353
5	4	2.132
6	5	2.015
7	6	1.943
8	7	1.895
9	8	1.860
10	9	1.833
11	10	1.812
12	11	1.796
13	12	1.782
14	13	1.771
15	14	1.761
16	15	1.753
17	16	1.746
18	17	1.740
19	18	1.734
20	19	1.729
21	20	1.725

3.2.2 ANALYTICAL SOLUTION

MBKs used for establishing a figure of merit for analytical solutions should represent a laboratory's normal operation over an extended period. Use of long term accumulated MBK results and more than the minimum number of measurements will provide values that are more appropriate.

- (1) Analytical solution detection limit (ASDL)—an estimate of the lowest analyte concentration that an instrument can detect according to the statistics of hypothesis testing, with a 95% confidence such that the probabilities of false positives (α) and false negatives (β) are both 0.05.

ASDL is based on the analyte concentration measurements (to at least 3 significant digits) of at least 5 independently prepared method blanks (MBKs) having analyte concentration between ASDL and the analytical solution quantification limit (ASQL). If an analyte's concentration in the MBK is below ASDL, then the MBK is fortified with the analyte at a level between ASDL and ASQL. This fortification should be accomplished gravimetrically so that the resulting variations will be due to the variations in MBK only and will not include pipetting variations. ASDL is calculated as follows and the result is rounded up to the next greatest two significant-digit number.

$$\text{ASDL} = 2 \times t_{0.95} \times \sqrt{1 + \frac{1}{n}} \times s$$

where

$t_{0.95}$ = one-sided Student's t at 95% confidence level

s = standard deviation of the concentration measurements of the MBKs (or MBKs fortified)

The value of $t_{0.95}$ is dependent on the number (n) of measurements and a list of $t_{0.95}$ values is provided in 3.2 Table 1. Units of ASDL are usually the same as for the standard solutions.

Note: The first time ASDL is determined, ASDL is estimated for assessing the need for MBK fortification. For example when using a GFAAS method, estimate ASDL as (a) $2 \times \text{characteristic mass}$ (converted to solution concentration), (b) $2 \times \text{IDL}$, or (c) a concentration that would be expected to give a relative standard deviation of about 50% for repeated measurements.

- (2) Analytical solution quantification limit (ASQL)—analytical solution's analyte concentration that has a relative standard deviation of 10%.

ASQL is equal to 30 times the standard deviation of the MBK's concentration measurements (or MBKs fortified with analyte). The same MBK concentration measurements used to calculate ASDL are used to calculate ASQL. ASQL is calculated as follows and the result is rounded up to the next greatest two significant-digit number.

$$\text{ASQL} = 30 \times s$$

3.2.3 ANALYTICAL PORTION

- (1) Limit of detection (LOD)—an estimate of the lowest analyte concentration that a method can detect in an analytical portion according to the statistics of hypothesis testing, with a 95% confidence such that the probabilities of false positives (α) and false negatives (β) are both 0.05.

LOD is the ASDL, derived from MBKs, adjusted for the analytical portion's mass and dilution. The result is rounded up to the next greatest two significant-digit number (round on basis of 3 digits only).

$$\text{LOD (mg/kg)} = \text{ASDL} \times \frac{V}{m \times \text{MCF}} \times \text{DF}$$

where

ASDL = Laboratory's ASDL (mg/L)

V = volume of analytical solution (L)

m = mass of analytical portion (kg)

MCF = mass correction factor (1 if water or other solvent not added to aid homogenization)

DF = dilution factor (1 if analytical solution not diluted)

Concentration may be converted to other convenient units (*e.g.*, $\mu\text{g/kg}$, ng/kg).

- (2) Limit of quantification (LOQ)—an estimate of the analyte concentration in an analytical portion that would have a total analytical uncertainty of 10% at 67% confidence (one sigma).

LOQ is the ASQL, derived from MBKs, adjusted for the analytical portion's mass and dilution. LOQ is calculated as follows and the result is rounded up to the next greatest two significant-digit number (round on basis of 3 digits only).

$$\text{LOQ (mg/kg)} = \text{ASQL} \times \frac{V}{m \times \text{MCF}} \times \text{DF}$$

where

ASQL = Laboratory's ASQL (mg/L)

V = volume of analytical solution (L)

m = mass of analytical portion (kg)

MCF = mass correction factor (1 if water or other solvent not added to aid homogenization)

DF = dilution factor (1 if analytical solution not diluted)

Concentration may be converted to other convenient units (*e.g.*, $\mu\text{g/kg}$, ng/kg).

Note: The procedures for determining LOD and LOQ are consistent with those given in documents of the International Union of Pure and Applied Chemistry and the International Organization for Standardization¹.

REFERENCES

- (1) Currie, L. A. (1999) Nomenclature in Evaluation of Analytical Methods Including Detection and Quantification Capabilities (IUPAC Recommendations 1995), *Anal. Chim. Acta* (1999) **391**, 105-126.