Metrologia

Supporting information

Calibration model averaging in chemical analysis: a case study for the method of standard additions

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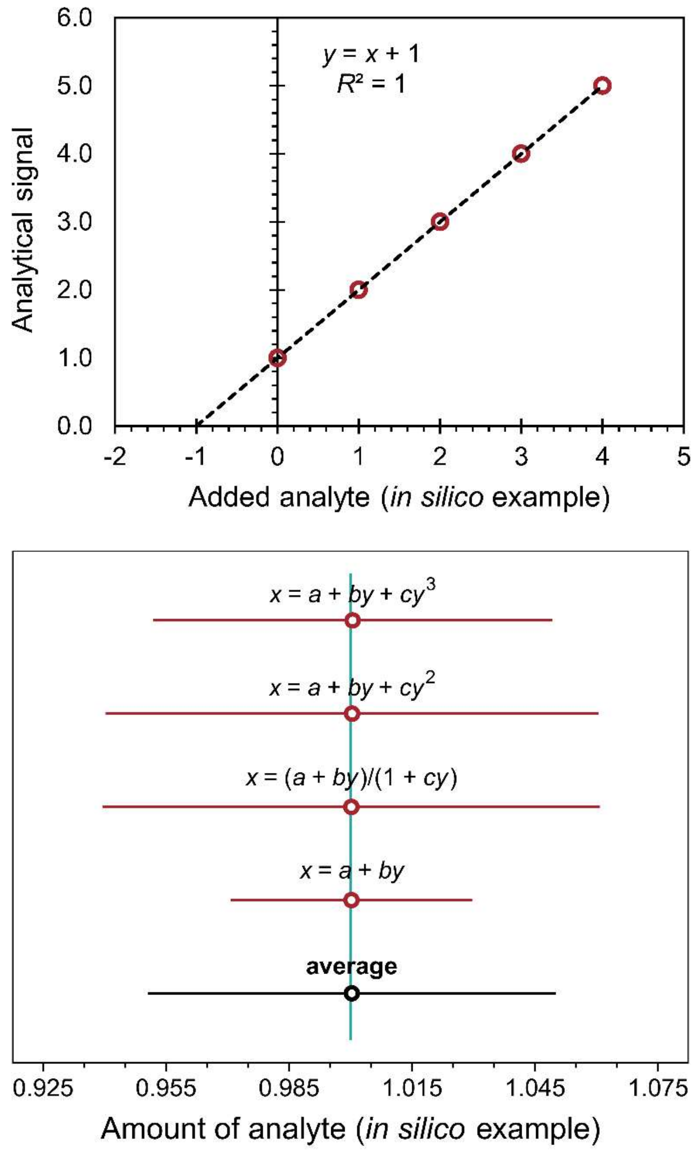


Figure S1. 5-level standard addition with linear data (*in silico*)

Top. Standard addition calibration plot. x = (0, 1, 2, 3, 4), y = (1, 2, 3, 4, 5), and $u(y)$ = 0.01 for all signals (homoscedastic). True value = 1.000 (blue line).

Bottom. Comparing different model equations for the calculation of standard addition results (Table S1). In this case, the linear model is the true model for the interpretation of this *in silico* data and yield w = 1.000 ± 0.030 (k = 2). The model average yield the same result with a larger uncertainty: w = 1.000 ± 0.050 (k = 2).

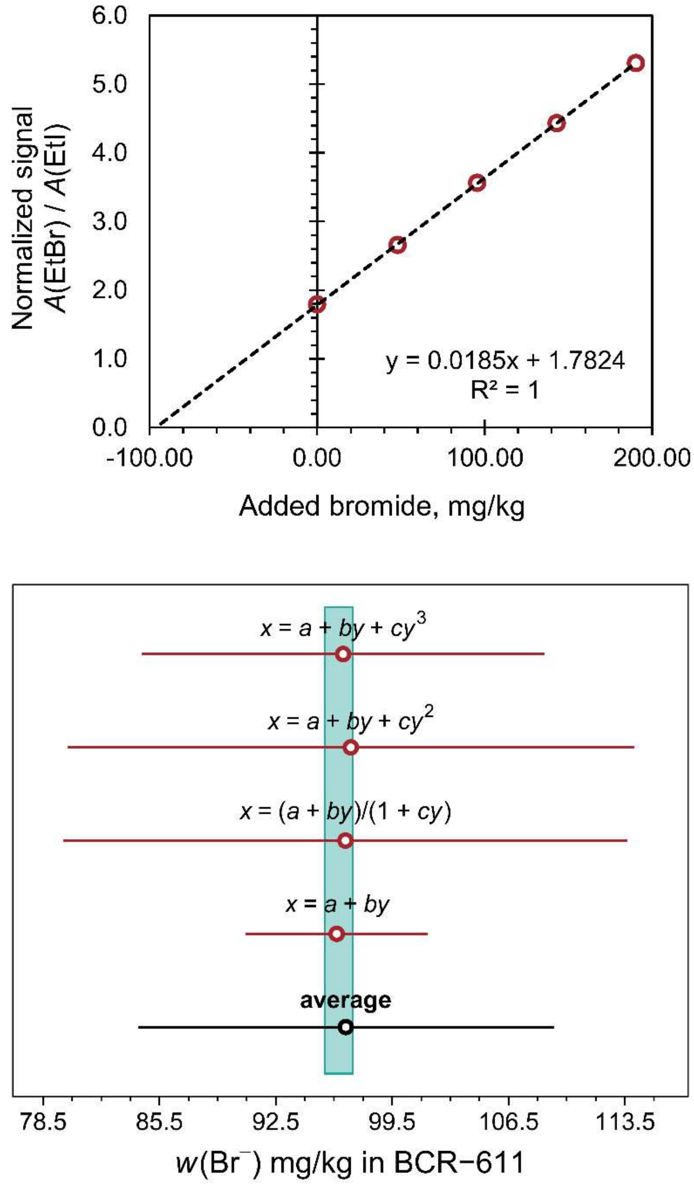
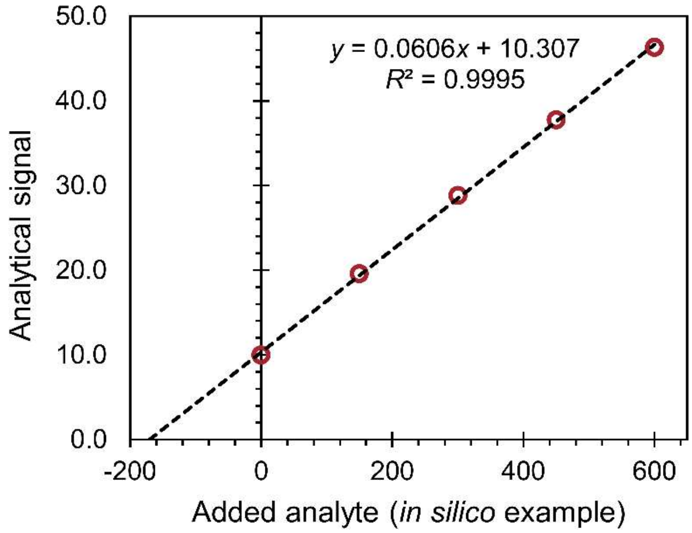


Figure S2. 5-level standard addition for the determination of bromide in groundwater BCR-611 by GC-MS

Top. Standard addition calibration plot. x = (0, 48.08, 95.53, 143.0, 190.3), y = (1.79, 2.66, 3.56, 4.43, 5.31), and $u_R(y)$ = 0.75 %. Isotope dilution data = 96.28 ± 0.84 mg/kg Br^- (k = 2, blue rectangle) [1]. Certified value = 93 ± 4 mg/kg Br^-. The measurement of bromide was performed by headspace GC-MS after ethylation with triethyloxonium tetrafluoroborate. Iodide was used as an endogenous internal standard. Experimental details can be found in ref. [1].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S2). In this case, a good agreement between all models was found.



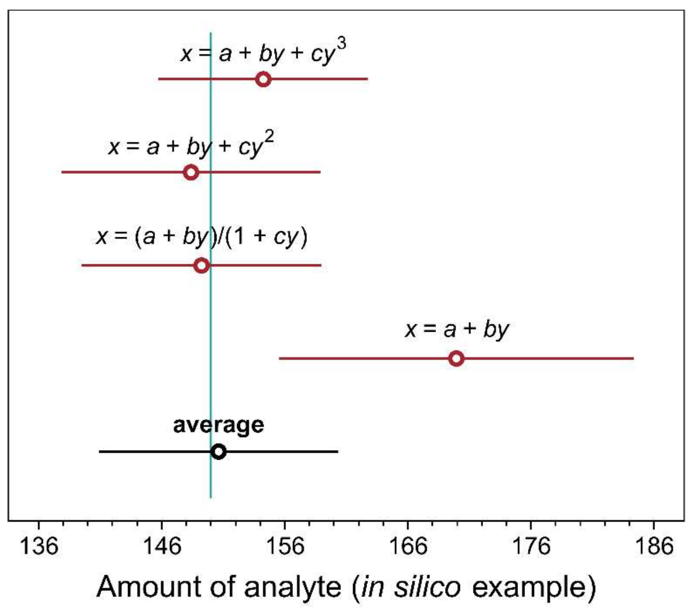


Figure S3. 5-level standard addition with nonlinear data (*in silico*)

Top. Standard addition calibration plot. x = (0, 150, 300, 450, 600), y = (9.961, 19.57, 28.82, 37.73, 46.31), and $u(y)$ = 0.100 for all signals (homoscedastic). True value = 150 (blue line). The data were chosen consistently to the equation proposed by Li et al. [2].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S3). All models are empirical approximations of the true model. In this case the standard addition result obtained by linear model w = 170 ± 14 (k = 2) is not in agreement with the true value whereas the estimate obtained by average w = 150.6 ± 9.8 (k = 2) is satisfactory.

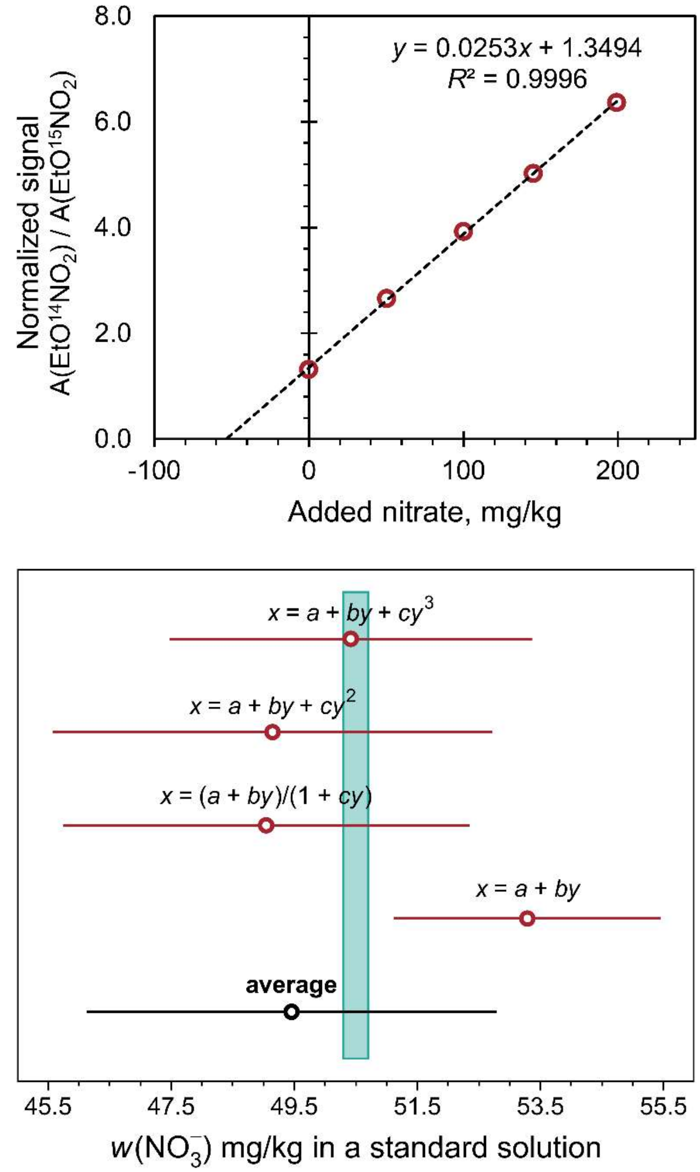


Figure S4. 5-level standard addition for NO_3^- quantitation by GC-MS (with $^{15}NO_3^-$ internal standard)

Top. Standard addition calibration plot. x = (0, 0, 0, 50.46, 50.46, 50.46, 100.20, 100.20, 100.20, 145.27, 145.27, 145.27, 199.19, 199.19, 199.19), y = (1.313, 1.308, 1.319, 2.645, 2.659, 2.647, 3.872, 3.969, 3.911, 5.003, 5.013, 5.045, 6.352, 6.342, 6.394), and $u_R(y)$ = 0.432 % for all signals (heteroscedastic). True value = 50.5 ± 0.2 (k = 2, blue rectangle). The data were acquired by electron ionization GC-MS [3].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S4). In this case the standard addition result obtained by linear model w = 53.3 ± 2.2 (k = 2) is not in agreement with the true value whereas, the estimate obtained by average w = 49.5 ± 3.3 (k = 2) is satisfactory.

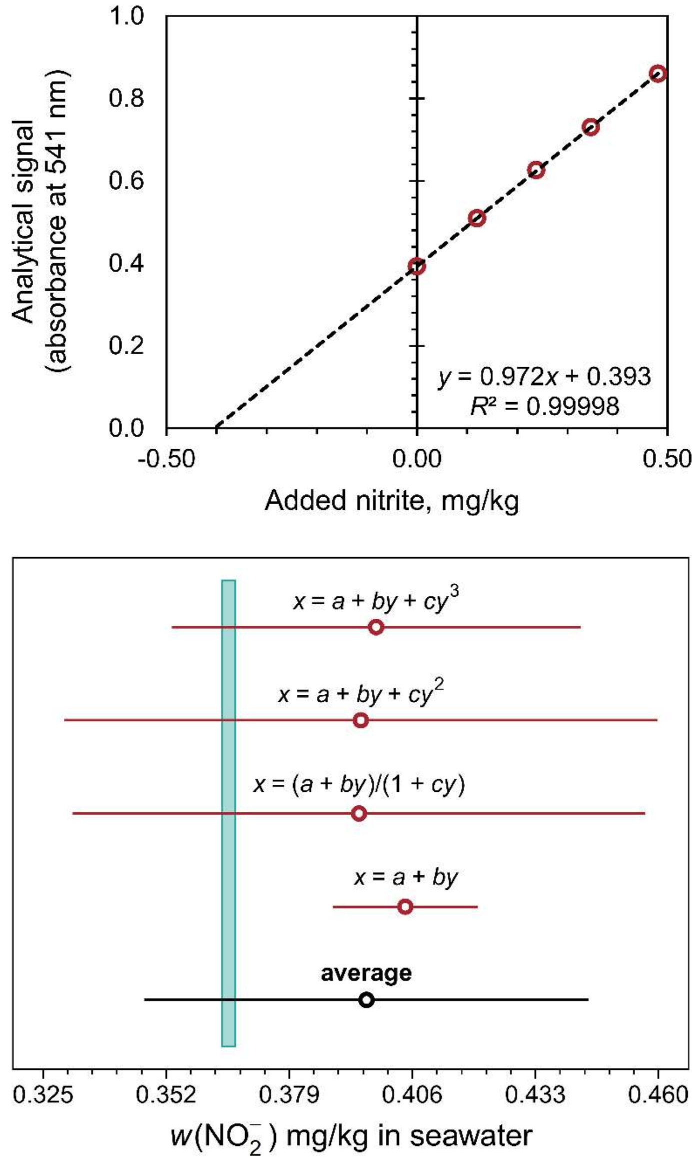


Figure S5. 5-level standard addition for NO_2^- quantitation in seawater by UV-vis

Top. Standard addition calibration plot. x = (0, 0.1200, 0.2381, 0.3473, 0.4809), y = (0.3923, 0.5096, 0.6258, 0.7300, 0.8597), and $u_R(y)$ = 0.5%. True value = 0.3657 ± 0.0015 mg/kg NO_2^- (k = 2, blue rectangle). The data were acquired by UV-vis at 541 nm after derivatization [4, 5].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S5). In this case the standard addition result obtained by linear model w = 0.404 ± 0.016 mg/kg NO_2^- (k = 2) is far off with respect to the true value of 0.3657 ± 0.0015 mg/kg NO_2^-. The model average approach improves the situation returning a result (0.396 ± 0.049 mg/kg NO_2^-, k = 2) closer to the true value.

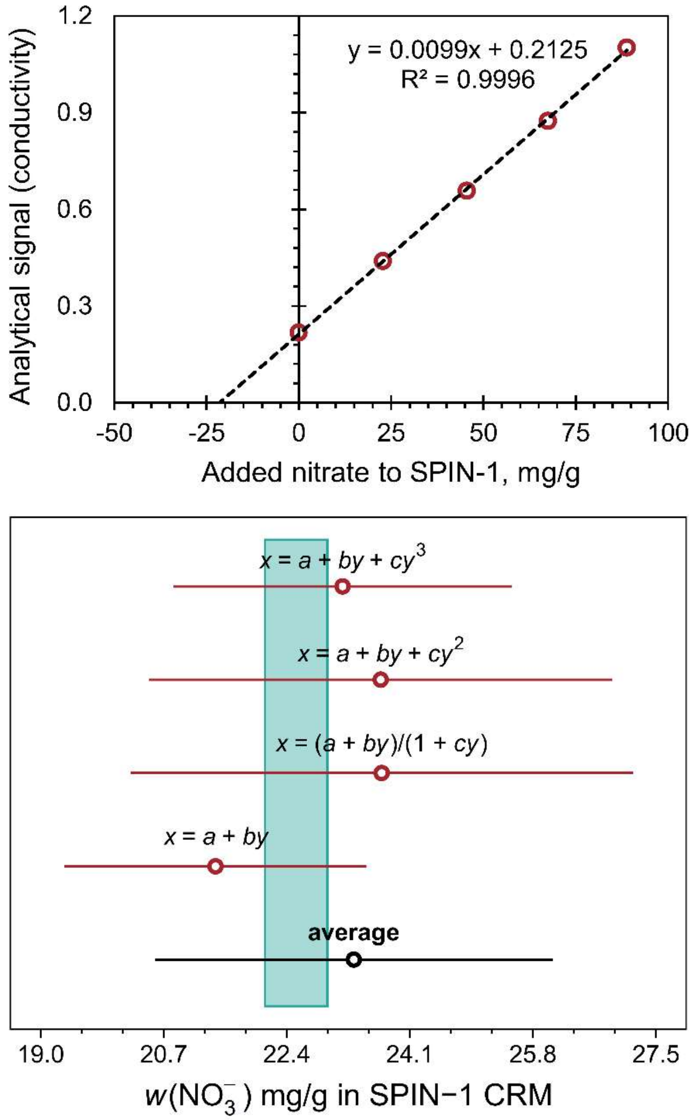


Figure S6. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

Top. Standard addition calibration plot. *x* = (0.0, 22.8, 45.5, 67.5, 88.8), *y* = (0.217, 0.439, 0.658, 0.874, 1.102), and *u*(y) = (0.003, 0.004, 0.001, 0.007, 0.005). True value = 22.53 ± 0.43 mg/g NO_3^- (*k* = 2, blue rectangle). The data were acquired by ion chromatography with conductivity detection and every data point was acquired in triplicates [6].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S6).

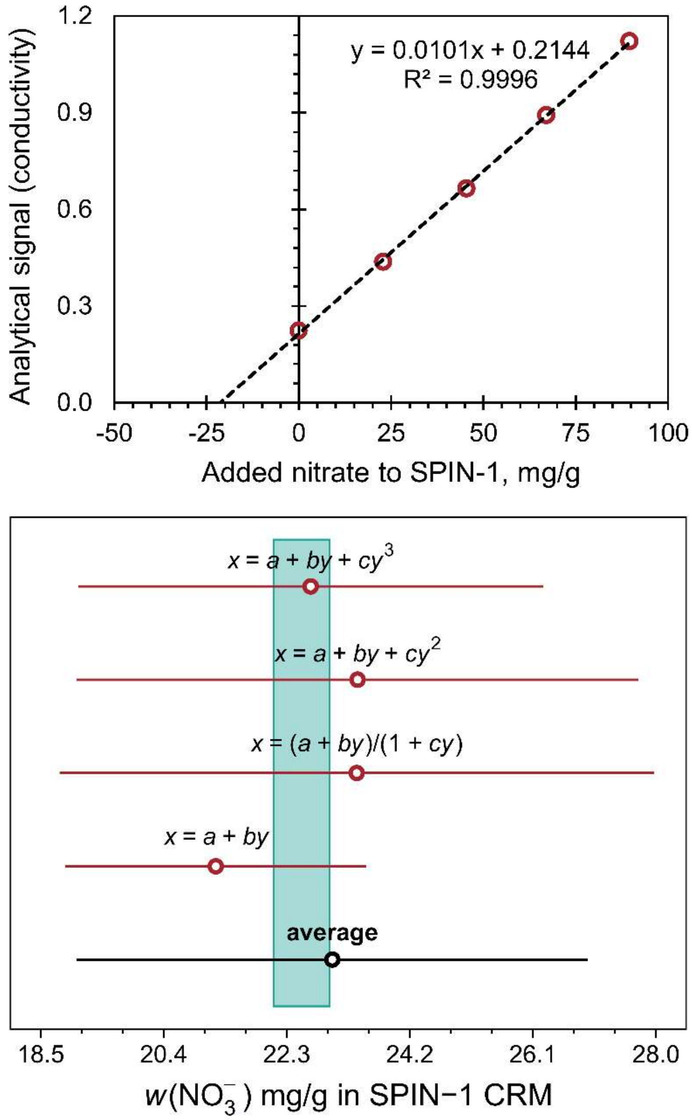


Figure S7. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

Top. Standard addition calibration plot. x = (0.0, 22.9, 45.4, 67.0, 89.6), y = (0.223, 0.437, 0.665, 0.893, 1.121), and u(y) = (0.003, 0.001, 0.011, 0.004, 0.003). True value = 22.53 ± 0.43 mg/g NO_3^- (k = 2, blue rectangle). The data were acquired by ion chromatography with conductivity detection and every data point was acquired in triplicates [6].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S7).

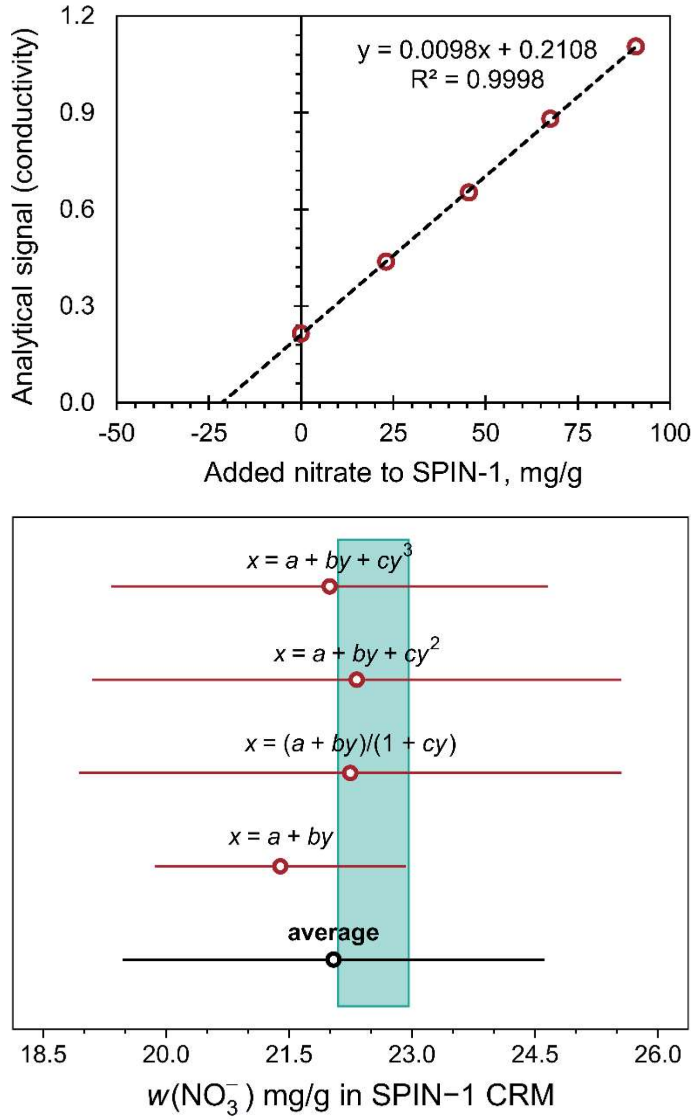


Figure S8. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

Top. Standard addition calibration plot. x = (0.0, 23.1, 45.6, 67.6, 90.8), y = (0.214, 0.437, 0.652, 0.881, 1.105), and u(y) = (0.001, 0.004, 0.004, 0.007, 0.003). True value = 22.53 ± 0.43 mg/g NO_3^- (k = 2, blue rectangle). The data were acquired by ion chromatography with conductivity detection and every data point was acquired in triplicates [6].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S8).

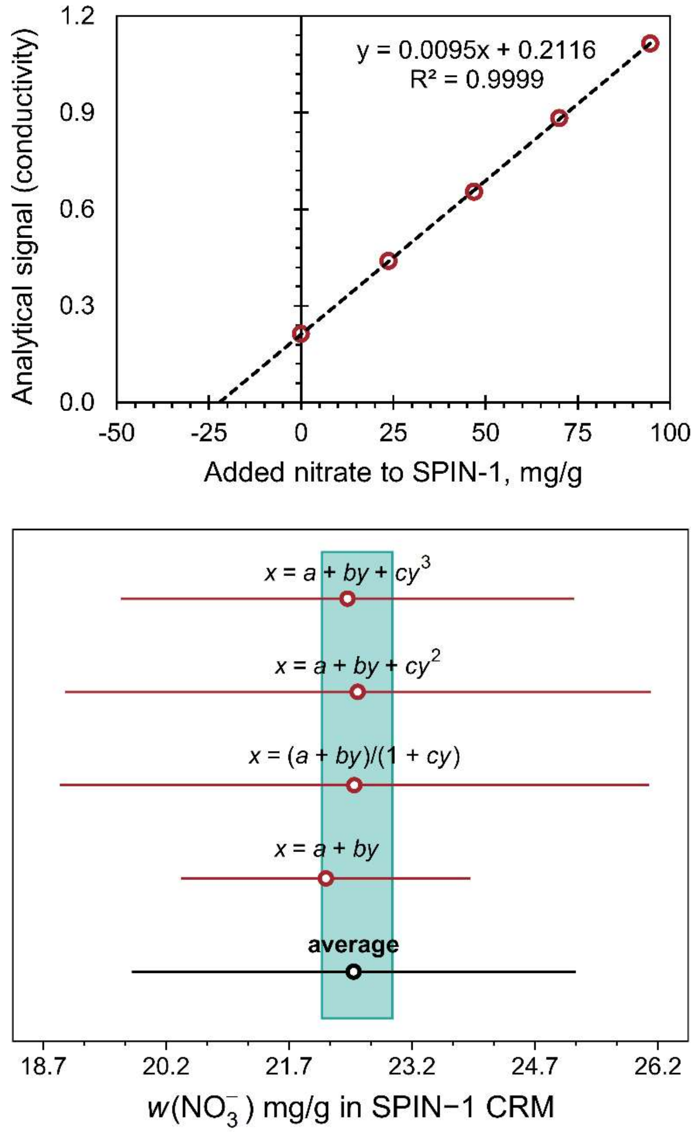


Figure S9. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

Top. Standard addition calibration plot. x = (0.0, 23.7, 46.9, 70.0, 94.6), y = (0.213, 0.439, 0.654, 0.882, 1.115), and u(y) = (0.002, 0.001, 0.003, 0.009, 0.010). True value = 22.53 ± 0.43 mg/g NO_3^- (k = 2, blue rectangle). The data were acquired by ion chromatography with conductivity detection and every data point was acquired in triplicates [6].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S9).

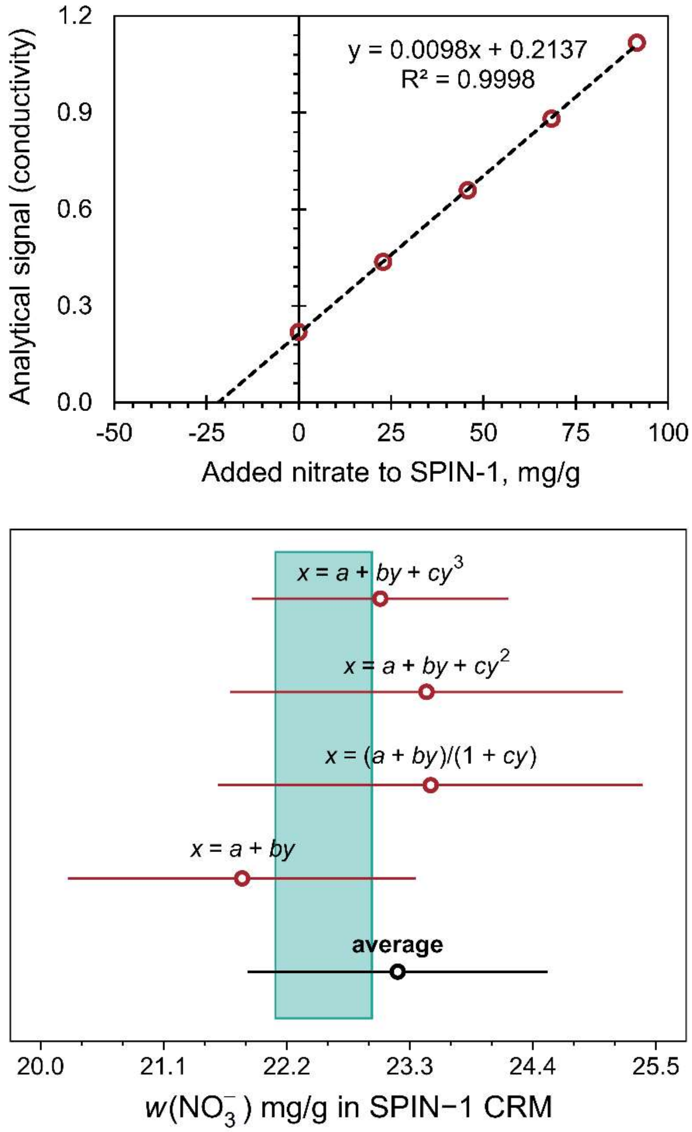


Figure S10. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

Top. Standard addition calibration plot. x = (0.0, 22.9, 45.8, 68.5, 91.6), y = (0.218, 0.437, 0.659, 0.880, 1.117), and u(y) = (0.001, 0.002, 0.002, 0.002, 0.009). True value = 22.53 ± 0.43 mg/g NO_3^- (k = 2, blue rectangle). The data were acquired by ion chromatography with conductivity detection and every data point was acquired in triplicates [6].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S10).

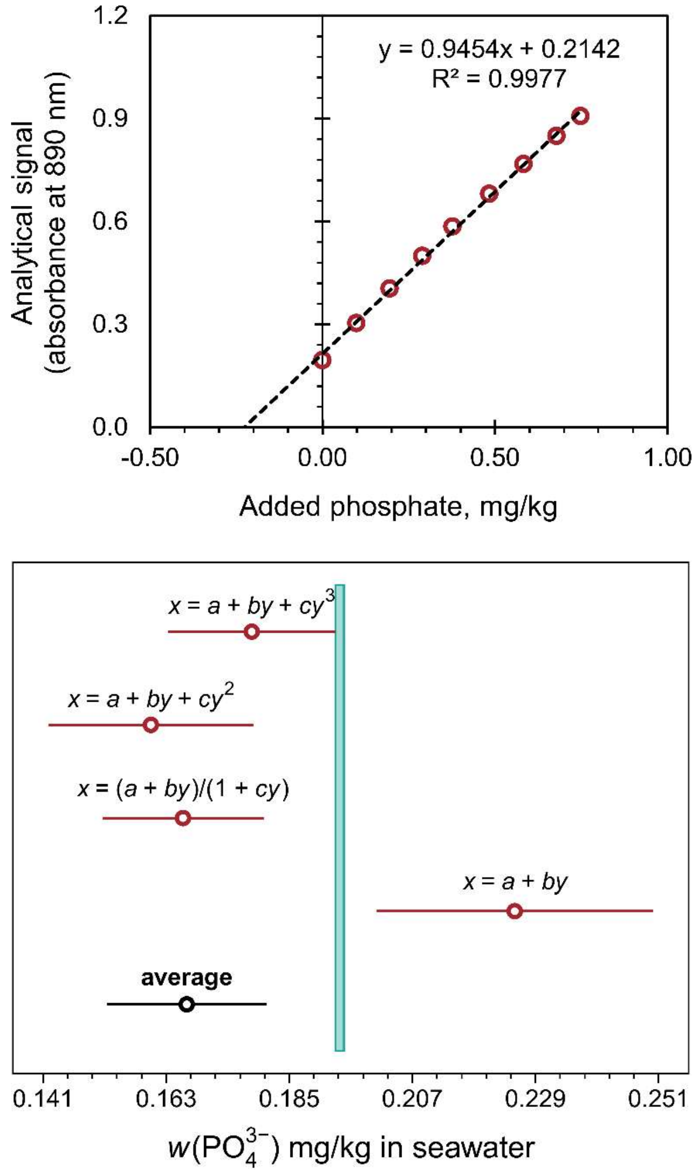


Figure S11. 9-level standard addition for PO_4^{3-} in seawater by UV-vis

Top. Standard addition calibration plot. x = (0, 0.09871, 0.1948, 0.2893, 0.3767, 0.4836, 0.5826, 0.6782, 0.7487), y = (0.196, 0.303, 0.404, 0.500, 0.586, 0.680, 0.767, 0.849, 0.907), and $u_R(y)$ = 0.5%. True value = 0.1940 ± 0.0010 mg/kg PO_4^{3-} (k = 2, blue rectangle). The data were acquired by UV-vis at 890 nm after derivatization [4, 5].

Bottom. Comparing different model equations for the calculation of standard addition results (Table S11).

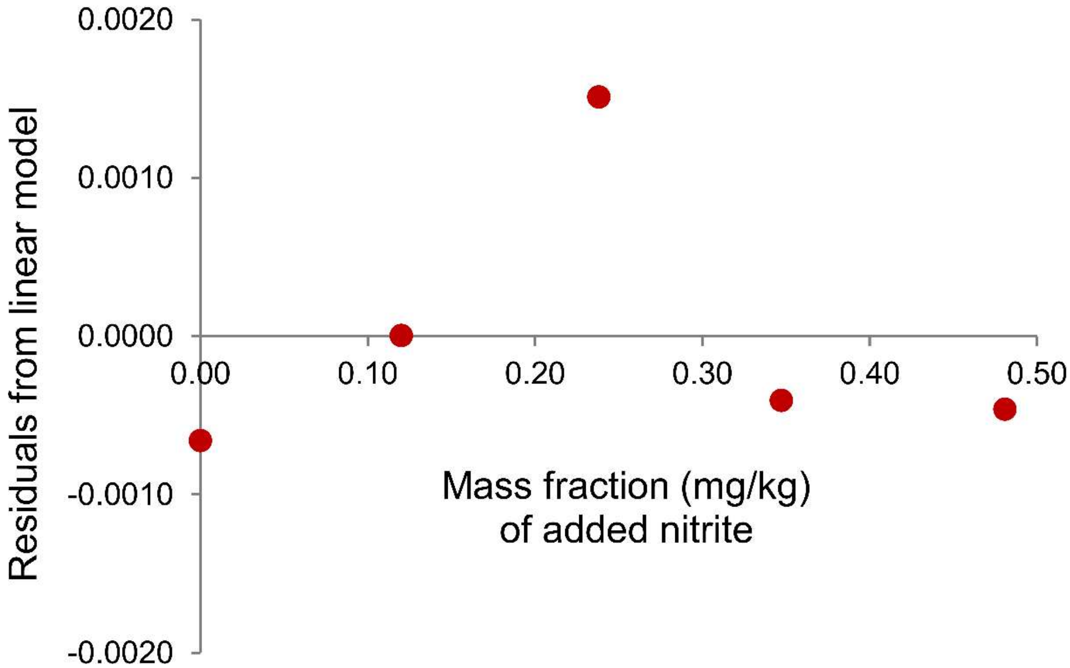


Figure S12. Residual graph for NO_2^- in seawater by UV-vis (Fig. S5)

S2. Supporting tables

BIC = Bayesian Information Criterion. The weight (*p*) is the contribution that the model is giving to the average. The uncertainties on BIC and on *p* were obtained using parametric bootstrap resampling

Table S1. 5-level standard addition with linear data (*in silico*)

model	BIC	*u*(BIC)	weight, *p*	*u*(*p*)	result, *w*	*u*(*w*)
$x = a + by$	-31.5	4.88	0.237	0.153	**1.000**	**0.015**
$x = (a + by)/(1 + cy)$	-32.96	6.47	0.25	0.071	**1.000**	**0.030**
$x = a + by + cy^2$	-32.96	6.46	0.25	0.071	**1.000**	**0.030**
$x = a + by + cy^3$	-32.96	6.43	0.262	0.122	**1.000**	**0.024**
average	-	-	-	-	**1.000**	**0.025**

Table S2. 5-level standard addition for the determination of bromide in groundwater BCR-611 by GC-MS

model	BIC	*u*(BIC)	weight, *p*	*u*(*p*)	result, *w*	*u*(*w*)
$x = a + by$	19.45	4.8	0.247	0.149	**96.2**	**2.7**
$x = (a + by)/(1 + cy)$	18.36	6.24	0.241	0.063	**96.7**	**8.5**
$x = a + by + cy^2$	18.33	6.29	0.244	0.063	**97.0**	**8.5**
$x = a + by + cy^3$	18.2	6.29	0.268	0.106	**96.6**	**6.1**
average	-	-	-	-	**96.7**	**6.3**

Table S3. 5-level standard addition with nonlinear data (*in silico*)

model	BIC	*u*(BIC)	weight, *p*	*u*(*p*)	result, *w*	*u*(*w*)
$x = a + by$	34.77	1.52	0.001	0.003	**169.9**	**7.2**
$x = (a + by)/(1 + cy)$	17.61	6.44	0.353	0.179	**149.2**	**4.9**
$x = a + by + cy^2$	18.34	6.39	0.301	0.207	**148.4**	**5.3**
$x = a + by + cy^3$	18.71	6.44	0.345	0.32	**154.3**	**4.3**
average	-	-	-	-	**150.6**	**4.9**

Table S4. 5-level standard addition for NO_3^- quantitation by GC-MS (with $^{15}NO_3^-$ internal standard)

model	BIC	*u*(BIC)	weight, *p*	*u*(*p*)	result, *w*	*u*(*w*)
$x = a + by$	63.21	3.51	0.046	0.064	**53.3**	**1.1**
$x = (a + by)/(1 + cy)$	56.31	5.19	0.503	0.059	**49.0**	**1.7**
$x = a + by + cy^2$	57.5	5.21	0.276	0.026	**49.1**	**1.8**
$x = a + by + cy^3$	58.43	5	0.175	0.025	**50.4**	**1.5**
average	-	-	-	-	49.5	1.7

Table S5. 5-level standard addition for NO_2^- quantitation in seawater by UV-vis

model	BIC	*u*(BIC)	weight, *p*	*u*(*p*)	result, *w*	*u*(*w*)
$x = a + by$	-42.26	4.95	0.22	0.154	**0.4040**	**0.0079**
$x = (a + by)/(1 + cy)$	-44.17	6.4	0.272	0.079	**0.394**	**0.031**
$x = a + by + cy^2$	-43.99	6.41	0.244	0.056	**0.395**	**0.033**
$x = a + by + cy^3$	-44.1	6.46	0.264	0.09	**0.398**	**0.022**
average	-	-	-	-	0.396	0.024

Table S6. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

model	BIC	*u*(BIC)	weight, *p*	*u*(*p*)	result, *w*	*u*(*w*)
$x = a + by$	14.87	3.1	0.058	0.074	**21.4**	**1.0**
$x = (a + by)/(1 + cy)$	9.96	6.22	0.185	0.087	**23.7**	**1.7**
$x = a + by + cy^2$	9.3	6.2	0.246	0.085	**23.7**	**1.6**
$x = a + by + cy^3$	7.89	6.42	0.511	0.185	**23.2**	**1.2**
average	-	-	-	-	23.3	1.4

Table S7. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

model	**BIC**	***u*(BIC)**	**weight, *p***	***u*(*p*)**	**result, *w***	***u*(*w*)**
$x = a + by$	16.01	2.96	0.159	0.133	21.2	**1.2**
$x = (a + by)/(1 + cy)$	13.73	3.87	0.292	0.065	23.4	**2.3**
$x = a + by + cy^2$	13.44	3.75	0.341	0.079	23.4	**2.2**
$x = a + by + cy^3$	14.41	3.28	0.207	0.033	22.7	**1.8**
average	**-**	**-**	**-**	**-**	**23.0**	**2.0**

Table S8. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

model	**BIC**	***u*(BIC)**	**weight, *p***	***u*(*p*)**	**result, *w***	***u*(*w*)**
$x = a + by$	11.57	3.88	0.252	0.148	21.4	**0.8**
$x = (a + by)/(1 + cy)$	10.53	6.13	0.24	0.064	22.2	**1.7**
$x = a + by + cy^2$	10.36	6.16	0.262	0.071	22.3	**1.6**
$x = a + by + cy^3$	10.55	6.11	0.246	0.109	22.0	**1.3**
average	**-**	**-**	**-**	**-**	**22.0**	**1.3**

Table S9. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

model	**BIC**	***u*(BIC)**	**weight, *p***	***u*(*p*)**	**result, *w***	***u*(*w*)**
$x = a + by$	10.92	5.27	0.237	0.151	22.1	**0.9**
$x = (a + by)/(1 + cy)$	10.05	6.26	0.225	0.046	22.5	**1.8**
$x = a + by + cy^2$	9.97	6.3	0.233	0.048	22.5	**1.8**
$x = a + by + cy^3$	9.56	6.43	0.305	0.133	22.4	**1.4**
average	**-**	**-**	**-**	**-**	**22.5**	**1.4**

Table S10. 5-level standard addition for NO_3^- in SPIN-1 CRM by ion chromatography with conductivity detection

model	**BIC**	***u*(BIC)**	**weight, *p***	***u*(*p*)**	**result, *w***	***u*(*w*)**
$x = a + by$	9.96	5.45	0.041	0.094	21.8	**0.8**
$x = (a + by)/(1 + cy)$	2.27	6.79	0.188	0.116	23.5	**0.9**
$x = a + by + cy^2$	1.71	6.63	0.229	0.112	23.4	**0.9**
$x = a + by + cy^3$	0	6.48	0.542	0.251	23.0	**0.6**
average	**-**	**-**	**-**	**-**	**23.2**	**0.7**

Table S11. 9-level standard addition for PO_4^{3-} in seawater by UV-vis

model	**BIC**	***u*(BIC)**	**weight, *p***	***u*(*p*)**	**result, *w***	***u*(*w*)**
$x = a + by$	-47.38	1.58	0	0	0.225	**0.012**
$x = (a + by)/(1 + cy)$	-74.58	6.29	0.664	0.109	0.1660	**0.0072**
$x = a + by + cy^2$	-71.57	6.2	0.19	0.122	0.1600	**0.0092**
$x = a + by + cy^3$	-70.83	6.36	0.147	0.144	0.1780	**0.0075**
average	**-**	**-**	**-**	**-**	**0.1670**	**0.0071**

S3. Supporting paragraph

Paragraph S1. Bayesian errors-in-variables linear regression model R code

```
################################################################################
# Example 1 # GC-MC analysis of nitrates in a standard solution
# containing 50.5 mg/kg nitrate with std. uncertainty 0.1 mg/kg
# by method of standard additions using Bayesian errors-invariables regression
################################################################################

##### DATA

##### Matrix of observed analytical signals
# each row corresponds to the different sample and each column shows the triplicate
observations
signal = t(array(c(1.313, 1.308, 1.319,
                 2.645, 2.659, 2.647,
                 3.872, 3.969, 3.911,
                 5.003, 5.013, 5.045,
                 6.352, 6.342, 6.394), c(3,5)))

##### Mass fraction of added nitrate to each of the five sample aliquots
stimulus   = c(50.46, 100.20, 145.27, 199.19)
u_stimulus = c(0.10, 0.2, 0.3, 0.4)

##### MEASUREMENT MODEL

##### Bayesian errors-in-variables regression (in Stan programming language)

code.EIV <- "data {
  matrix[5,3] signal;   // analytical response (five samples each measured in
triplicate)
  vector[4] stimulus;   // non-zero stimulus (mass fraction of the added nitrate) to
each sample
  vector[4] u_stimulus; // uncertainty associated with the non-zero stimulus values
}
parameters {
  real intercept;           // regression intercept
  real slope;               // regression slope
  real<lower=0> u_signal;   // measurement uncertainty associated with the analytical
signal
  vector[4] stimulus_true; // true value of stimulus to each sample
}
transformed parameters {
  vector[5] stimulus_true_adj;
  stimulus_true_adj[1] = 0; // zero-stimulus applied to the unspiked sample aliquot
  for(i in 1:4) stimulus_true_adj[1+i] = stimulus_true[i];
}
model {
  // weakly informative prior for u_signal //
  u_signal ~ cauchy(0, 1);

  // likelihood for stimulus //
  stimulus ~ normal(stimulus_true, u_stimulus);

  // likelihood for analytical signals //
  for(i in 1:5) signal[i] ~ normal(intercept + slope * stimulus_true_adj[i],
u_signal);
}
```

```
generated quantities{
  real result = intercept / slope;
}
"

data = list(stimulus = stimulus,
            u_stimulus = u_stimulus,
            signal = signal)

# plot classical OLS for standard additions
ols = lm(c(signal) ~ rep(c(0, stimulus),3))

plot(x=rep(c(0, stimulus),3), y=c(signal), pch=19,
     ylim=c(0,max(signal)), xlim=c(-ols$coef[1]/ols$coef[2], max(stimulus)))
abline(v=0, lty=2)
abline(ols$coef, lwd=3, col=2)

require(rstan)
init.OLS = function() list(intercept = ols$coef[1],
                           slope = ols$coef[2],
                           u_signal = median(apply(signal,1,sd)),
                           stimulus_true = stimulus)
fit <- stan(model_code = code.EIV, data = data, init = init.OLS, iter=5000, cores=4,
chains=4)
print(fit, pars=c('intercept','slope','result'))
# result = 53.3 mg/kg
# standard unc = 1.0 mg/kg
```

S4. References

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