PAC Technical Note

Antek ElemeNtS Limit Of Detection calculation according to ISO 11843

- Low level Sulfur and/or Nitrogen measurements
- Software integrated LOD calculation according ISO 11843
- LOD of 20 ppb for Sulfur & 30 ppb for Nitrogen

Keywords: ElemeNtS, sulfur, nitrogen, detection limit (LOD), ISO 11843

INTRODUCTION

“Detection limit” or “lower limit of detection” are frequently used terms in the (instrumental) analytical chemistry and say something about the lowest concentration level of a substance one can measure.

The concept/definition of the limit of detection (LOD) has been, and still is, regularly subject of discussion in the instrumental analysis industry if only because of the importance of the parameter. There are multiple definitions and calculation methods, however LOD is usually defined as the lowest quantity or concentration of a component that can be reliably detected with a given analytical method. So one could consider the LOD to be the lowest concentration obtained from the measurement of a sample (containing the element) that we would be able to discriminate from the concentration obtained from the measurement of a blank sample (a sample not containing the element).

ANTEK ELEMENTS

Recently PAC introduced the Antek ElemeNtS, being the most advanced, modular analytical system for the measurement of total Sulfur and/or Nitrogen in liquids, gases and LPG samples. The ElemeNtS analyzer detects these substances using an Ultraviolet (UVF) or Chemiluminescence detection technique.

Measuring and detecting total Sulfur and/or Nitrogen at the lowest possible concentration is of great importance in the Hydrocarbon Processing Industry (HPI), as Sulfur and/or Nitrogen have many undesirable effects like catalyst poisoning, detrimental product quality and ecosystem pollution.

$$R - S + O_2 \xrightarrow{1050°C} CO_2 + SO_2 + H_2O$$

$$SO_2 + hv \rightarrow SO_2^*$$

$$SO_2^* \rightarrow SO_2 + hv$$

Figure 1A: UVF analysis principle for Sulfur detection

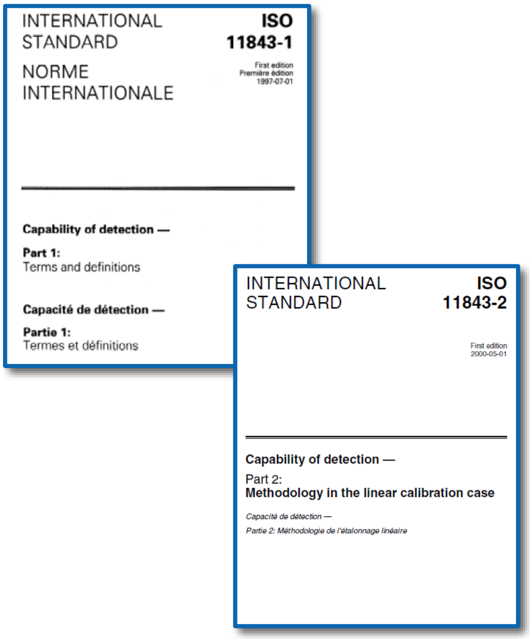
$$R - N + O_2 \xrightarrow{1050°C} CO_2 + NO + H_2O$$

$$\mathrm{NO} + hv \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + hv$$

Figure 1B: Chemiluminescence analysis principle for Nitrogen detection

ISO 11843 INTRODUCTION



INTERNATIONAL STANDARD
NORME INTERNATIONALE
ISO 11843-1
First edition
Première édition
1997-07-01

Capability of detection —

Part 1:
Terms and definitions

Capacité de détection —

Partie 1:
Termes et définitions

INTERNATIONAL STANDARD
ISO 11843-2
First edition
2000-05-01

Capability of detection —

Part 2:
Methodology in the linear calibration case

Capacité de détection —

Partie 2: Méthodologie de l'étalonnage linéaire

ISO creates documents that, amongst others, provides specifications and guidelines, that can be used consistently to ensure that products, processes and services are fit for their purpose.
PAC has therefore integrated in the ElemeNtS software an LOD calculation according to "***ISO 11843 – Capability of detection***". ISO 11843 consists of multiple parts where Part 1 describes the used "Terms and definitions" and part 2 the actual methodology in a linear calibration case (as used for the ElemeNtS). The other parts are of less importance for this analysis technique.

The software calculates the "***critical concentration***" and "***LOD***" as defined by the ISO 11843 based on an actual calibration in a 0 – 1 mg/l concentration range. These parameters (critical concentration and LOD) are including all uncertainties like the number of calibration levels, number (and quality) of calibration standard preparation, number of injections ("repeats"), detector sensitivity, etc.

The ISO 11843 calculation model is based on three assumptions:

- The calibration is a linear function.
- Measurements are normally distributed around a mean value.
- The standard deviation is constant, or it forms a linear function of the values of the net state variable.

CRITICAL CONCENTRATION

The **critical concentration** is defined as "*the value of the net concentration (or amount) the exceeding of which leads, for a given error probability α, to the decision that the concentration (or amount) of the analyte in the analyzed material is larger than that in the blank material*" (see fig 2).

One could also describe critical value as the minimum response which can be differentiated significantly (95%) from the blank response.

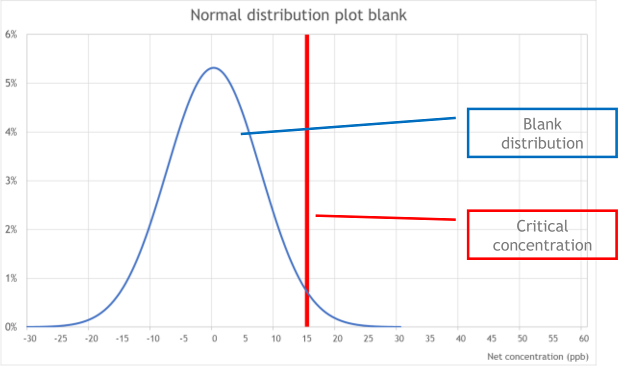


Figure 2: Normal distribution plot of multiple blank analysis

The calculation is using a "95% certainty", and α is defined in the method "*as the probability of detecting (erroneously) that a system is not in the basic state when it is in the basic state (blank)*" (so in this case 5% or "1 out 20").

MINIMUM DETECTABLE NET CONCENTRATION

The minimum detectable net concentration (x_d) is defined as "true net concentration (or amount) of the analyte in the material to be analyzed which will lead, with probability (1-ß), in this case again 95%, to the conclusion that the concentration of the analyte in the analyzed material is larger than that in the blank material.

Or as described in the ISO method: "*the probability is β of (erroneously) not detecting that a system, for which the value of the net state variable is equal to the minimum detectable value (x_d), is not in the basic state*".

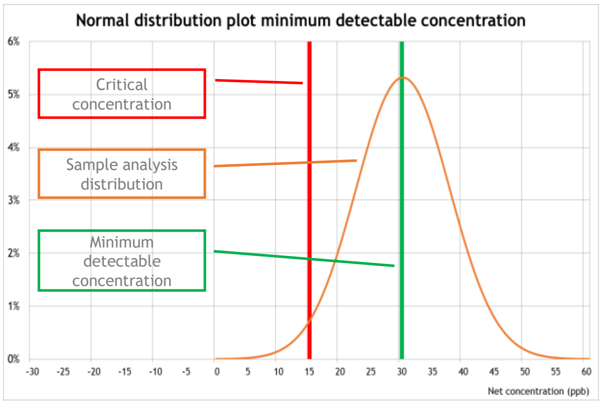


Figure 3: Normal distribution plot minimum detectable concentration

The minimum detectable value derived from a particular calibration indicates the capability of detection of the actual system measurement process ("detection limit").

The software calculates the LOD (x_d = minimum detectable concentration) as an approximate by 2 * critical concentration (x_c). This is based on paragraph 5.2.4 of ISO 11843-2 where it is described that with an error probability (for both α and ß) of 5% and a sufficient numbers of freedom (should be >3) the minimum detectable concentration is two times the critical concentration ($x_d = 2\,xc$).

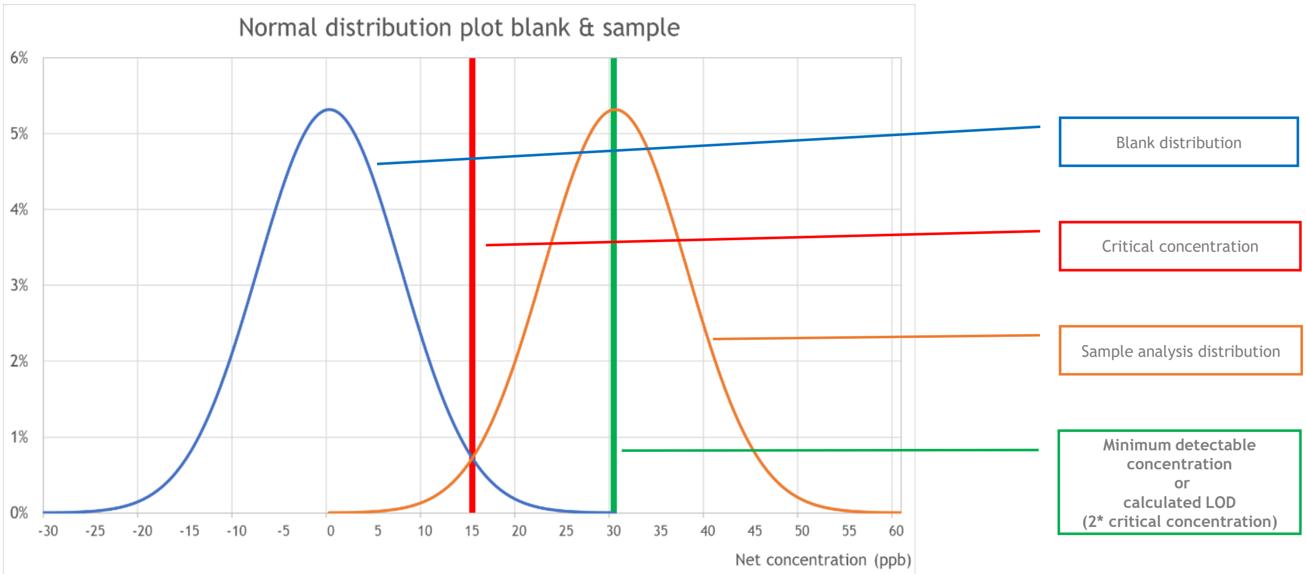


Figure 4: Normal distribution plot minimum detectable value (or LOD)

ANTEK ELEMENTS SOFTWARE

To calculate the critical concentration and minimum detectable net concentration of the system one needs to calibrate it at a 0 – 1 mg/L range (or lower). Each level should be analyzed from duplicate samples/vials in five repeated analysis, from these analysis a linear calibration curve is calculated.

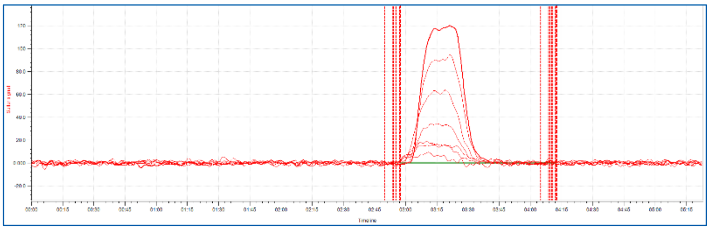


Figure 5A: Overlay of Sulfur 0-1 mg/L *calibration analysis*

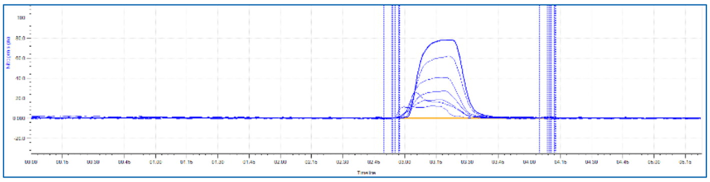
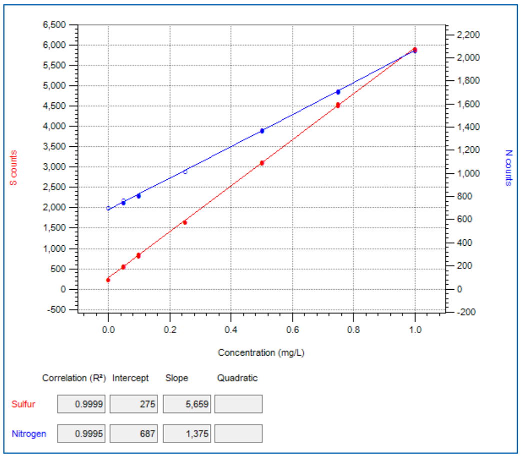


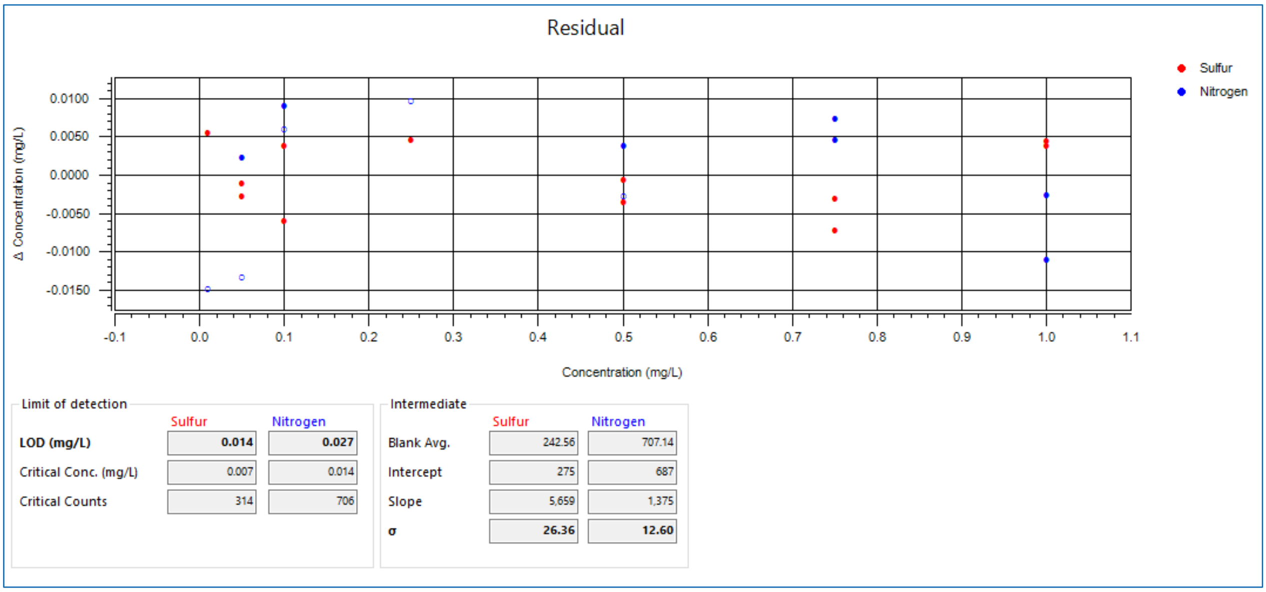
Figure 5B: Overlay of Nitrogen 0-1 mg/L *calibration analysis*



	Correlation (R²)	Intercept	Slope	Quadratic
Sulfur	0.9999	275	5,659	
Nitrogen	0.9995	687	1,375	

Figure 5C: Calibration curve 0-1 mg/L *for both Sulfur & Nitrogen*

For all the calibration points the residuals are calculated relative to the best fit correlation as displayed in the calibration tab (found value for calibration point minus the predicted value from linear calibration curve). The statistical tab in the instrument method (fig 6) shows a graphical overview of these residuals.



Limit of detection

	Sulfur	Nitrogen
LOD (mg/L)	**0.014**	**0.027**
Critical Conc. (mg/L)	0.007	0.014
Critical Counts	314	706

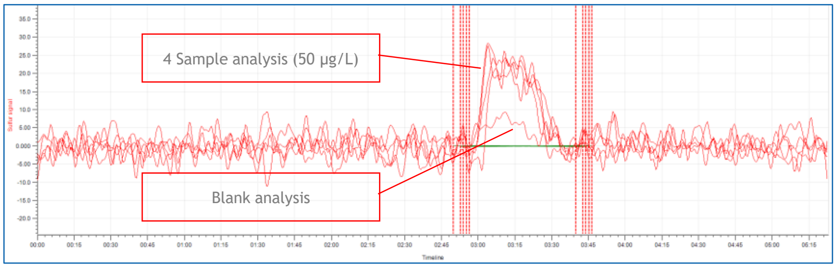
Intermediate

	Sulfur	Nitrogen
Blank Avg.	242.56	707.14
Intercept	275	687
Slope	5,659	1,375
σ	**26.36**	**12.60**

Figure 6: Residual plot for 0-1 mg/L S & N calibration

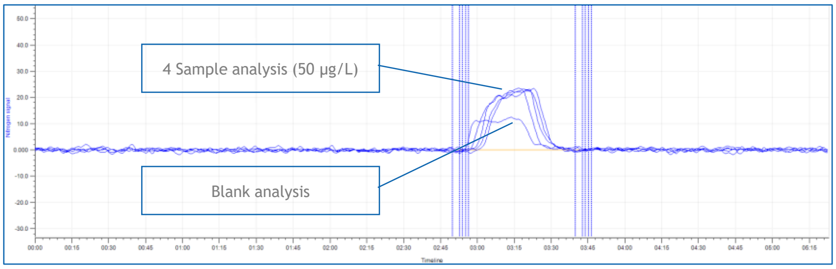
Based on this residual data and other parameters the Critical Concentration and LOD (minimum detectable limit) are calculated as described in ISO 11843. From this calculation, we can conclude that for the selected range (0-1 ppm) the response of the ElemeNtS instrument is linear since the residuals are evenly distributed over the complete range. In accordance to ISO-11843 a good fit of the model and low RSD's will result in a low calculated limit of detection.

For this specific data the calculated LOD (based on above described procedure) is 0.014 mg/L Sulfur and 0.027 mg/L. The following plots (fig 7) show an analysis of a 50 µg/L S & N sample and the results of it calculated based on the above calibration.



Sulfur results in µg/L		
target	found	RSD (n=5)
50	51	6.4
50	54	12.5
50	53	1.1
50	46	2.9

Figure 7A: Overlay of multiple analysis of a 50 µg/L *Sulfur standard analyzed as sample and a blank*



Nitrogen results in µg/L		
target	found	RSD (n=5)
50	51	0.7
50	51	3.6
50	49	0.1
50	55	1.8

Figure 7B: Overlay of multiple analysis of a 50 µg/L *Nitrogen standard as sample and a blank*

CONCLUSION

Since the limit of detection or minimum detectable limit is of great importance and often subject of discussion PAC has integrated a functionality in the Antek ElemeNtS software to calculate the minimum detectable level (LOD) according ISO 11843 part 1 & 2.

This method uses a statistical calculation to define the critical concentration (using a 95% certainty), based on an actual calibration of the system. The minimum detectable limit is derived from the critical concentration (again using a 95% certainty). These calculations include all variable effecting the results, like calibration standard accuracy, repeatability of sample introduction, etc.

Paragraph 11.6 of ISO 11843: ***The minimum detectable value of the measurement method may be used for the selection of measurement processes and method for further measurements. And the measurement processes or measurement method is suitable for a certain measurement task if the minimum detectable value is equal to or smaller than a specified concentration (e.g. a specified requirement on scientific, legal or other reasons regarding the capability of detection).***

The Antek ElemeNtS is capable of reaching an **LOD** of **20 ppbw for Sulfur** and **30 ppbw for Nitrogen**. These values have been determined using hydrocarbon matrices, dedicated calibration and optimized instrument configurations with analysis conform ISO 11843. For specific applications, LOD needs to be validated.

Antek's lab instruments provide reliable, precise elemental analysis for total nitrogen and sulfur, speciated nitrogen and sulfur, fluoride, chloride, and bromide. Antek products are recognized by global regulating bodies, leading scientific research institutions, and process laboratories as the instrument of choice for selective multi-element detection.