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# An Experimental Estimation of Two Detection Limit Models

Chang-Jin Ma*, Susumu Tohno, Mikio Kasahara and Gong-Unn Kang[1)]
*Department of Socio-Environmental Energy Science,*
*Graduate School of Energy Science,*
*Kyoto University, Uji, Kyoto 611-0011, Japan*
[1)]*Department of Environmental Science, Wonkwang Health Science College,*
*Iksan, Jeonbuk 570-750, Korea*

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## Abstract

In environmental studies, decisions are often made on the analytical data indicating certain contaminants as being "detected" or "non-detectible." Since detection limits are analytical method specific, one has to first review the concepts and definitions associated with analytical method systems and specifications. In this study, the experimental analytical values for a series of low level standards (for an ionic species) were used as an example to estimate two different method detection limits (MDL). The scores of EPA's MDL and Pallesen's MDL determined by real analytical scores are 0.0575 and 0.0561 mg/L, respectively for our nitrate data. These scores determined by two different MDL models are roughly similar, while there are apparent differences between two methods with respect to statistical and systematical procedure. However, determination of MDL for one's laboratory provides some practical applications which helps to assure one's regulating authorities that one's measured scores are accurate.

**Key words** : Detection limit, Quality assurance/Quality control, Data interpretation, Environmental measurement.

## 1. INTRODUCTION

Sound environmental analytical measurements are essential to provide the data required to ensure the quality of the environment and the health of the public. A quality assurance program including quality assesment (QA) and quality control (QC) is a prerequisited part of a sound data interpretation. Though QA/QC is not a new concept, there is a clear need for its wider use by researcher engaged in analytical measurement. Individual investigators as well as a laboratory organization should use QA/QC to detect and correct problems and take reasonalbe steps needed to keep the measurement process reliable (MacDougall and Warren, 1980).

The literatures in the field of analytical chemistry reveal numerous and often confliction definitions and prodedures for estimating a lower limit of detection for nonrepeated determinations. It is generally agreed that the formulation of a detection limit should account for the uncontrolled, random fluctuations of the entire anlytical process and protect against making misclassification errors (Holland and McElroy, 1986; Oppenheimer *et al.*, 1983; Currie, 1968). More infor-

* Corresponding author.
E-mail : ma@uji.energy.kyoto-u.ac.jp, Tel : +82-(0)63-840-1274

mation can be gained when a numerical result and an estimate of measurement precision are reported for every measurment, as opposed to reporting "not detected"or "less than" (Porter *et al.*, 1988).

The detection limit exprimment is intended to estimate the lowest concentraton of an analyte that can be measured. There are several different types of detection limits depending what is being defined. However, the MDL is the only one designed to be determined in one's laboratory using chemicals, equipment, and technicians. The other detection limits are either determined by the instrument manufacturer or are calculated from the MDL. While each has its place, not all are useful in one's day to day analyses.

In this study, to estimate two different MDLs, an experimental data set for an ionic component were applied.

## 2. MODEL DISCRIPTION

### 2.1 EPA's MDL

The U.S. Environmental Protection Agency (EPA) guidelines establishing test procedures for the analysis of pollutants, procedures for detection and quantitation.

EPA's MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Per the Code of Federal Regulations 40, part 136, the practical protocol to determine MDL specifies mathematically to take a minimum of 7 replicates of given spiking concentration in a range of one to five times from the projected lowest concentration that a detector in the analytical method can measure. The MDL is calculated according to the following formula:

$$MDL = t_{df,\ \alpha=0.01} \cdot S \qquad (1)$$

where $t_{df,\ \alpha=0.01}$ is Student's t-distribution table value for 99% with the degree of freedom (n-1).

$S$ is standard deviation, $\left[\frac{1}{n-1}\sum_{i=1}^{n}(X_i-\overline{X})^2\right]^{\frac{1}{2}}$

where $X_i$ = spiking replicates concentration (mg/L ) ($i = 1 \cdots n$) ($n = 7$ in this case), $\overline{X}$ is the mean of spiking concentrations (mg/L). As we can see, the so-called 99% confidence is really based on the t-distribution in statistics. Of course, this assumes that the distribution of the low level spiking concentrations follows the t-distribution. The definition of EPA's MDL was illustrated in Figure 1.

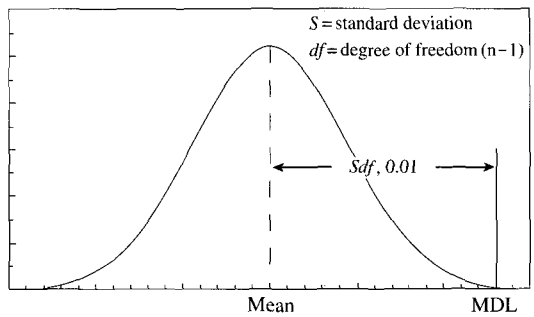



**Fig. 1. The definition of EPA's MDL.**

If one has another slightly different concentration spike, the procedure of MDL can be continued by pooling the two sample variances as follows:

$$S^2_{pooled} = \frac{df_1 S_1^{\ 2} + df_2 S_2^{\ 2}}{df_1 + df_2} \qquad (2)$$

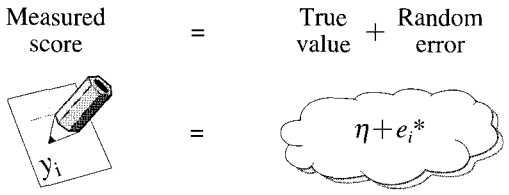
$$= \frac{S_1^{\ 2} + S_2^{\ 2}}{2} \text{ (if degree of freedom (n-1) is same} \qquad (3)$$

However the difference between the variances has to be statistically insignificant. If two variances are not significantly different from each other, the MDL can be calculated as the product of the new critical t-value and the pooled standard deviation as follow:

$$MDL = t_{df_1+df_2,\ \alpha=0.01} \cdot S_{pooled} \qquad (4)$$

### 2.2 Pallesen's MDL

Pallesen (1985) suggested that detection limit is the least concentration of the target component which can be certainly detected with surpassing the background noise in the analysis of blank sample. This MDL is difined in terms of the background noise in the process of target component analysis. In




*two components: $a_i$ analytic error, $b_i$ background noise

$$y_i=\eta+a_i+b_i$$

**Fig. 2. The structure of errors in the Pallesen's MDL.**

this model, analytic error and background noise are taken into consideration, respectively. In the near of true mean related detection limit, as shown in Figure 2, the structure of errors can be explained ass follow:

$$y_i=\eta+e_i=\eta+a_i+b_i \quad (5)$$

where $y_i$ is the concentration of target component, $\eta$ is true concentration, $e_i$ is total random error caused by analysis and background noise, $a_i$ is analytic error , and $b_i$ is backgroun noise. $a_i$ and $b_i$ are two random errors which affect the value of measurement. Also $a_i$ and $b_i$ are random respectively and supposed to follow the normal distribution. Background noise, $b_i$, will exit in the blank sample and supposed to satisfy the same variance ($\sigma_b^2$). On the other hand, analytic error, $a_i$, derived from the process of signal analysis is related to signal $\eta$. Under this assumption, total error distribution ($\sigma_e^2$) can be represented as follows:

$$\sigma_e^2=\sigma_a^2+\sigma_b^2=\sigma_b^2+\kappa^2\eta^2 \quad (6)$$

In the case of blank sample (e.g., $\eta$ is zero), $\sigma_b^2$ is to be zero. Thus error distribution of blank sample will be $\sigma_e^2=\sigma_b^2$. One has to pay attention to the fact that distribution of analytic error ($\sigma_e^2=\kappa^2\eta^2$) will be able to smaller than that of background noise when $\eta$ is small. MDL is the maximum value of y which cannot reject the assumption of $\eta=0$ in the established confidence interval. Pallesen (1985) defined MLD as follows:

$$\text{MDL}=\kappa_d\cdot\sigma_b \quad (7)$$

where $\kappa_d$ is the z-value of standard normal distribution.

Pallesen (1985) supposed that $y$ was followed the normal distribution whose mean and variance are zero and, $\sigma_d^2$ respectively. In general, $\kappa_d$ can be selected to be the smaller probability which $y$ is larger than MDL. In the case of blank sample, the probability of $y>$MDL is to be $\sigma$. Thus the value of $\kappa_d$ is the $z$-value of normal distribution. The examples of $\kappa_d$ are $\kappa_d=1.63$ $\sigma=0.05$ (5%), $\kappa_d=2.00$ $\sigma=0.023$ (2.3%), $\kappa_d=2.33$ $\sigma=0.01$ (1%), and $\kappa_d=3.00$ $\sigma=0.0013$ (0.13%). Here, $\kappa_d=3.00$ ($\sigma=0.0013$) is used in Pallesen's MDL.

## 3. RUN MDLS BY EXPREMENTAL DATA AND DISCUSSION

The calculation procedure of detection limits by experimental data was displayed in Figure 3. A spike is a standard containing the analyte at a known concentration and goes through the entire analytic process like a real sample on a given instrument. Since spikes mimic real samples, we can measure the efficiency of the instrument performance and establish the MDL of the spike sample media. We made the solution of 0.25 mg/L, 0.5 mg/L, 2 mg/L, 5 mg/L nitrate, respectively. These solutions were analyzed seven times by ion chromatography (Shimadzu LC-10A) over the course of several days. Blank sample and each step of spiked

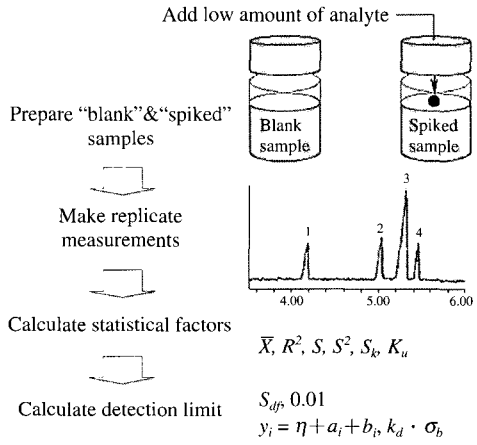



**Fig. 3. The calculation procedure of detection limits by experimental data.**

samples were analyzed with Shima-A1 column. More detailed analytical conditions of ion chromatography are listed in Table 1.

The actual laboratory data used to estimate the MDLs for a series of experiments are tabulated in Table 2 as the stem and leaf plot with their statistical summary. In Table 2, the skewness and kurtosis scores indicate the shape of distribution for measured scores.

As mentioned earlier, EPA's MDL can be determined by the low level spiking concentrations. Also the pooled MDL can be calculated by another slightly different concentration spike. Thus, in this study EPA's MDL was calculated by pooling the two spike samples with 0.25 mg/L and 0.5 mg/L. The pooled standard deviation of this data set calculated to be 0.0214. By substituting the numbers into the Eq. (1), we got an MDL of 0.0575 mg/L for our nitrate data.

To assume the value of $\kappa^2$, $\sigma_b^2$ which are the parameters of the Pallesen's MDL, as shown Figure 4, a regression curve was drawn by using each data.

**Table 1. Analytical condition of ion chromatography.**

| | | | |
|---|---|---|---|
| Sensitivity | 0.1-5120 μs cm$^{-1}$ | Speed | 3 mm min$^{-1}$ |
| Noise | 0.004 μs cm$^{-1}$ | Sample loop | 200 μL |
| Drift | 0 μV min$^{-1}$ | Flow rate | 1.5 mL min$^{-1}$ |
| Slope | 635.04 μV min$^{-1}$ | Press | 18 KG m$^3$ |
| Attenuation | $2^4$ mV | Eluent solution | 6.6 mM NaOH |

In the regression equation ($S_e^2 = a + b\overline{X}^2$) of Figure 4, $a$ and $b$ will be $\sigma_b^2$ and $\kappa^2$, respectively. From the values of $\sigma_b^2$ and $\kappa_d$, the Pallesen's MDL was finally calculated to be 0.0561 mg/L.

As a consequence, the scores of MDL determined by two different methods are roughly similar, however there are several differences between two methods. One of differences can be derived from the considering about the separation between analytic error and background noise in the Pallesen's MDL.

As discribed above the EPA's MDL is computed as the product of the standard deviation and the critical t-value. Also the EPA's single or double concentration procedures take a very simple route to computing the MDL. Unfortunately, with this very simple method there comes a major inaccuracy. This inaccuracy is the assumption of uniform variance across all possible concentration spikes. It should be apparent that as one measures increasing higher concentrations that there will be larger variabilities associated with these measurements as shown in Table 2, however, EPA performs no calibration to account for such trends.

As can be seen from the procedures illustrated above, Pallesen's MDL should result in much more accurate MDL than what would result if one were to use EPA's MDL on the identical set of data.

**Table 2. Stem an leaf plot of the measured scores of blank and nitrate and statistical summary.**

| Frequence | True value* | Stem | Leaf | n | $\overline{X}$ | $S$** | $S^2$*** | $S_k$**** | $K_u$***** |
|---|---|---|---|---|---|---|---|---|---|
| 3 | 0 | 0.00 | 8, 9, 9 | 7 | 0.011 | 0.002 | 3.6E-6 | −0.154 | −1.870 |
| 4 | | 0.0 | 11, 12, 12, 13 | | | | | | |
| 7 | 0.25 | 0.2 | 38, 41, 44, 59, 59, 69, 72 | 7 | 0.255 | 0.014 | 1.9E-4 | 0.022 | −1.953 |
| 3 | 0.5 | 0.4 | 82, 99, 99 | 7 | 0.518 | 0.027 | 7.3E-4 | 0.208 | −1.478 |
| 4 | | 0.4 | 11, 34, 43, 56 | | | | | | |
| 2 | 2 | 1.9 | 84, 86 | 7 | 2.031 | 0.038 | 1.4E-3 | −0.013 | −1.008 |
| 5 | | 2.0 | 17, 41, 43, 59, 86 | | | | | | |
| 1 | | 5.0 | 27 | | | | | | |
| 3 | 5 | 5.1 | 01, 67, 89 | 7 | 5.164 | 0.075 | 5.6E-3 | −1.223 | 0.693 |
| 3 | | 5.2 | 11, 17, 35 | | | | | | |

Stem width is 0.1 for 0.5, 2, 5 true values; Each leaf is 1 case; * mg/L; ** Standard deviation; *** Variance

**** Skewness, $\frac{n}{(n-1)(n-2)} \cdot \sum_{i=1}^{n} \frac{(X_i-\overline{X})^3}{S^3}$; ***** Kurtosis, $\frac{n(n+1)}{(n-1)(n-2)(n-3)} \cdot \sum_{i=1}^{n} \frac{(X_i-\overline{X})^4}{S^4} - \frac{3(n-1)^2}{(n-2)(n-3)}$

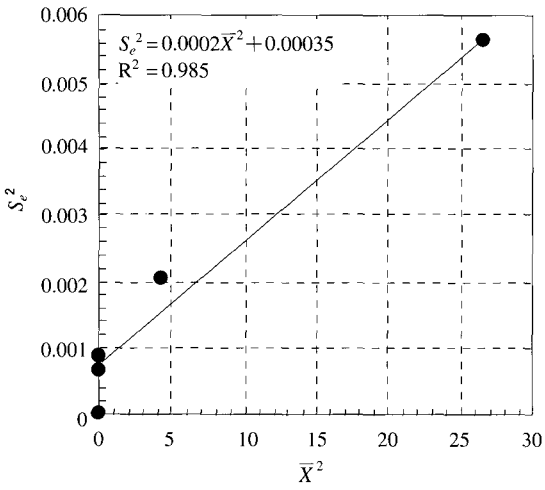



**Fig. 4. Regression curve to assume $\kappa^2$ and $\sigma_b^2$.**

## 4. CONCLUSIONS

Though the performance of analytical methods especially in terms of sensitivity, precision and accuracy is significantly increased, the most dominant source of error is analysis with sampling in the field of environment. For this reason it should be emphasized that the quality assessment (QA)/quality control (QC) procedures should be conducted as closely as possible to avoid missing of data analysis. In this study, as one of the QA/QC programs, two different MDLs suggested by EPA and Pallesen were determined by running a series of low-level nitrogen standards. The determined MDL scores give us an idea of just how low the concentration of the sample can be significantly detected by the instrument. Also more information can be gained when a numerical result and an estimate of measurement precision are reported for every measurement, as opposed to reporting "not detected" or "less than". In conclusion, these numerical detection limit values can provide the measurement precision to researcher engaged in analytical measurement, more particularly environmental experiment.

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