

Determination of cadmium and lead in water – new recommended way of evaluating the limits of detection and quantification

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Abstract Traditional and the new IUPAC recommended calculation methods for determining the limit of detection and the limit of quantification are applied to the trace determination of cadmium and lead in water. The new method is based on the upper limit approach (ULA), which utilises the one-sided confidence band around the calibration line. The residual standard deviation of the calculated calibration line as well as the *t*-distribution critical value are used for the calculation of both limits. An appropriate design of the calibration experiment is described. The calculation of both limits in the new way is extremely easy when the calibration experiment is equidistantly designed.

Keywords cadmium; lead; differential pulse anodic stripping voltammetry; inductively coupled plasma atomic emission spectroscopy; limit of detection; limit of quantification; water analysis

Introduction

A representative characteristic of an analytical method is the smallest concentration (or the mass) of the analyte that can be detected with a specified degree of certainty. The related quantity, the *limit of detection* (LOD), was defined by IUPAC in the nineteen-seventies in the signal domain as

$$y_D = \mu_b + k_D \sigma_b \quad (1)$$

where μ_b denotes the expected mean blank value (the population mean), commonly approximated by the arithmetic mean of the blank \bar{y}_b , σ_b is the population standard deviation of the blank, approximated by the blank standard deviation s_b , and $k_D=3$ (IUPAC, 1978).

The *limit of quantification* (LOQ) refers to the smallest analyte concentration (or mass), which can be quantitatively analysed with a reasonable reliability by a given procedure. Its traditional definition is similar to the LOD definition, but the numerical factor k_Q is used:

$$y_Q = \mu_b + k_Q \sigma_b \quad (2)$$

The same approximations were assumed as described below equation (1) but the factor of 10 was chosen for k_Q as the value recommended by ACS (ACS Committee, 1980).

The mentioned traditional methods of the LOD and LOQ calculation have many weak aspects therefore they have been criticized in numerous papers. Problems with the traditional definitions were encountered especially when a relatively small number of the blank measurements were performed (since the population statistics is not valid in such a case) and when the *concentration* values of both limits were required. Nevertheless, mainly due

to its simplicity and long term usage, they have still been used despite several new ways described in the literature and IUPAC documents (Currie, 1994a,b; Mocak, 1997). The recent IUPAC recommendation appeared more than two years ago (Mocak, 1997) and the whole document is accessible on the Internet (IUPAC, 1999). A list of previously published papers on this topic was also given there. Concerning this document and in accordance with our recent paper at the “Water supply and water quality” conference (Mocak, 2000), the main objective of this work is to apply the recommended new approach of the LOD and LOQ evaluation to the cadmium and lead trace determination in water matrices and to make comparisons with the traditional approach.

Theory

The main task of an analytical chemist is to know the concentration counterparts of the signal LOD and LOQ values, for which the slope of the calibration straight-line, usually in the form $y = q_0 + q_1x$, is commonly used:

$$\text{LOD} = (y_D - \bar{y}_b) / q_1 = k_D s_b / q_1 \quad (3)$$

$$\text{LOQ} = (y_Q - \bar{y}_b) / q_1 = k_Q s_b / q_1 \quad (4)$$

Traditional approach

The traditional approach employs the mean blank signal, \bar{y}_b , as the reference point value for the calculation of the LOD and LOQ signals and *neglects the intercept* of the calibration straight line. The usual way of *inverse regression*, transforming the sample signal to the concentration domain by means of the function inverse to the calibration function, is not applied here, even though it is always applied in analytical calibration. The simplifications assumed in the traditional method of the LOD calculation are equivalent to the following assumptions: (i) $q_0 = \bar{y}_b$, (ii) $\bar{y}_b = \mu_b$, which means that the measured mean blank signal equals to the population mean (i.e. the expected blank signal value), (ii) all calibration points lie exactly on the calibration line, which means that the measured signals are errorless and the slope and intercept of the calibration line are theoretical. Such assumptions are never valid in real experiments.

Upper limit approach

The upper limit approach, ULA, which is fundamental for the new way of the LOD and LOQ calculations, makes use of the *one-sided upper confidence limit* (Mocak, 1997) for a future individual observation (Green, 1978; Massart, 1988) – the so-called prediction (or dispersion) band – for predicting the maximum signal value corresponding to the zero analyte concentration (the blank) at the $100(1-\alpha)$ % probability level. As the most suitable, the level 99% has been recommended ($\alpha = 0.01$) in the IUPAC Technical Report (Mocak, 1997). In this way, the uncertainty of the calibration line is respected and the calculation is consistent with the original IUPAC definition of the LOD. The residual standard deviation $s_{y,x}$, expressing the error of regression, is used here instead of the blank standard deviation s_b . The multiplication factors k_D and k_Q are not fixed, but depend on the number of experiments performed, as it affects the critical t -distribution value. In the ULA the *concentration* LOD and LOQ values are correctly estimated by *inverse regression*. It also means that the LOD and LOQ calculations are always calibration-model dependent.

Methods

Differential Pulse Anodic Stripping Voltammetry (DPASV) was performed using a standard three-electrode voltammetric cell with the static mercury drop electrode SMDE-1 (Laboratorní Přístroje, Prague), a reference 3 mol/L silver-silver chloride electrode, and a platinum wire auxiliary electrode. An AUTOLAB/PGSTAT 20 Electrochemical Instrument, The Netherlands, was used in all electrochemical measurements. The following parameters were set for the Cd(II) and Pb(II) determination: deposition potential -1 V, equilibration time 10 s, modulation time 0.04 s, interval time 0.1 s, initial potential -0.8 V, end potential -0.2 V, step potential -0.002 V, modulation amplitude -0.05 V. All electrochemical experiments were made at $25 \pm 0.5^\circ\text{C}$.

Inductively coupled plasma atomic emission spectroscopy (ICP AES) was made using a Perkin-Elmer Plazma-40 ICP spectrometer and the following parameters were set: frequency 40 MHz, power 950 W, constant slit, sample delivery efficiency $1\text{cm}^3/\text{min}$, wavelength 220.353 nm for lead and 214.438 nm for cadmium.

All chemicals used were of analytical reagent grade. Distilled and de-ionised water was used in all measurements. Experimental data were sampled by the DPASV or ICP AES instruments and written to the computer hard disk. Then they were exported to ORIGIN (Microcal Software, Inc., Northampton, MA) or Microsoft EXCEL software package, and treated by linear regression.

Results and discussion

Signal values of the LOD and LOQ

For obtaining the correct signal LOD and LOQ values, the factors k_D and k_Q , multiplying the blank standard deviation, have to be properly adjusted, since in practice the unknown values of the population mean μ_b and the population standard deviation σ_b are substituted by the experimentally accessible sample statistics \bar{y}_b and s_b . Then the correct value of the LOD signal, if expressed by means of the blank standard deviation (Mocak, 1997), is:

$$y_D = \bar{y}_b + k_D s_b = \bar{y}_b + t(n-1, 1-\alpha) (1 + 1/n)^{1/2} s_b \quad (5)$$

where the term $(1 + 1/n)^{1/2}$ corrects for the uncertainty of \bar{y}_b with respect to μ_b , $t(v, 1-\alpha)$ is the critical t -distribution value for $v = n-1$ degrees of freedom, and $1-\alpha$ is the confidence level. The k_Q factor is defined in analogous way and its value is simply three times larger:

$$y_Q = \bar{y}_b + k_Q s_b = \bar{y}_b + 3 t(n-1, 1-\alpha) (1 + 1/n)^{1/2} s_b \quad (6)$$

If the signal variance is constant (homoscedasticity), then the signal sample standard deviation corresponding not only to the blank but also to other non-zero concentrations (but not too far from zero) can be used instead of s_b as a better statistical estimate of σ_b . This way is applied when deriving the concentration LOD and LOQ values in the next paragraph.

LOD and LOQ in concentration domain

The *concentration* LOD and LOQ values for the general straight line calibration model, $y = q_0 + q_1 c$, are given by the ULA2 variant, derived just for this calibration model, as:

$$\text{LOD} = \left[t(n-2, 1-\alpha) s_{yx} / q_1 \right] \left[1 + 1/n + \bar{c}^2 / \sum_{i=1}^n (c_i - \bar{c})^2 \right]^{1/2} \quad (7)$$

$$\text{LOQ} = 3 \left[t(n-2, 1-\alpha) s_{yx} / q_1 \right] \left[1 + 1/n + \bar{c}^2 / \sum_{i=1}^n (c_i - \bar{c})^2 \right]^{1/2} \quad (8)$$

where n concerns the number of all points involved in the regression procedure, c_i is the i -th point concentration coordinate, \bar{c} is the mean concentration of all points. The obtained values for the determination of cadmium and lead are summarised in Table 1. Closer inspection of the results reveals that: (1) the LOD and LOQ values are significantly lower in the case of the cadmium analyses compared to those for lead, (2) the electrochemical DPASV method gives both limits much lower compared to the ICP method for both analysed elements, (3) the obtained results depend on how the calibration experiment is designed.

In the case of the ICP lead determination, considerably smaller LOD and LOQ values were found by the ULA2 than by the traditional approach. The explanation of such a relatively large difference in the LOD and LOQ calculation results is based on the fact that the traditional calculation of both limits is much more influenced by a large variation of the blank signal values (expressed by s_b) compared to the value of s_{yx} used in ULA2, which reflects the blank signals as well as the signals at the adjacent concentrations, so that the number of signals is much larger and the result is more reliable.

Design of calibration experiment

For a larger number of the replicate signal measurements, a smaller residual standard deviation s_{yx} is expected if the *averaged* signal values are used in regression calculations, in contrast to the use of individual signal measurements, since the averaged values are generally better estimates of the unknown population means compared to the individual signal values. Our observations were in accordance with this expectation – as shown in Figure 1.

Table 1 Determination of lead and cadmium by DPASV and ICP AES – comparison of the traditional (part A) and ULA2 (part B) methods of the LOD and LOQ calculation*

| | Calculated Parameter | Pb by DPASV | Pb by ICP AES | Cd by DPASV | Cd by ICP AES |
|---|----------------------|-------------|---------------|-------------|---------------|
| A | n_b^{**} | 4 | 9 | 6 | 10 |
| | \bar{y}_b | 20.6800 | 0.03002 | 1.19333 | 0.00361 |
| | s_b | 0.60553 | 0.01639 | 0.15488 | 0.00188 |
| | $3s_b$ | 1.8166 | 0.04917 | 0.46464 | 0.00564 |
| | $10s_b$ | 6.0553 | 0.16390 | 1.5488 | 0.01880 |
| | q_1 | 7.44881 | 0.0000998 | 10.3786 | 0.00105 |
| | LOD ($3s_b$), ppb | 0.244 | 49.3 | 0.0448 | 5.36 |
| | LOQ ($10s_b$), ppb | 0.813 | 164 | 0.149 | 17.9 |
| B | n | 8 | 10 | 6 | 9 |
| | n_r | 4 | 9 | 6 | 10 |
| | v | 6 | 8 | 4 | 7 |
| | s_{yx} | 0.48681 | 0.00784 | 0.11218 | 0.00150 |
| | k_D | 3.741 | 3.360 | 4.625 | 3.519 |
| | k_Q | 11.223 | 10.08 | 13.875 | 10.56 |
| | q_0 | 20.8583 | 0.002623 | 1.32121 | 0.00394 |
| | q_1 | 7.44881 | 0.0000998 | 10.3786 | 0.00105 |
| | LOD (ULA2), ppb | 0.245 | 26.4 | 0.0500 | 4.99 |
| | LOQ (ULA2), ppb | 0.734 | 79.2 | 0.150 | 15.0 |

* The measured quantities and corresponding units of the blank signal mean \bar{y}_b and the blank standard deviation s_b are: (a) the maximum peak current in nA in DPASV, (b) intensity in arbitrary units in ICP AES. The ratio of the signal unit to the concentration unit (ppb) makes the slope unit.

** n_b – number of blank measurements, n – number of calibration points (equal to the number of calibration standards plus one (the blank), since the mean values of the replicate measurements were used in regression in this case), n_r – number of replicate measurements for each standard, v – number of degrees of freedom, $v = n - 2$, s_{yx} – residual standard deviation, k_D – multiplication factor for the given n and $\alpha = 0.01$ (one-sided) is given by the product $t(v, 1 - \alpha) [1 + 1/n + \bar{c}^2 / \sum(c_i - \bar{c})^2]^{1/2}$, the multiplication factor $k_Q = 3 k_D$.

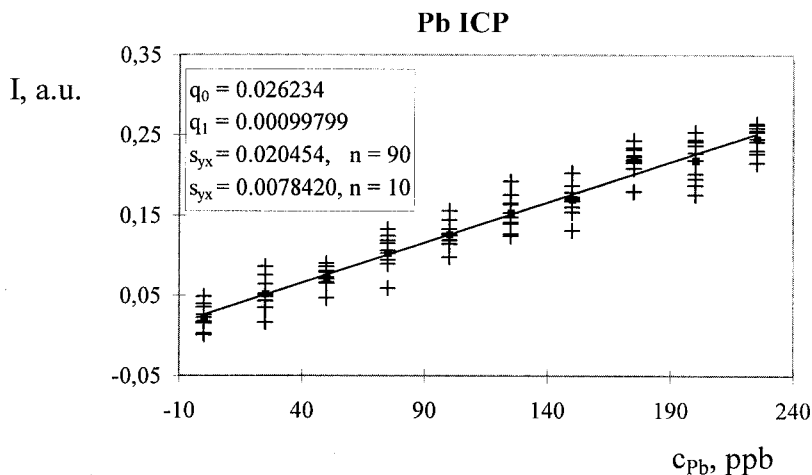


Figure 1 Regression calculations for the ICP AES determination of lead – two ways of the calibration design. Symbols + denote individual points, ■ denote the mean values of the replicate measurements.

The LOD and LOQ values depend on the calibration design in a complicated way. If the replicate signal measurements are averaged (for all calibration standards as well as the blank), then the smaller value of the residual standard deviation s_{yx} makes the LOD and LOQ values smaller compared to the situation when all individual signal measurements are involved in regression calculations. On the other hand, the critical t -values are larger if averaging the replicates, since the number of degrees of freedom is considerably smaller. However, the rise in the t -values does not fully compensate the decrease in the s_{yx} value, so that the use of the mean signal values is more advantageous – the LOD and LOQ values are smaller. An important feature of the correct way of signal averaging in this case is the use of an *equal number of replicates* for each calibration standard as well as the blank, otherwise more complicated weighted regression has to be used, with the weights reflecting the unequal number of the replicates.

For example, two calibration designs, depicted together in Figure 1, consist of either all $10 \times 9 = 90$ points involved in linear regression, or only 10 points represented by the mean values of 9 replicates made for each standard as well as the blank. Due to the constant number of the replicate measurements, a standard way of regression analysis is appropriate when the mean values are used. The comparison of both residual standard deviations, given in Figure 1, shows a favourable 61.7% decrease (0.007842 vs. 0.020454) when using the mean values, whilst the growth in the critical t -values, i.e. $t(8, 0.99) = 2.89647$ vs. $t(88, 0.99) = 2.36947$, is only 22.4%. In accord with these data, the LOD and LOQ values calculated for all individual signal measurements are much higher and therefore less recommended. Similar results were found in the case of other performed analyses, although the observed effect was smaller.

The best design of the calibration experiment is *equidistant*, with at least one point, except the blank, located in the region below or at the LOQ, otherwise the LOD and LOQ are calculated from the points located faraway. The usage of the calibration points at concentration levels much higher than the limits of detection and quantification is quite frequent in practice but is not permissible (Massart, 1988) because of errors caused by the distant extrapolation. Therefore a special calibration experiment is needed for determining the LOD and LOQ, different from that used in routine laboratory work.

Using a table of multiplication factors for equidistant calibration

For an *equidistant calibration* experiment, it is advantageous to use a table of the k_D and k_Q values, which are pre-calculated for this type of the calibration design in Table 2. The LOD and LOQ values can be then calculated in a way similar to the traditional approach:

$$\text{LOD} = k_D(n, \alpha) s_{yx} / q_1 \tag{9}$$

$$\text{LOQ} = k_Q(n, \alpha) s_{yx} / q_1 \tag{10}$$

The $C(n)$ term and $B(n)$ term introduced in Table 2 are exclusively concentration dependent; they do not depend on the signal values, therefore they can be pre-calculated:

$$C(n) = \bar{c}^2 / \sum_{i=1}^n (c_i - \bar{c})^2 = 1 / \sum_{i=1}^n (c_i / \bar{c} - 1)^2 \tag{11}$$

$$B(n) = [1 + 1/n + C(n)]^{1/2} \tag{12}$$

$$k_D(n, \alpha) = t(n - 2, 1 - \alpha) B(n) \tag{13}$$

The k_Q factor is simply three times the corresponding k_D value, $k_Q = 3 k_D$, therefore

$$k_Q(n, \alpha) = 3 t(n - 2, 1 - \alpha) B(n) \tag{14}$$

The LOD and LOQ calculations with the use of Table 2 are very comfortable and quick. It is just necessary to find the factor $k_D(n - 2, 0.99)$ corresponding to the number of points n involved in the linear regression $y = q_0 + q_1 x$ and relevant to the ULA2. For comparison purposes, one can also find in this table the values of the factor $k_D(n - 2, 0.95)$, however, the probability 95% has not been recommended since the obtained LOD values would be too low. A detailed inspection of the data in Table 2 enables us to find such an n value, at which the multiplication factor is close to 3, which is the value used unalterably in the traditional approach. As can be seen, the $k_D(n - 2, 0.99) = 3.006$ corresponds to $n = 14$. If $n > 14$, the factor is smaller than 3, if $n < 14$ the opposite is true; the multiplication factor always reflects the number of degrees of freedom, dependent on n . When n is large, the $C(n)$ term is insignificant and $B(n)$ converges to $(1 + 1/n)^{1/2}$, which is consistent with equation (6).

Pre-calculation of the multiplication factors can be also made for another type of equidistant calibration model, e.g. the straight line passing through a fixed point (mostly the origin), $y = qx$, to which the ULA1 is relevant (Mocak, 1997). Even though one can find in practice a lot of models of this type, the general straight line is much more widespread and therefore is treated in this paper. The upper limit approach can be generally used for any type of calibration function, since the calculation of the prediction band is generally feasible and known in statistics (Mocak, 1990). Nevertheless, matrix algebra is necessary for more complex calibration models.

Finally, it should be stressed that the calibration is not considered equidistant if an equal number of replications (two or more) is made and the calibration standards are equally spaced along the concentration axis. Such a case can be considered *pseudo-equidistant* and the best way of computing the

LOD and LOQ is the same as in the general case – by means of equations (7) and (8), nevertheless the use of Table 2 is possible but more complicated. If a given non-equidistant

Table 2 Dependence of the k_D factors and other quantities used in the LOD and LOQ calculation for $\alpha = 0.01$ and $\alpha = 0.05$ (one-sided) on the number of experiments n assuming equidistant calibration*

| n | $1/n$ | $(1+1/n)^{1/2}$ | $C(n)$ | $B(n)$ | $t(v, 0.99)$ $v = n-2$ | $k_D(v, 0.99)$ for ULA2 $v = n-2$ | $k_D(v, 0.95)$ for ULA2 $v = n-2$ |
|----------|---------|-----------------|---------|---------|---------------------------|---|---|
| 2 | 0.50000 | 1.22474 | 0.50000 | 1.41421 | – | – | – |
| 3 | 0.33333 | 1.15470 | 0.50000 | 1.35401 | 31.821 | 43.086 | 8.549 |
| 4 | 0.25000 | 1.11803 | 0.45000 | 1.30384 | 6.965 | 9.081 | 3.807 |
| 5 | 0.20000 | 1.09545 | 0.40000 | 1.26491 | 4.541 | 5.744 | 2.977 |
| 6 | 0.16667 | 1.08012 | 0.35714 | 1.23443 | 3.747 | 4.625 | 2.632 |
| 7 | 0.14286 | 1.06905 | 0.32143 | 1.21008 | 3.365 | 4.072 | 2.438 |
| 8 | 0.12500 | 1.06066 | 0.29167 | 1.19024 | 3.143 | 3.741 | 2.313 |
| 9 | 0.11111 | 1.05409 | 0.26667 | 1.17379 | 2.998 | 3.519 | 2.224 |
| 10 | 0.10000 | 1.04881 | 0.24546 | 1.15994 | 2.897 | 3.360 | 2.157 |
| 11 | 0.09091 | 1.04447 | 0.22727 | 1.14812 | 2.821 | 3.239 | 2.105 |
| 12 | 0.08333 | 1.04083 | 0.21154 | 1.13792 | 2.764 | 3.145 | 2.062 |
| 13 | 0.07692 | 1.03775 | 0.19780 | 1.12904 | 2.718 | 3.069 | 2.028 |
| 14 | 0.07143 | 1.03510 | 0.18571 | 1.12122 | 2.681 | 3.006 | 1.998 |
| 15 | 0.06667 | 1.03280 | 0.17500 | 1.11430 | 2.650 | 2.953 | 1.973 |
| 16 | 0.06250 | 1.03078 | 0.16544 | 1.10813 | 2.624 | 2.908 | 1.952 |
| 17 | 0.05882 | 1.02899 | 0.15686 | 1.10258 | 2.602 | 2.869 | 1.933 |
| 18 | 0.05556 | 1.02740 | 0.14912 | 1.09758 | 2.583 | 2.836 | 1.916 |
| 19 | 0.05263 | 1.02598 | 0.14211 | 1.09304 | 2.567 | 2.806 | 1.901 |
| 20 | 0.05000 | 1.02470 | 0.13571 | 1.08891 | 2.552 | 2.779 | 1.888 |
| 21 | 0.04762 | 1.02353 | 0.12987 | 1.08512 | 2.539 | 2.756 | 1.876 |
| 22 | 0.04545 | 1.02247 | 0.12451 | 1.08165 | 2.528 | 2.734 | 1.866 |
| 23 | 0.04348 | 1.02151 | 0.11957 | 1.07844 | 2.518 | 2.715 | 1.856 |
| 24 | 0.04167 | 1.02062 | 0.11500 | 1.07548 | 2.508 | 2.698 | 1.847 |
| 25 | 0.04000 | 1.01980 | 0.11077 | 1.07274 | 2.500 | 2.682 | 1.839 |
| 26 | 0.03846 | 1.01905 | 0.10684 | 1.07019 | 2.492 | 2.667 | 1.831 |
| 27 | 0.03704 | 1.01835 | 0.10317 | 1.06781 | 2.485 | 2.654 | 1.824 |
| 28 | 0.03571 | 1.01770 | 0.09975 | 1.06558 | 2.479 | 2.641 | 1.817 |
| 29 | 0.03448 | 1.01709 | 0.09655 | 1.06350 | 2.473 | 2.630 | 1.811 |
| 30 | 0.03333 | 1.01653 | 0.09355 | 1.06155 | 2.467 | 2.619 | 1.806 |
| 31 | 0.03226 | 1.01600 | 0.09073 | 1.05970 | 2.462 | 2.609 | 1.801 |
| 32 | 0.03125 | 1.01550 | 0.08807 | 1.05800 | 2.457 | 2.600 | 1.796 |
| 33 | 0.03030 | 1.01504 | 0.08556 | 1.05630 | 2.453 | 2.591 | 1.791 |
| 34 | 0.02941 | 1.01460 | 0.08319 | 1.05480 | 2.449 | 2.583 | 1.787 |
| 35 | 0.02857 | 1.01419 | 0.08095 | 1.05330 | 2.445 | 2.575 | 1.783 |
| 36 | 0.02778 | 1.01379 | 0.07883 | 1.05200 | 2.441 | 2.568 | 1.779 |
| 37 | 0.02703 | 1.01342 | 0.07681 | 1.05060 | 2.438 | 2.561 | 1.775 |
| 38 | 0.02632 | 1.01307 | 0.07490 | 1.04940 | 2.435 | 2.555 | 1.772 |
| 39 | 0.02564 | 1.01274 | 0.07308 | 1.04820 | 2.431 | 2.549 | 1.768 |
| 40 | 0.02500 | 1.01242 | 0.07134 | 1.04710 | 2.429 | 2.543 | 1.765 |
| ∞ | 0 | 1 | 0 | 1.00000 | 2.326 | 2.326 | 1.645 |

* $C(n) = (\bar{c}^2 \sum_{i=1}^n (c_i - \bar{c})^2) = 1 / \sum_{i=1}^n (c_i / \bar{c} - 1)^2$; $B(n) = [1 + 1/n + C(n)]^{1/2}$

$k_D(n, \alpha) = t(n-2, 1-\alpha) B(n)$; $k_Q(n, \alpha) = 3 t(n-2, 1-\alpha) B(n)$

calibration design is repeatedly used in the laboratory, then it is economic to pre-calculate the $C(n)$ and $B(n)$ terms for the particular case.

Conclusions

The new method for LOD and LOQ calculation, recommended by IUPAC (Mocak, 1997), overcomes problems caused by statistical incorrectness of the common traditional approach and, as shown in this paper, it can be applied easily. An appropriate design of the calibration experiment enables us to achieve lower as well as correct LOD and LOQ values.

The best design of the calibration experiment is equidistant, with at least one point, except the blank, located in the region below or at the LOQ.

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References

- ACS Committee of Environmental Improvement (1980). Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry. *Anal. Chem.*, **52**, 2242–2249.
- Currie, L.A. and Horwitz, W. (1994). IUPAC recommendations for defining and measuring detection and Quantification limits. *Analisis*, **22**, m24–m26.
- Currie, L.A. and Svehla, G. (1994). Nomenclature for the presentation of results of chemical analysis. *Pure Appl.Chem.*, **66**, 595–608.
- Green, J.R. and Margerison, D. (1978). *Statistical Treatment of Experimental Data*. Elsevier, Amsterdam, Chapter 14.3.
- IUPAC, Analytical Chemistry Division (1978). Nomenclature, symbol, units and their usage in spectrochemical analysis. II. Data interpretation. *Spectrochim. Acta*, **33 B**, 241–246.
- IUPAC Commission V5 web site (1999): <http://users.unimi.it/ape/V5>.
- Massart, D.L., Vandeginste, B.G.M., Deming, S.N., Micotte, Y. and Kaufman, L. (1988). *Chemometrics: a Textbook*. Elsevier, Amsterdam, pp. 86–91; pp. 113–114.
- Mocak, J., Varga, S., Polak, P., Gergely, S., Izak, J. (1990). Calibration – Some Newer Chemometrical Aspects in Instrumental Analysis. *Wiss. Zeitschr. (Merseburg)* **32**, 43–49.
- Mocak, J., Bond, A.M., Mitchell, S., and Schollary, G. (1997). A Statistical Overview of Standard (IUPAC and ACS) and New Procedures for Determining the Limits of Detection and Quantification: Application to Voltammetric and Stripping Techniques. *Pure & Appl.Chem.*, **69**, 297–328.
- Mocak, J. and Bobrowski, A. (2000). Determination of Cadmium and Lead in Water – New Way of Calculating Detection and Quantification Limits. In: *Conference Proceedings IV. International Conference “Water Supply and Water Quality”*. M.S. Sozanski (ed.), Cracow, Poland, pp. 121–132.