

### On the $s(M) \sim M$ dependence

The  $s(M) \sim M$  or, otherwise, the  $Var(M) \sim M^2$  dependence plays an essential role in derivations related to the mathematical description of the double stochasticity of ICPMS signals and also explains the relative decrease of the excess variance component in the total uncertainty of weak signals: the excess variance scales in quadrature with decreasing  $M$ , while the number of counts scales linearly. This dependence is not given axiomatically and has to be explained. One way to explain it is to propose a probabilistic model describing the supply of analyte to the ICP, as it is done in the main text (see eqn 29 and its notation):

$$Var(M^*) = (\bar{c}^*)^2 \bar{N}^* (1 - p^*) + \bar{c}^* \bar{N}^*$$

This way is practical, and, as such, it depends on the particular processes connected with the operation of the sample introduction system. An other practical way is to refer to empirical data supporting the  $s(M) \sim M$  dependence (the relevant literature is rich and is frequently referred to in the main text).

However, more general considerations in support of this dependence can be given. Let us imagine that the whole amount of an analyte contained in a sample is divided in two sub-portions (populations), for example by labelling the atoms (ions) of the same isotope as ( $A$ ) and ( $B$ ). Let us consider the total variance

$$Var(M^A + M^B) = Var(M^A) + Var(M^B) + 2Cov(M^A, M^B)$$

For several reasons, including the sample introduction system instability and, probably, processes operating during ion extraction from the ICP through the interface, the ion supply to the ion channel fluctuates. Such fluctuation happens, for example, when a large droplet, or a pack containing a large number of droplets arrives to the ICP. It is reasonable to think that the analyte atoms present in that droplet (droplets) are proportionally sampled from the populations  $A$  and  $B$ . Hence,  $M^A$  and  $M^B$  are perfectly correlated. A perfect correlation means that the corresponding Pearson's coefficient is equal to unity:

$$\rho(M^A, M^B) = \frac{Cov(M^A, M^B)}{[Var(M^A)Var(M^B)]^{1/2}} = 1 \Rightarrow Cov(M^A, M^B) = [Var(M^A)Var(M^B)]^{1/2} = s(M^A)s(M^B)$$

Thus,

$$Var(M^A + M^B) = Var(M^A) + Var(M^B) + 2s(M^A)s(M^B) = [s(M^A) + s(M^B)]^2$$

$$\Downarrow$$

$$s(M^A + M^B) = s(M^A) + s(M^B)$$

It follows immediately that  $s(M) \sim M$ ; for example, doubling the concentration, we obtain:

$$s(M^A + M^A) = 2s(M^A); \quad \frac{s(M^A + M^A)}{s(M^A)} = \frac{M^A + M^A}{M^A} = 2$$

Interestingly, the property of correlation between the sampled parts of populations  $A$  and  $B$  is conditional. For example, if the sub-portions of populations  $A$  and  $B$  in a droplet or incremental gas volume are obtained by the Poisson selection (e.g., in the sense of Landau and Lifshitz, ref. 1), then the number of atoms of type  $A$  and the number of atoms of type  $B$  entering a sub-volume of the main sample volume are independent from each other, as are independent outcomes of any two different ordinary Poisson processes. We obtain:

$$Cov(M^A, M^B) = 0; \quad Var(M^A + M^B) = Var(M^A) + Var(M^B)$$

This time, doubling the concentrations results in the Poissonian, square-root based relationship:

$$Var(M^A + M^A) = 2Var(M^A); \quad \frac{s(M^A + M^A)}{s(M^A)} = \sqrt{\frac{M^A + M^A}{M^A}} = \sqrt{2}$$

The both processes - the proportional selection of the analyte and its Poisson scattering - are actually concomitant. At higher concentrations, the proportional selection dominates, while at lower concentrations - the Poisson scattering, which is formalised in the first equation of this Appendix (see eqn 29 and its notation in the main text).

### References

- 1 L.D. Landau and E.M. Lifshitz, *Course of theoretical physics, vol. 5, Statistical physics, part I*, Pergamon Press, 3rd edn, 1980, p. 387.