

Theoretical calculation of the standard deviation in inductively coupled plasma mass spectrometry†

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The theoretical calculation of the standard deviation in inductively coupled plasma mass spectrometry (ICP-MS) was investigated. The theoretical dependence of the standard deviation on instrument parameters and element concentration was examined. The connection between the standard deviation and the detection limit was demonstrated. The theoretical results were compared with experimental data and showed good agreement. The theory proposed may be used for the improvement of the detection limit in ICP-MS.

The method of inductively coupled plasma mass spectrometry (ICP-MS) is widely used in the determination of trace elements.¹ Study of the theoretical and practical aspects of ICP-MS permits improvements of the instrument and method parameters.¹⁻⁵ The calculation of the standard deviation and detection limit theoretically is useful for future developments in ICP-MS analysis. In analytical practice, an empirical linear approximation has been used for the characterization of the connection between element concentration and standard deviation.⁶⁻⁸

$$s_c = a + bc \quad (1)$$

where s_c is the standard deviation of a single analytical determination in units of concentration, c is the element concentration in units of concentration (ng ml⁻¹ or others) and a and b are coefficients (a in concentration units and b dimensionless). In the theory of measurements a determines the additive error and bc determines the multiplicative error. In practical analysis, the standard deviation of the analytical method is calculated by methods of mathematical statistics.⁸⁻¹⁰ For the calculation of the detection limit Kaiser's statistical criterion can be used.⁷ Different methods are used for the calculation of the detection limit from experimental data. In inductively coupled plasma atomic emission spectrometry (ICP-AES), Boumans¹¹ proposed the determination of the detection limit by the 'SBR-RSDB approach' using the signal-to-background ratio (SBR) and the relative standard deviation of the background (RSDB) as the objective criteria for instrumental performance. Boumans¹² also proposed an empirical relationship for the connection between standard deviation and detection limit:

$$s_c = (c_m^2 k^{-2} + \Delta^2 c^2)^{1/2} \quad (2)$$

where c_m is the detection limit in concentration units, k is a numerical factor chosen according to the confidence level desired and Δ is the instability coefficient of the apparatus, otherwise this is the relative standard deviation (RSD) of a strong signal which is determined by flicker noise.

The theoretical calculation of the standard deviation and detection limit may be helpful for the improvement of practical methods and for characterization of standard deviation and

detection limit. The theoretical calculation of the standard deviation in ICP-MS was the aim of this work.

Theory

Prudnikov and co-workers¹³⁻¹⁵ showed the possibility of the theoretical calculation of the standard deviation in AES and AAS. This approach was based on classical papers concerning the theoretical calculation of the SBR and detection limit in AES and AAS.¹⁶⁻¹⁸ The theory allows one to examine the noise in analytical chemistry, to propose practical methods for the study of standard deviation and detection limit, and to calculate theoretically the standard deviation and detection limit in ICP-AES.¹⁹⁻²¹ These investigations allow one to give a mathematical description of the process of an analytical measurement.²² They may be the basis for the theoretical calculation of the standard deviation and the detection limit in ICP-MS.

According to previous papers,¹⁹⁻²² five kinds of random errors may be distinguished in different analytical systems. These fluctuations depend on the system parameters and the element concentration. Their values are proportional to the power 0, 1/2, 1, 3/2 and 2 of the mentioned parameters. The standard deviation of the analytical measurement may be written in the following manner:

$$s = [s_b^2 + (k_d + 2RA s_{bl}) S_v c + \Delta^2 S_v^2 c^2 + k_k S_v^3 c^3 + k_n S_v^4 c^4]^{1/2} \quad (3)$$

where s is the instrumental value of the standard deviation in arbitrary units (counts s⁻¹ or others), s_{bl} is the blank fluctuations (counts s⁻¹), k_d is the coefficient of shot noise if produced by the detector (counts s⁻¹), R is the coefficient of correlation (cross-correlation) of the net and interfering signals, S_v is the instrumental sensitivity of the apparatus (counts s⁻¹ ng⁻¹ mL) and k_k and k_n are the coefficients of the non-linear noise. The first three terms on the right-hand side characterize the measurements in the linear range of the calibration function, whereas the following two terms determine the non-linearity in the analytical conditions. The term including the correlation coefficient R concerns the correlation fluctuations between the net and interfering signals. The non-linear processes break the theoretical relationship between the element concentration and the analytical signal. For a high concentration and strong signal, non-linearity can occur during the processes of nebulization, ionization and ion counting and

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processes in the mass spectrometer. For a small signal, the non-linearity can be due to the matrix interferences.

For the theoretical calculation of the standard deviation in ICP-MS, we do not consider the non-linearity in the calibration function and ignore the correlation moment for the net and interfering signals, because this moment plays a major role for considerable matrix interferences. The examination of these factors may be the subject of more detailed investigation.

The expression for the theoretical standard deviation in ICP-MS taking into account the method theory¹ and the theoretical eqn. (1) is given as

$$s = (s_{\text{bl}}^2 + S_v c + \Delta^2 S_v^2 c^2)^{1/2} \quad (4)$$

where s is the instrumental standard deviation in ICP-MS (counts s^{-1}), s_{bl} is the blank fluctuations (counts s^{-1}), S_v is the instrumental sensitivity of the ICP mass spectrometer (counts $\text{s}^{-1} \text{ ng}^{-1} \text{ mL}$), c is the element concentration (ng mL^{-1}) and Δ is the instability coefficient of the ICP mass spectrometer. Eqn. (4) is a particular case of eqn. (3) and shows the general principle of the theoretical calculation of the standard deviation. The value of the standard deviation is the sum of blank fluctuations and the shot and flicker noise of the useful net signal. Taking into consideration also the co-correlation between net and interfering signals, eqn. (4) may be rewritten as

$$s = [s_{\text{bl}}^2 + (1 + 2RA s_{\text{bl}}) S_v c + \Delta^2 S_v^2 c^2]^{1/2} \quad (5)$$

The blank fluctuations in eqns. (4) and (5) include the blank counts from the ion detector, the ICP source and mass spectrometer and also the blank counts from spectral and matrix interferences. For the blank standard deviation, we can write a relationship without matrix interferences:

$$s_{\text{bl}}^2 = n_{\text{bl i.d.}} + n_{\text{bl ICP}} + \Delta^2 n_{\text{bl ICP}}^2 \quad (6)$$

where $n_{\text{bl i.d.}}$ is the number of the blank ions from the ion detector (counts s^{-1}) and $n_{\text{bl ICP}}$ is the number of blank ions from the ICP source and mass spectrometer (counts s^{-1}). The blank fluctuations and the standard deviation also depend on the measurement time as a power of a number $s_{\text{bl}} = f(\tau^{-1/2})$. We accept the measurement time constant for all theoretical and experimental data as $\tau = 1 \text{ s}$. For a change in measurement time, the results can be recalculated by use of the above-mentioned equation.

The instrumental sensitivity of ICP-MS can be estimated using the results of the calculations for the ICP-AES method:²¹

$$S_v = 6 \times 10^{23} a_r T_s F_s \alpha \beta \beta_i / A T_{\text{ICP}} V_g n_{T/298} \times 10^9 \quad (7)$$

where 6×10^{23} is Avogadro's number, a_r is the natural relative abundance of various element isotopes, T_s is the introduced sample temperature (K), F_s is the solution flow rate (mL min^{-1}), α is nebulization efficiency, β is the ionization efficiency, β_i is the coefficient of the mass spectrometer processing efficiency (or the ion use efficiency), A is the element atomic mass, T_{ICP} is the ICP source temperature (K), V_g is the nebulizer gas flow rate (mL min^{-1}), $n_{T/298}$ is the number of moles present or the change in the number of moles of gas during the transition from the sample temperature to the plasma temperature (for Ar this coefficient is equal to 1) and 10^9 is the coefficient for the recalculation of concentration from g to ng. Eqns. (4) and (5) have been considered for a time registration of $\tau = 1 \text{ s}$. For any registration time, it is necessary to apply the coefficient $1/\tau^{1/2}$. According to IUPAC recommendations (Inf. Bull. No. 27, November 1972), S_v is determined by the value of the first derivative of the calibration function at a given concentration of an element, or S_v is the slope of the calibration function. In practice, the instrumental sensitivity may be determined like the value of an analytical signal (V , in ICP-MS counts s^{-1}) for an element concentration $c = 1$ (in g mL^{-1} , or for ICP-MS more preferably in ng mL^{-1}).

According with this comment, we have in the denominator of eqn. (7) the single element concentration 1 g mL^{-1} , and also in the numerator of this equation the ion detector efficiency is 1 count s^{-1} for a single ion.

Eqns. (4)–(7) represent the process of analytical determinations by ICP-MS theoretically. These expressions include the parameters of the apparatus, the sensitivity of measurement, the blank fluctuations, the measured element concentration and the standard deviation of a measurement. These expressions are also connected with the detection limit of the measurement. Taking into account the statistical Kaiser's criterion and the data in previous papers,^{20,21} one can write

$$c_m = k S_v^{-1} s_{\text{bl}}$$

and for the $3s$ criterion (k is the confidence level coefficient) we have

$$c_m = 3 S_v^{-1} s_{\text{bl}} \quad (8)$$

Using eqn. (8), we can include the detection limit in eqns. (4) and (5):

$$s = [c_m^2 S_v^2 k^{-2} + (1 + 2RA c_m S_v k^{-1}) S_v c + \Delta^2 S_v^2 c^2]^{1/2} \quad (9)$$

Eqn. (9) includes all the parameters of the analytical method of ICP-MS without the non-linear noise.

For practical use, the relative standard deviation ($\text{RSD} = s_r$) is more convenient than the absolute standard deviation. The instrumental RSD is $s_r = s/S_v c$, and for the calculation of RSD in concentration units we have $s_r = s_c/c$. The theoretical relative standard deviation (s_r) of the ICP-MS method can be obtained from the eqn. (4):

$$s_r = (s_{\text{bl}}^2 S_v^{-2} c^{-2} + 2RA s_{\text{bl}} S_v^{-1} c^{-1} + \Delta^2)^{1/2} \quad (10)$$

Eqn. (10) will be used for the calculation of the instrumental RSD in ICP-MS. For the detection limit, one can use eqns. (8) and (9).

Experimental

The experimental results utilize archived data. The experiments were performed on a Perkin-Elmer SCIEX (Thornhill, ON, Canada) Elan 250 ICP-MS system. The conditions of the measurements were as follows: plasma gas (argon) flow rate, 11.9 L min^{-1} ; rf power, 1.25 kW; nebulizer gas flow rate, 1 L min^{-1} ; auxiliary gas flow rate, 1.41 L min^{-1} ; and solution flow rate, 1 mL min^{-1} .

The standard deviations for the ICP-MS determinations of ^{89}Y , ^{52}Cr , ^{139}La , ^{142}Nd , ^{140}Ce , ^{90}Zr were measured experimentally. The concentrations of these elements in solution were 0.1, 0.5, 1.0, 2.0, 5.0, 20.0 and 100.0 ng mL^{-1} in a 2% solution of HNO_3 . Standard methods for calibration curve construction were used. The computer-processed results for the standard deviation values for above element concentrations were taken. Table 1 gives the blank values and their fluctuations for the listed elements. The experimental data for the standard deviation of the ICP-MS determination of the listed elements are given in Tables 2–7.

The value of the blank count due to the ion detector is $n_{\text{i.d.}} = 20$, the nebulization efficiency is $\alpha = 0.02$,^{1,7,21} the temperature of the sample is $T_s = 300 \text{ K}$, the temperature of the ICP source is $T_{\text{ICP}} = 8000 \text{ K}$ ^{1,21} and the number of moles present for argon is $n_{T/298} = 1$. The other parameters for the theoretical calculations are examined further.

Results and discussion

First we will calculate theoretically the minimum value of the detection limit for ICP-MS with sample nebulization. We apply the ICP-MS instrument parameters. To predict theoretically the blank count and the efficiency of ion use is difficult;

Table 1 Blank value and standard deviation of the blank in ICP-MS

Element	Experimental data/counts s ⁻¹		Theoretical/counts s ⁻¹	
	Blank value 1 and 2 measured	Absolute standard deviation of blank	Blank value	Absolute standard deviation of blank
⁸⁹ Y	1035; 984	26; 22	1000	32
⁵² Cr	592; 633	47; 37	600	25
¹³⁹ La	666; 669	45; 20	670	26
¹⁴² Nd	60; 75	10; 15	65	8
¹⁴⁰ Ce	77; 81	12; 8	81	9
⁹⁰ Zr	2107; 1182	216; 23	1600	40

Table 2 Theoretical and experimental RSDs and detection limits for ⁸⁹Y in ICP-MS

Concentration/ng mL ⁻¹	RSD (%)	
	Theoretical	Experimental
0.1	0.65	0.71
0.5	0.14	0.08
1.0	0.075	0.05
2.0	0.045	0.037
5.0	0.024	0.005
20.0	0.011	0.007
100.0	0.0068	0.008
Detection limit	0.2	0.2

Table 3 Theoretical and experimental RSDs and detection limits for ⁵²Cr in ICP-MS

Concentration/ng mL ⁻¹	RSD (%)	
	Theoretical	Experimental
0.1	0.36	0.64
0.5	0.085	0.38
1.0	0.05	0.27
2.0	0.031	0.086
5.0	0.018	0.038
20.0	0.010	0.018
100.0	0.007	0.01
Detection limit	0.1	0.5

Table 4 Theoretical and experimental RSDs and detection limits for ¹³⁹La in ICP-MS

Concentration/ng mL ⁻¹	RSD (%)	
	Theoretical	Experimental
0.1	0.84	≥1.0
0.5	0.17	0.074
1.0	0.099	0.05
2.0	0.055	0.037
5.0	0.03	0.004
20.0	0.014	0.007
100.0	0.007	0.007
Detection limit	0.25	0.25

Table 5 Theoretical and experimental RSDs and detection limits for ¹⁴²Nd in ICP-MS

Concentration/ng mL ⁻¹	RSD (%)	
	Theoretical	Experimental
0.1	0.99	0.45
0.5	0.24	0.18
1.0	0.14	0.075
2.0	0.089	0.043
5.0	0.051	0.011
20.0	0.025	0.013
100.0	0.011	0.01
Detection limit	0.27	0.25

Table 6 Theoretical and experimental RSDs and detection limits for ¹⁴⁰Ce in ICP-MS

Concentration/ng mL ⁻¹	RSD (%)	
	Theoretical	Experimental
0.1	0.37	0.42
0.5	0.10	0.067
1.0	0.067	0.029
2.0	0.045	0.019
5.0	0.027	0.01
20.0	0.014	0.011
100.0	0.008	0.008
Detection limit	0.1	0.12

Table 7 Theoretical and experimental RSDs and detection limits for ⁹⁰Zr in ICP-MS

Concentration/ng mL ⁻¹	RSD (%)	
	Theoretical	Experimental
0.1	1.56	0.16
0.5	0.32	0.16
1.0	0.16	0.106
2.0	0.089	0.13
5.0	0.042	0.036
20.0	0.017	0.047
100.0	0.010	0.011
Detection limit	0.46	0.25

$n_{i.d.} \forall 10\text{--}100$, for example, for a mass spectrometer with a medium resolving power up to 1000–2000. For the Perkin-Elmer SCIEX Elan 250 the blank ion detector count is about 20, and we used this value for the calculation. The ionization efficiency may be calculated theoretically.^{1,2,7} The value for many elements is approximately 0.5–1 for ICP. The most difficult problem is the theoretical characterization of ion use efficiency (β_i) (or the mass spectrometer processing efficiency). We cannot calculate theoretically the loss of ions in the mass spectrometer. This is a problem of theory in mass spectrometry.^{1–5} We tried to estimate the efficiency of ion use with the application of some general parameter in ICP-MS. A large

loss of ions occurs at the sampler and skimmer. For plasma diameters up to 15–20 mm and inner sampler and skimmer diameters up to 0.8–1 mm, the coefficient of ion use is $<2 \times 10^{-3}$ – 5×10^{-3} . Further, the intermediate nebulizing gas (argon) is diluted by the outer argon flow, and for argon intermediate flow rates up to 0.8–1 L min⁻¹ and outer argon flow rates up to 10–15 L min⁻¹ the loss of ions can reach up to 0.1–0.05. The loss of ions in the mass spectrometer must also be considered. Tanner *et al.* have shown^{1,2} that losses immediately after the skimmer based space charge are very significant. For the product of all these coefficients of ion losses, we can use the value $\beta_i = 1 \times 10^{-4}$ for the calculation

of the standard deviation and detection limits in ICP-MS. This coefficient is in keeping with literature data.^{1,2} Then for ⁸⁹Y we have:

$$s_{bl}=4.5$$

$$S_v=6 \times 10^{23} \times 300 \times 1 \times 0.02 \times 10^{-4} / 89 \times 8000 \times 1000 \times 1 \times 10^9 = 5 \times 10^2$$

$$c_m=3 \times 4.5/5 \times 10^2 \approx 2.5 \times 10^{-2} \text{ ng ml}^{-1}=25 \text{ ng L}^{-1} \quad (11)$$

The theoretical results obtained for the detection limit in ICP-MS correspond to the literature data for the instrument used.¹

In real measurement conditions, the blank ion count increases owing to the influence of the ICP source and mass spectrometer blank value. In this case the overall blank count also increases and may reach a value much more than 100–1000. The maximum contribution for real samples with a complicated composition make matrix interferences of a different type.^{1,2} The experimental data in Table 1 for the blank confirm this theoretical calculation. The pure theoretical calculations of the detection limits give results which are lower than those of measurements under real conditions. Because we cannot predict theoretically the influence of different factors in the determination of the real blank value, we use the real conditions of the measurement. For the theoretical calculation we take the real experimental results as the blank count, but the value of the fluctuation of the blank is calculated theoretically (see Table 1).

The theoretical calculation of the standard deviation in ICP-MS was realized with the use of experimental and theoretical measurement parameters. For the theoretical calculations we applied eqn. (10). All the necessary parameters for the calculations are given above. The results of the theoretical calculation are given in Tables 2–7. Good agreement between the theoretical and experimental data is observed. The differences may be explained by the errors in the experimental standard deviation calculation and the theoretical data calculation. The random error for the standard deviations of our experiments may be equal to 0.5 of the values given in Tables 2–7 for the experimental data. According to the mathematical statistics, the random error of RSD determination in our experiments can be calculated using the equation: relative random error of $RSD=RSD^{1/2}$.^{8,9} For concentrations near the detection limit the value of this error is about 0.5. For Cr we can see also the influence of the non-instrumental blank, resulting from the presence of Cr in the solution and the other systems of the mass spectrometer. The molecular ion overlap can also increase the blank and RSD for Cr. In Tables 2–7 are also given the theoretical and experimental results of the calculation of the detection limits of the ICP-MS method. Using the Kaiser 3s criterion, the detection limits were determined like the concentration with the standard deviation $s=0.33$ (see the data in Tables 2–7). The theoretical detection limits are controlled also by eqn. (8). These results agree with the limits of the experimental error of the detection limit determination and the errors of the theoretical parameter characterization.

Hence the proposed theory shows the possibility of the theoretical study of the standard deviation and detection limit in ICP-MS. One can demonstrate the viability of this theory with Voigtman's computer simulation program for analytical instruments.²³ First it is necessary to emphasize that this theory gives a strict mathematical description of the process of the analytical measurement in ICP-MS. Some problems arise only because it is difficult to give the theoretical value of some parameters of the analytical instrument and measurement. In this case the theory requires some assumptions and practical data.

The combination of this theory with a computer simulation program may be useful for the more precise and rapid characterization of the possibility of instrumental improvements. However, because the theory proposed in eqns. (4)–(10) describes all the parameters of ICP-MS determination, it may be used for the indication of means for the improvement of the characteristics of the ICP-MS method. According to eqns. (8) and (9), the detection limit in ICP-MS and any other analytical method decreases with increase in the instrumental sensitivity and decrease in the blank signal fluctuations. This corresponds to a decrease in the noise of the trace element concentration determinations. According to eqn. (7), the instrumental sensitivity in ICP-MS may be increased by improvements in the nebulization efficiency, ionization efficiency and ion use efficiency, and also the solution flow rate. The application of the method of direct introduction of the sample into the plasma¹ allows one to increase the absolute detection limit more than 10-fold in comparison with the sample nebulization method.^{24–27} The theory permits the estimation of this possibility exactly. A decrease in the blank fluctuations and matrix interferences is the other way to decrease the detection limit and improve the accuracy and instrumental parameters in ICP-MS. This approach is also widely used in practice.¹ Hence the theory shows a direct way to improve the characteristics of the ICP-MS method.

The demonstration of the possibilities of the practical use of this theory is also valuable. Practical methods for the characterization of the standard deviation and detection limit under conditions of real analysis of different samples were given in a previous paper.²⁰ With the theoretical eqns. (4)–(10) and the practical standard deviations for minimum numbers of samples, one can calculate the standard deviation for any other concentration and the detection limit in real analysis.²⁰ This permits one to control the results of the analysis and the operation of the equipment. The results in Tables 2–7 demonstrate these possibilities.

Under real analysis conditions non-instrumental errors play an important role. In Fig. 1 and 2 the theoretical and experimental results for real samples are shown, with application of archive data for ⁵²Cr and ⁸⁹Y, respectively. The higher values of RSD for the experimental data do have a place within the theory, particularly for Cr and for trace concentrations (see also Table 3). We can see that the non-instrumental errors are prevalent in the analysis of real samples. For Cr the importance of the non-instrumental errors is particularly clear. The proposed theory permits us to examine and study also the non-instrumental errors. The next step in the progress of the theory may be the theoretical study of non-instrumental errors and a search for ways to eliminate the influence of different non-instrumental errors in ICP-MS analysis.

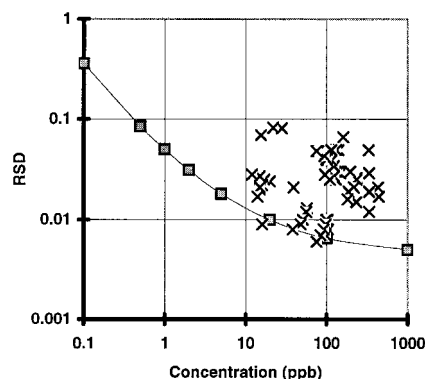


Fig. 1 Theoretical and experimental RSDs for the determination of ⁵²Cr in practical samples. Line, theory; x, experimental data.

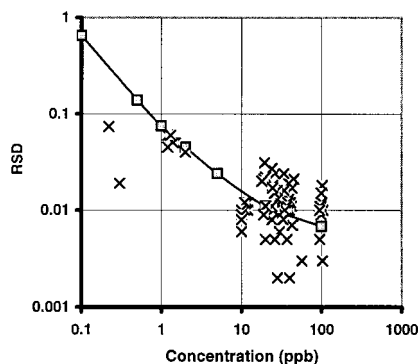


Fig. 2 Theoretical and experimental RSDs for the determination of ^{89}Y in practical samples. Line, theory; \times , experimental data.

Conclusions

The theoretical calculation of the standard deviation and detection limit in ICP-MS has been presented and theoretical expressions for the standard deviation in ICP-MS have been proposed. These expressions include all the parameters of the ICP-MS instrument, the sensitivity of measurements, the blank fluctuations and the element concentration. The proposed theory may be useful for the further development of the instrumental and analytical characteristics of ICP-MS. A comparison of theoretical and experimental results showed good agreement. The proposed theory may be used in practice for the characterization of the standard deviation and detection limit in the analysis of different samples by ICP-MS. The possibilities of using this theory for the examination of non-instrumental errors in analysis have been demonstrated.

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