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Calibration of the electron-capture detector for the determination of polychlorinated biphenyls

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The response of the constant current electron capture detector (CC-ECD) to 21 polychlorinated biphenyls is discussed. Responses were non-linear from the detection limit upwards, showing that the CC-ECD is a fundamentally non-linear detector. The extra sum of squares principle was used to assess systematically the validity of several non-linear calibration functions with their respective calibrated ranges. The power function could be applied in the small amount range. The maximum amount to which the power function applied was of the order of several tens to several hundreds of picograms, depending on the compound. Using a slightly modified power function, the calibrated range could be extended by a compound specific factor of 2–45 (maximum amount of the order of several hundred to > 1000 pg). Logarithmic and linear interpolation could be used to increase the calibrated range substantially without significant loss of accuracy, from the detection limit to > 1000 pg injected. Model calculations showed that the use of appropriate internal standards can limit the effect of volume errors on the quantification to less than 1%.

Keywords: *Electron-capture detector; polychlorinated biphenyls; calibration; statistical methods; organochlorine contaminants; gas chromatography; models*

The electron-capture detector (ECD) is widely used in the determination of compounds containing halogens, sulfur, nitrogen and oxygen after separation by gas chromatography. Its principle of operation basically is as follows.[1] High-energy electrons are emitted by a radioactive source (^{63}Ni or ^{3}H), and these electrons produce secondary electrons of lower energy by the ionisation of a make-up gas (nitrogen or argon/methane). The secondary electrons are sampled by the application of an electrical potential between the source and an anode. The presence of an electron-capturing compound reduces the number of free electrons. This reduction is detected as a decrease in electrical current through the detector. In the early days of the ECD, a constant potential was applied, which caused irreproducible and erratic responses.[1] In a later version of this detector, the free electrons were sampled by application of a pulsed potential at a constant frequency (CF-ECD). This mode of operation increased the stability of the ECD and reduced its sensitivity for non-electron-capture processes.[1] The CF-ECD showed a largely non-linear response. In a new mode of operation, the current through the detector was kept constant by adjusting the frequency of the pulses.[2] This detector is referred to as the constant-current ECD (CC-ECD). The relationship between the change in frequency (Δf) and the amount (a) of an electron-capturing compound was established as

$$\Delta f = \frac{k_1}{K} a^{\varphi} \qquad (1)$$

where K is a proportionality constant, k_1 is the rate constant for the electron-capture reaction, and φ is the response index. Although the values of φ are close to unity, small deviations were observed; depending on the compound and the detector temperature, values of φ were found in the range 0.95–1.03.[2,3] The linear dynamic range was defined as the interval for which the logarithm of the response was linearly proportional to the logarithm of the amount injected.[2]

For quantitative analysis, the non-linearity of the CC-ECD should be taken into account. It has been suggested that the linearity can be evaluated by plotting the response per unit mass against the mass injected[4–6] (see Fig. 1). It was proposed to define a true linear range as the range of amount where the slope of this plot was approximately equal to zero. Storr-Hansen[7] evaluated several non-linear calibration functions for polychlorinated biphenyls (PCBs). She found the power fit [eqn. (1)] to be valid from the detection limit up to 250 pg injected. For larger amounts, the power fit underestimated the injected amounts, and a second-order equation with non-zero intercept fitted the data better. The second-order fit overestimated the amounts near the detection limit, however.

For proper detector calibration, both the type of response function and its range of application should be identified. Biased results can be expected when the number of parameters in the response function is too small, or the concentration range too large. On the other hand, response functions with too many parameters will result in over-fitting the data. For example, fitting detector response data for n different concentrations with a polynomial of degree $n - 1$ gives a perfect fit, but may result in local maxima and minima that give rise to erratic results.

The non-linearity of the ECD raises the question of the extent to which the internal standards correct for volume losses during sample extraction, clean-up and analysis. When the detector response is linear, the calculations are straightforward:[8]

$$c_{j,\text{sample}} = \frac{(H_j)_{\text{sample}}}{(H_j)_{\text{standard}}} c_{j,\text{standard}} \qquad (2)$$

with

$$H_j = \frac{h_j}{h_i} \qquad (3)$$

where h_j and h_i are the responses of the analyte (j) and the internal standard (i), respectively, and c_j is the concentration of the analyte. When the detector response is non-linear, the use of relative responses may give rise to errors, since the non-linearity of analyte and internal standard responses are not necessarily equal.

In the following, we make an analysis of ECD response functions of PCBs. We apply statistical methods to identify systematically the validity of a number of calibration functions with their respective ranges. In addition, we discuss the extent to which internal standards correct for volume losses. Although the actual values of response function parameters and calibrated ranges may be specific for the ECD used in this study, we believe the present assessment method to be applicable to other systems. Throughout this paper, CB118 will be used as a typical example in the figures.

Experimental

Two stock standard solutions containing 21 PCBs (see Table 1, IUPAC numbering[9]) were prepared from solutions of the pure compounds in 2,2,4-trimethylpentane at concentrations of approximately 1000 and 300 ng ml^{-1}. The stock standard solutions were diluted by mass, covering a concentration range of 0.1–1000 ng ml^{-1}. From each dilution, a 900 μl sample was taken, and 100 μl of a solution of CB112 was added (130 ng ml^{-1}). Samples were injected four times, starting at the lowest concentrations. Between each series, the injection system was cleaned. Cross-contamination was shown to be negligible by the injection of 2,2,4-trimethylpentane.

Samples were injected on to an HP 5880 gas chromatograph equipped with an HP 7673A autosampler and a constant-current ECD (Hewlett-Packard, Avondale, PA, USA). Analytes were separated on a 60 m × 0.15 mm id CP-Sil 19 capillary column with a film thickness of 0.20 μm (Chrompack, Middelburg, The Netherlands). The carrier gas was hydrogen, the injector temperature was 250 °C, the injection mode was splitless (4.5 min) and the detector temperature was 340 °C. The column temperature programme was initial temperature 90 °C (held for 4.5 min), increased at 10 °C min^{-1} to 215 °C (held for 25 min), then increased at 5 °C min^{-1} to 270 °C (held for 25 min). The detector output was sampled by a data acquisition program at a rate of 3 Hz. Baselines were set manually with a data processing program. Responses were measured as peak heights relative to the peak height of the internal standard. Peaks with a signal-to-noise ratio smaller than 10 were not considered.

Results and discussion

Single-level calibration

The definition of the linear range from a plot of the response per unit mass *versus* the mass injected depends on the largest amount considered. A typical example (CB118) is shown in Fig. 1, for three amount ranges. The dashed lines represent the intervals where differences in sensitivity are smaller than 10%. Depending on the largest amount considered, the approximate linear range is 160–360, 80-180 and 40–90 pg [Fig. 1, (*a*), (*b*) and (*c*) respectively]. Clearly, the apparent linear range is not a characteristic of the ECD, but instead of the maximum amount considered. Furthermore, Fig. 1 shows that the CC-ECD response is non-linear from the detection limit upwards. The errors involved in adopting an apparent linear range of 160–360 pg are shown in Fig. 2. The relative error in the calculated response (Δ_H) is defined as

$$\Delta_H = \frac{H_{\text{calc}} - H_{\text{exp}}}{H_{\text{exp}}} \quad (4)$$

At the lower limit of the apparent linear range, responses are underestimated by 5% and at the higher limit they are overestimated by 5%. Outside this range, the errors increase rapidly to unacceptable levels. The adoption of an apparent linear range is both incorrect and impractical. It is incorrect because systematic errors should be avoided unless the random errors are much larger. The approximate linear range concept is impractical because the relative concentrations of PCB congeners in environmental samples differ by orders of magnitude. Moreover, the relative concentrations also depend on the nature of the samples to be studied (sediments, water, invertebrates, fish, mammals). Hence a detailed knowledge of the concentrations of all PCB congeners in the samples is needed before a standard can be prepared to determine these concentrations accurately, when a single-level calibration is used.

Multi-level calibration

Error structure of the response data

Before least-squares parameter estimation can be applied, the error structure in the data must be known, since a basic assumption in ordinary least-squares (OLS) estimation is that the error variance is constant for all values of the independent variable, *i.e.*, the amount injected in our case.[10] If, however, the error variance is concentration dependent, a weighted least-squares procedure should be used. We assessed the error structure by plotting the repeatability of the response (*H*) *versus* the amount injected. As an example, this is shown for CB118 in Fig. 3. The repeatability increases with increasing amount injected in an approximately linear manner. Therefore, OLS estimation would produce erroneous results, and weighted least-squares estimation should be used instead.[10]

Statistical analysis

When the range to which a particular calibration function is applied increases, the weighted residual sum of squares (RSS) also increases. The judgement to be made is whether this increase is statistically significant or not. The extra sum of squares principle[11] is a systematic approach to make this judgement. Considering a range comprising *M* groups of *n* observations per group, the smallest RSS is obtained with a function that passes exactly through the group averages: the 'complex model' (*e.g.*, a polynomial of degree $M - 1$). The complex model gives an independent estimate of the error variance based on $df_{\text{complex}} = M(n - 1)$ degrees of freedom. When applying a simpler model with *p* parameters, the RSS increases. When the RSS of the simpler model is significantly larger than that for the complex model, it must be concluded that the simpler model fails to describe the data accurately. The error variance is first estimated from the difference in RSS between

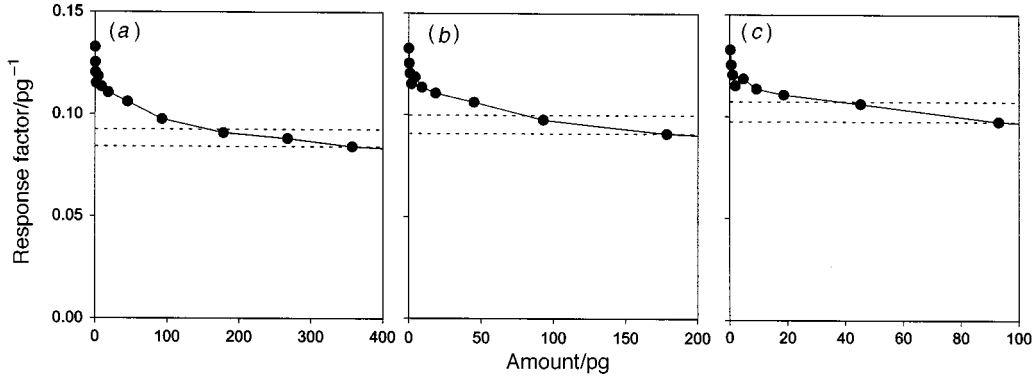

Fig. 1 Response factor (*H/a*) of CB118 for the amount ranges (*a*) 0–360 pg, (*b*) 0-180 pg and (*c*) 0–90 pg. Dashed lines indicate the intervals for which the response factor is constant to within ±5%.

the simple and the complex model. This estimate is associated with $df_{simple} - df_{complex}$ degrees of freedom. In the case of a perfect fit, the variance estimate equals the residual variance of the complex model. Using a one-tailed *F*-test, we can evaluate whether or not the error variance estimated from the added RSS is significantly larger than the estimate obtained from the complex model:

$$F = \frac{\dfrac{RSS_{simple} - RSS_{complex}}{df_{simple} - df_{complex}}}{\dfrac{RSS_{complex}}{df_{complex}}} \quad (5)$$

The number of degrees of freedom equals $M(n - 1)$ for the complex model and $Mn - p$ for the simple model. The range of validity of the simple model can be assessed by applying eqn. (6) to increasing amount ranges until the calculated variance ratio becomes larger than the appropriate critical *F*-value $[F_{0.05}(df_{simple} - df_{complex}, df_{complex})]$.

Power fit. A linear relationship between the log-transformed response and amount has been observed in the small amount range.[2,3,7] The validity of this log–log relationship was limited to amounts injected smaller than 300–3000 pg for various halogenated hydrocarbons. This relation is identical with the logarithmically transformed power function [eqn. (1)]. Using the peak height (*H*) instead of the change in frequency as a variable, eqn. (1) becomes

$$H = Aa^{\varphi} \quad (6)$$

and

$$\log H = \log A + \varphi \log a \quad (7)$$

where *A* is a constant. Eqn. (6) was fitted to the data for increasing amount ranges (*i.e.*, 0.1–1, 0.1–2 , 0.1–5 pg, *etc*.),

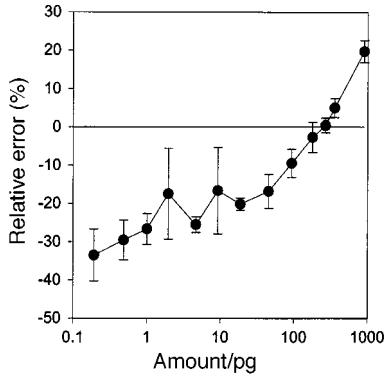

Fig. 2 Relative error (average ± standard deviation) in the calculated response of CB118 when an apparent linear range of 160–360 pg is used.

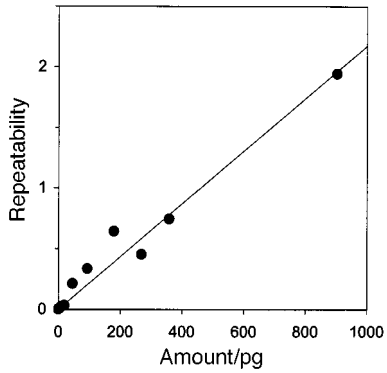

Fig. 3 Repeatability of the response (*H*) of CB118.

and the RSS were calculated. The relative errors in the calculated response of CB118 are shown in Fig. 4. The results for all congeners are summarised in Table 1. Values of the response index (φ) were in the range 0.93–1.00, similar to literature values.[7] The maximum amount for which eqn. (6) applies is of the order of several tens to several hundreds of picograms, depending on the compound.

Modified power fit. The calibrated range may be extended by using more complicated calibration functions. Eqn. (6) should be the limiting case in the small amount range, however. A possible candidate is a modified power function:

$$H = \frac{Aa^{\varphi_j}}{1 + Ba^{\varphi_j}} \quad (8)$$

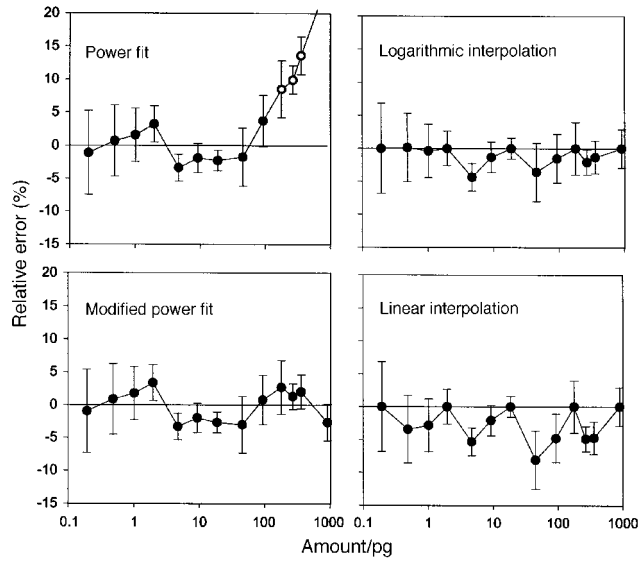

Fig. 4 Relative errors (average ± standard deviation) in the calculated response of CB118 for the power fit, the modified power fit, logarithmic interpolation and linear interpolation. Data points falling outside the calibrated range are indicated with open circles.

Table 1 Calibration results for the power fit [eq. (6)]. Parameter values are listed as estimate ± standard deviation

Compound	*N*	a_{max}/ pg	*s* (%)	Log *A*	φ
CB11	10	10	3.2	−1.239 ± 0.011	1.022 ± 0.015
CB15	30	50	7.8	−1.240 ± 0.007	0.982 ± 0.008
CB28	48	900	5.9	−0.677 ± 0.005	0.958 ± 0.003
CB31	45	300	5.8	−0.712 ± 0.005	0.953 ± 0.003
CB52	30	20	3.5	−0.740 ± 0.003	0.960 ± 0.004
CB77	14	20	2.7	−1.136 ± 0.008	0.996 ± 0.009
CB101	26	20	2.2	−0.899 ± 0.002	0.954 ± 0.003
CB105	44	900	4.7	−0.896 ± 0.005	0.968 ± 0.003
CB114	48	900	4.3	−0.882 ± 0.004	0.977 ± 0.002
CB118	34	100	4.3	−0.913 ± 0.004	0.958 ± 0.004
CB126	33	400	6.8	−1.055 ± 0.012	0.945 ± 0.007
CB128	45	400	5.8	−0.871 ± 0.005	0.953 ± 0.004
CB138	37	300	5.6	−0.846 ± 0.006	0.948 ± 0.004
CB153	26	50	4.1	−0.858 ± 0.005	0.955 ± 0.005
CB156	36	900	7.6	−0.993 ± 0.013	0.970 ± 0.007
CB169	35	900	10.6	−1.120 ± 0.019	0.923 ± 0.009
CB170	48	900	13.2	−1.072 ± 0.012	0.977 ± 0.007
CB180	20	900	8.3	−0.664 ± 0.049	0.882 ± 0.021
CB194	48	900	13.6	−1.170 ± 0.012	0.958 ± 0.007
CB202	34	200	7.6	−0.914 ± 0.009	0.919 ± 0.006
CB209	48	900	16.1	−1.242 ± 0.015	0.927 ± 0.009

The range to which eqn. (8) applies was identified in the same way as described above. The relative errors in the calculated response of CB118 are shown in Fig. 4. Results for all tested chlorobiphenyl congeners are summarised in Table 2. By applying eqn. (8) instead of eq. (6) the calibrated range is extended by a factor of 2–45.

Interpolation. Interpolation may be used as an alternative to fitting one function to multiple standards. To illustrate this, the injected amounts of 0.2, 2, 20, 200 and 1000 pg were arbitrarily treated as standards and the other amount levels were treated as samples. For each amount interval a calibration function was calculated from the amounts and responses of two subsequent standards. For logarithmic interpolation, eqn. (7) was applied; for linear interpolation, the untransformed variables were used. The results are summarised in Tables 3 and 4. The relative errors in the calculated responses of CB118 are shown in Fig. 4. With logarithmic interpolation, the errors are similar to those obtained for the modified power fit (Tables 1 and 3). Values of the response index (φ) decrease from 0.98 in the amount range 0.2–2 pg to 0.87 in the range 200–1000 pg (Table 3). Averaged over all compounds, the errors occurring in linear interpolation are about 1% higher than for logarithmic interpolation.

Internal standard method. The non-linear response of the ECD necessitates a further analysis of the quantification method with internal standards. We will show that the errors resulting from differences in the response index between the internal standard and analyte are negligible. We consider the injection of a volume (v) from a solution containing analyte (j) and internal standard (is) at concentrations c_j and c_{is}, respectively. The amounts injected are $a_j = vc_j$ and $a_{is} = v\ c_{is}$. The relative

Table 2 Calibration results for the modified power fit [eqn. (8)]. Parameter values are listed as estimate ± standard deviation

Compound	N	a_{max}/pg	s (%)	Log A	φ	Log B
CB11	22	100	4.4	−1.232 ± 0.014	1.024 ± 0.019	−2.33 ± 0.06
CB15	45	400	7.1	−1.238 ± 0.007	0.988 ± 0.008	−2.78 ± 0.06
CB28	48	900	5.2	−0.680 ± 0.005	0.970 ± 0.004	−3.62 ± 0.12
CB31	52	900	5.6	−0.711 ± 0.004	0.959 ± 0.004	−3.47 ± 0.10
CB52	42	900	4.2	−0.739 ± 0.003	0.959 ± 0.004	−2.66 ± 0.06
CB77	26	200	3.1	−1.134 ± 0.008	0.999 ± 0.009	−2.79 ± 0.06
CB101	38	200	2.6	−0.897 ± 0.002	0.956 ± 0.003	−2.81 ± 0.05
CB105	44	900	4.1	−0.902 ± 0.005	0.979 ± 0.004	−3.77 ± 0.12
CB114	48	900	4.1	−0.883 ± 0.004	0.982 ± 0.003	−3.99 ± 0.18
CB118	48	900	4.1	−0.912 ± 0.004	0.958 ± 0.003	−3.38 ± 0.06
CB126	36	900	6.0	−1.074 ± 0.012	0.970 ± 0.009	−3.33 ± 0.09
CB128	48	900	6.0	−0.871 ± 0.006	0.958 ± 0.005	−3.67 ± 0.15
CB138	44	900	4.8	−0.850 ± 0.005	0.960 ± 0.005	−3.38 ± 0.07
CB153	41	400	4.1	−0.856 ± 0.005	0.957 ± 0.005	−2.95 ± 0.05
CB156	36	900	7.1	−1.013 ± 0.015	0.990 ± 0.010	−3.68 ± 0.18
CB169	35	900	9.3	−1.161 ± 0.021	0.962 ± 0.015	−3.40 ± 0.13
CB170	48	900	11.6	−1.077 ± 0.011	1.003 ± 0.009	−3.34 ± 0.12
CB180	20	900	8.3	−0.761 ± 0.109	0.935 ± 0.057	−3.50 ± 0.32
CB194	48	900	12.3	−1.175 ± 0.011	0.982 ± 0.010	−3.34 ± 0.14
CB202	44	900	6.3	−0.918 ± 0.007	0.935 ± 0.007	−3.09 ± 0.07
CB209	48	900	14.8	−1.250 ± 0.014	0.957 ± 0.013	−3.21 ± 0.15

Table 3 Calibration results for logarithmic interpolation ($\log H = \log A + \varphi \log a$)

	Range 0.2–2 pg			Range 2–20 pg			Range 20–200 pg			Range 200–1000 pg		
Compound	φ	Log A	s (%)	φ	Log A	s (%)	φ	Log A	s (%)	φ	Log A	s (%)
CB11				0.986	−1.230	5.1	0.861	−1.077	5.6	0.802	−0.931	7.3
CB15	0.990	−1.246	9.0	0.997	−1.248	5.0	0.869	−1.086	4.6	0.834	−1.007	6.9
CB28	0.948	−0.686	6.8	0.993	−0.699	3.1	0.946	−0.639	4.1	0.904	−0.545	5.5
CB31	0.951	−0.720	7.2	0.986	−0.730	3.2	0.920	−0.647	4.2	0.885	−0.568	5.4
CB52	0.962	−0.746	4.1	0.960	−0.746	2.9	0.856	−0.614	3.9	0.846	−0.591	5.0
CB77				0.999	−1.145	3.1	0.903	−1.022	3.7	0.866	−0.939	2.9
CB101	0.940	−0.906	2.3	0.964	−0.914	2.6	0.878	−0.802	2.7	0.846	−0.731	3.4
CB105				0.992	−0.922	3.4	0.963	−0.885	5.4	0.925	−0.799	4.2
CB114	0.949	−0.893	5.4	0.995	−0.906	2.6	0.983	−0.891	3.9	0.933	−0.779	3.7
CB118	0.939	−0.921	4.7	0.982	−0.934	3.2	0.912	−0.845	3.9	0.872	−0.754	3.0
CB126				0.990	−1.095	5.9	0.916	−1.002	8.3	0.868	−0.893	5.7
CB128	0.892	−0.881	4.9	0.981	−0.908	4.4	0.949	−0.867	7.5	0.883	−0.719	5.9
CB138				0.979	−0.870	3.9	0.913	−0.787	6.1	0.873	−0.695	4.5
CB153				0.968	−0.868	3.0	0.872	−0.747	4.4	0.848	−0.692	2.9
CB156				0.986	−1.014	6.1	0.968	−0.990	9.8	0.925	−0.893	8.1
CB169				0.959	−1.158	8.4	0.911	−1.093	13.3	0.859	−0.976	10.2
CB170	1.014	−1.070	14.2	0.989	−1.063	8.1	0.944	−1.007	12.4	0.884	−0.870	9.7
CB180										0.876	−0.660	8.1
CB194	0.949	−1.181	14.1	0.989	−1.192	11.1	0.938	−1.128	17.1	0.858	−0.947	13.9
CB202				0.959	−0.943	5.3	0.861	−0.818	8.3	0.810	−0.704	6.1
CB209	0.845	−1.253	14.8	0.977	−1.291	13.7	0.922	−1.222	19.7	0.795	−0.935	15.5

response can be obtained from eqn. (6) (power fit/logarithmic interpolation):

$$H_j = \frac{h_j}{h_{is}} = \frac{A_j}{A_{is}} \frac{(a_j)^{\varphi_j}}{(a_{is})^{\varphi_{is}}}$$

$$= \frac{A_j}{A_{is}} \left(\frac{a_j}{a_{is}} \right)^{\varphi_j} (a_{is})^{\varphi_j - \varphi_{is}} \quad (9)$$

Substitution of a_{is} from eqn. (6) gives

$$H_j = \frac{A_j}{A_{is}} \left(\frac{a_j}{a_{is}} \right)^{\varphi_j} \left(\frac{h_{is}}{A_{is}} \right)^{\frac{\varphi_j - \varphi_{is}}{\varphi_{is}}} \quad (10)$$

Once the internal standard has been added, the amount ratio of analyte to internal standard is free of experimental error. Errors may be observed in the peak height of the internal standard (h_{is}), which can be regarded as having an average part (h_{avg}) and an error term (Δh_{is}):

$$h_{is} = h_{avg} + \Delta h_{is} \quad (11)$$

Inserting eqn. (11) into eqn. (10) and rearranging gives

$$H_j = \frac{A_j}{A_{is}} \left(\frac{h_{avg}}{A_{is}} \right)^{\frac{\varphi_j - \varphi_{is}}{\varphi_{is}}} \left(\frac{a_j}{a_{is}} \right)^{\varphi_j} \left(1 + \frac{\Delta h_{is}}{h_{avg}} \right)^{\frac{\varphi_j - \varphi_{is}}{\varphi_{is}}} \quad (12)$$

(constant) (variable) (error factor)

On the right-hand side of eqn. (12) three groups of parameters and variables can be identified: the first group is a constant, the second group is the relative amount variable and the third group is an error term. When $\Delta h_{is} << h_{avg}$, the relative error in H_j equals

$$\Delta_H \approx \left(1 + \frac{\Delta h_{is}}{h_{avg}} \right)^{\frac{\varphi_j - \varphi_{is}}{\varphi_{is}}} - 1 \quad (13)$$

An approximate expression may be obtained by making a power series expansion of eqn. (13):

$$\Delta_H \approx \frac{\varphi_j - \varphi_{is}}{\varphi_{is}} \frac{\Delta h_{is}}{h_{avg}} \quad (14)$$

Since differences in the response index are smaller than 0.2 (Table 3), the relative response calibration reduces all volume errors by a factor of > 5. Hence a repeatability of the injection volume of 5% results in a repeatability of $< 1\%$ in the calibration. For samples, an internal standard recovery of 90% results in a bias of $< 2\%$. Combined with a repeatability of 1% for the volumetric addition of the internal standard, the total repeatability as a result of volume errors is smaller than 2%. This estimate is smaller than the value of 3–16% observed in this study, which indicates that fluctuations in the sensitivity of the ECD also are important [proportionality constants *A* in eqn. (6)]. Irreproducible discrimination in the injector, interaction of the sample matrix with the stationary phase in the column and column bleed might also be causes of poor repeatability. The above-mentioned estimates represent a lower limit which may be attained when the chromatographic conditions are fully optimised.

Conclusion

The power fit is a valid response function for the small amount range. The calibrated range can be extended by using either a slightly modified power function, or logarithmic or linear interpolation. Volume errors are virtually eliminated by the use of internal standards provided that the response indices of internal standards and analytes are similar.

Although the use of appropriate calibration functions is a necessary condition for obtaining a valid quantitation for real samples, it is not necessarily a sufficient condition. Detector fouling, and co-elution of compounds with low electron-capture affinity may interfere with the electron capture by the target compounds, thereby changing their amount-response relationship. A number of measures should be taken to validate the quantification of real-world samples. First, a thorough sample clean-up procedure minimises the amount of co-eluting compounds. Second, frequent re-calibration limits the effect of progressive detector fouling. Third, recovery studies using spiked and unspiked samples indicate whether or not co-eluting

Table 4 Calibration results for linear interpolation ($H = \alpha + \beta a$)

	Range 0.2–2 pg			Range 2–20 pg			Range 20–200 pg			Range 200–1000 pg		
Compound	β	α	*s* (%)	β	α	*s* (%)	β	α	*s* (%)	α	α	*s* (%)
CB11				0.056	0.004	5.5	0.037	0.331	10.1	0.027	3.162	7.3
CB15	0.056	0.000	9.2	0.056	0.001	5.1	0.040	0.297	6.3	0.030	2.188	6.8
CB28	0.196	0.005	7.2	0.195	0.007	3.3	0.171	0.470	4.3	0.142	5.596	5.4
CB31	0.182	0.005	7.6	0.178	0.013	3.6	0.146	0.615	4.8	0.118	5.661	5.3
CB52	0.173	0.003	4.7	0.158	0.033	4.2	0.110	0.923	5.9	0.084	4.697	4.9
CB77				0.071	0.000	3.1	0.056	0.295	6.3	0.043	2.511	4.2
CB101	0.117	0.004	3.8	0.109	0.021	3.8	0.080	0.569	5.4	0.060	4.180	4.1
CB105				0.117	0.004	3.5	0.107	0.194	6.1	0.092	2.758	5.4
CB114	0.122	0.003	6.2	0.122	0.003	2.7	0.117	0.097	4.2	0.103	2.697	4.7
CB118	0.113	0.004	5.3	0.110	0.010	3.8	0.088	0.414	6.0	0.070	3.785	4.6
CB126				0.078	0.004	6.0	0.063	0.281	10.1	0.049	2.780	7.5
CB128	0.118	0.008	6.2	0.116	0.011	4.7	0.103	0.271	8.5	0.082	4.043	7.6
CB138				0.126	0.013	4.4	0.102	0.470	8.1	0.080	4.336	6.3
CB153				0.122	0.020	3.9	0.089	0.646	7.7	0.067	4.525	5.0
CB156				0.093	0.007	6.3	0.086	0.137	10.3	0.074	2.230	9.2
CB169				0.060	0.016	8.5	0.049	0.272	14.5	0.037	2.481	12.5
CB170	0.086	−0.001	14.0	0.083	0.005	8.2	0.073	0.209	13.4	0.058	2.888	11.2
CB180										0.089	4.685	9.8
CB194	0.063	0.002	14.7	0.062	0.003	11.2	0.053	0.168	18.1	0.040	2.479	15.6
CB202				0.100	0.021	6.2	0.071	0.569	11.5	0.049	4.369	8.5
CB209	0.048	0.005	15.5	0.047	0.006	14.0	0.039	0.160	21.1	0.026	2.535	17.8

compounds interfere with the quantification of the target compounds. Fourth, repetitive analyses of samples using different GC columns and different detectors will also indicate whether co-eluting compounds play a significant role in analyte quantification.

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