



Extending the working calibration ranges of four hexachlorocyclohexane isomers in gas chromatography–electron capture detector by radial basis function neural network

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ABSTRACT

A radial basis function neural network (RBFNN) method was developed for the first time to model the nonlinear calibration curves of four hexachlorocyclohexane (HCH) isomers, aiming to extend their working calibration ranges in gas chromatography–electron capture detector (GC–ECD). Other 14 methods, including seven parametric curve fitting methods, two nonparametric curve fitting methods, and five other artificial neural network (ANN) methods, were also developed and compared. Only the RBFNN method, with logarithm-transform and normalization operation on the calibration data, was able to model the nonlinear calibration curves of the four HCH isomers adequately. The RBFNN method accurately predicted the concentrations of HCH isomers within and out of the linear ranges in certified test samples. Furthermore, no significant difference ($p > 0.05$) was found between the results of HCH isomers concentrations in water samples calculated with RBFNN method and ordinary least squares (OLS) method ($R^2 > 0.9990$). Conclusively, the working calibration ranges of the four HCH isomers were extended from 0.08–60 ng/ml to 0.08–1000 ng/ml without sacrificing accuracy and precision by means of RBFNN. The outstanding nonlinear modeling capability of RBFNN, along with its universal applicability to various problems as a “soft” modeling method, should make the method an appealing alternative to traditional modeling methods in the calibration analyses of various systems besides the GC–ECD.

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1. Introduction

Electron capture detector (ECD) is widely applied in the determination of analytes containing halogen atoms, cyano groups or nitro groups. It has been recognized to be an indispensable, simple, sensitive and selective detector for gas chromatography (GC) in the past four decades [1]. Nevertheless, it also suffers from various disadvantages, one of them being its narrow linear dynamic range (LDR) [2]. Quantification in GC–ECD is mostly done from cal-

ibration curves in LDR based on the linear regression hypothesis of ordinary least squares (OLS). It may lead to inaccurate results if analyte concentration in a sample exceeds the upper concentration limit on the calibration curve. In that case the analyst may be forced to dilute the sample or reduce the sensitivity of the analytical measurement with the ensuing risk of contamination, increase of time consumption and analysis costs [3]. These procedures, however, are not always practical especially in the multi-component or multi-sample analyses where analyte concentrations may cover very wide concentration ranges. Moreover, there remain some questions as to whether the increased accuracy of fitting a linear calibration curve compensates for the loss in signal-to-noise ratio (S/N) that may result from dilution or sensitivity reduction [4].

Fortunately, several instrumental, analytical, and mathematical methods with various degrees of success have been proposed to tackle the above problems [5–9]. Apparently, the mathematical approach, which is actually the focus of the present work, exhibits more advantages in cost, time consumption and universality than the former two. Because of the potential nonlinearity of calibration curve in GC–ECD, various curve fitting methods were employed as alternatives to OLS method. Table 1 lists several curve fitting methods available in the software packages of four leading world GC instrument manufactures. These methods could be

Abbreviations: ANN, artificial neural network; ANNs, artificial neural networks; ANOVA, analysis of variance; BPNN, back propagation neural network; ECD, electron capture detector; EI, electron impact; GC, gas chromatography; GRNN, generalized neural network; HCH, hexachlorocyclohexane; I.S., internal standard; LDR, linear dynamic range; r , correlation coefficient; LOD, limit of detection; LODs, limit of detections; MS, mass spectrometer; LOQ, limit of quantification; LOQs, limit of quantifications; m/z , mass-to-charge ratio; OLS, ordinary least squares; PCNB, pentachloronitrobenzene; R^2 , coefficient of determination; RBF, radial basis function; RBFNN, radial basis function neural network; RMSE, root mean square error; RMSPD, root mean square of the percentage deviations; RSD, relative standard deviation; S/N, signal-to-noise ratio; SIM, selected ion monitoring.

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Table 1
Curve fitting methods adopted in the software packages of different GC instrument manufactures.

Manufacturer	Software	Curve fitting method
Agilent Technologies	ChemStation A.09	Linear, quadratic, log, power, exponent, piecewise linear
Thermo Electron	Xcalibur 1.4	Linear, quadratic, linear log–log, quadratic log–log, average response factor, point-to-point, cubic spline, locally weighted
Shimadzu	GCsolution 2.0	Linear, quadratic, cubic, point-to-point, average response factor, exponent, manual response factor
Varian	Star Workstation 6.0	Linear, quadratic, cubic

generally classified into two groups: parametric and nonparametric methods. The former commonly involves the use of polynomial, logarithm, power, exponent, linear log–log, and quadratic log–log. Theoretically, parametric curve fitting method will perform well if the assumed structure of the function is sufficiently close to the global relation of $y-x$ (y and x indicating response and quantum, respectively). Unfortunately, if such precondition does not meet, parametric curve fitting method will not achieve satisfactory results [10].

Nonparametric curve fitting method, in contrast, tries to avoid modeling the global relation of $y-x$. It focuses only on the local relation around a point of interest. If the global relation of $y-x$ to be modeled is unknown, however, it can be expected that a nonparametric method will, on average, have better performance than the parametric counterpart [10]. Linear interpolation and cubic spline are the commonly utilized nonparametric curve fitting methods [7].

Recently, artificial neural networks (ANNs) are increasingly applied in analytical chemistry as a powerful complement to traditional statistical and modeling methods [11–14]. ANNs represent so-called “soft” modeling without the need to know or establish a mathematical model. The models have an ability to learn and extract $y-x$ mapping relations from the presentation of a set of training samples [15]. Among the types of ANN already applied in calibration method, back propagation neural network (BPNN) is the most widely used one. Radial basis function neural network (RBFNN) and generalized regression neural network (GRNN) are ANNs, which both use radial basis functions as transfer functions, offering interesting alternatives to BPNN in the sense that they allow local and fast training [16].

ANNs have been widely applied in chemometrics, concerning the fields of modeling [17,18], signal processing [19], curve resolution [20], calibration [21,22], parameter estimation [23–25], quantitative structure activity relationship [26–28], pattern recognition [29–31], and artificial intelligence [32]. As for the section of calibration, ANNs have been employed as very typical way to improve the working calibration ranges in different analytical techniques, such as voltammetry [20,21], optical sensor [22], spectrometry [3,33] and GC [19]. Taking the work of Fu et al. as an example, the performance of a thermoionic detector in GC was improved 10-fold in its detection limit thanks to the employment of an ANN processing [19]. Nevertheless, as far as we know, no literature has been reported on the ANNs applied to extend the working calibration range of GC–ECD up to now.

Hexachlorocyclohexane (HCH) used to be extensively applied as a broad-spectrum organochlorine pesticide. It has been listed as the persistent organic pollutant in the Stockholm Convention for its tendency to accumulate along the food chain, together with harmful effects on human beings and the environment [34]. Its residues in diverse environmental samples were distributed in wide concentration ranges [35–38]. Its linear range in GC–ECD, however, is relatively narrow.

In this study, seven parametric curve fitting methods, two nonparametric curve fitting methods and six ANN methods belonging to three types of ANN (i.e. BPNN, GRNN and RBFNN) were developed and evaluated for modeling the nonlinear calibration curves of four HCH isomers, aiming to explore the best method that could extend

the working calibration ranges of HCH in GC–ECD. The accuracy and precision of the best method was further validated by analyses of certified test samples and comparison with OLS method in the determination of HCH residues in water samples.

2. Materials and methods

2.1. Standards and reagents

Five certified analytical standards of α -HCH, β -HCH, lindane, δ -HCH in petroleum ether ($100.00 \pm 0.13 \mu\text{g/ml}$) and pentachloronitrobenzene (PCNB) in benzene ($100.00 \pm 0.10 \mu\text{g/ml}$) were purchased from China Standard Technology Development Corporation (Beijing, China). *n*-Hexane was HPLC grade and other reagents were analytical grade. These were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). PCNB was used as internal standard (I.S.).

Individual stock standard solutions of each HCH isomer ($10 \mu\text{g/ml}$) and PCNB ($1 \mu\text{g/ml}$) were prepared in *n*-hexane and stored in a freezer at -20°C . Composite stock standard solutions containing four HCH isomers at concentration of $1 \mu\text{g/ml}$ were prepared by diluting the individual stock standard solutions with *n*-hexane and stored at 4°C in the dark. Calibration standards were made up, which covered five orders of magnitude of concentrations using 26 standards. These were prepared by serial dilution of composite stock standard solutions with *n*-hexane and adding a constant amount of I.S. stock standard solution. Concentration ranges of HCH isomers were 0.010 – 1000 ng/ml . I.S. was at the constant concentration of 100 ng/ml . Each order of magnitude of concentration was characterized using five standards (1, 2, 4, 6, 8 series). Certified test samples were prepared by serial dilution of each HCH individual stock standard solution with *n*-hexane and adding a constant amount of I.S. stock standard solution to yield each HCH concentration at three levels: 1 ng/ml , 10 ng/ml and 100 ng/ml and I.S. concentration of 100 ng/ml . The concentrations of HCH were selected to be inside and outside their linear calibration ranges in GC–ECD.

2.2. Samples preparation

Water samples were collected from four lakes around Huazhong Agricultural University in Hubei province of China. They were pre-filtered through Millipore PTFE-membrane filters of $0.45 \mu\text{m}$ pore size to remove algae and suspended materials. The method of sample extraction and concentration was referred to US EPA Method 3510C [39]. The final volume of extraction, extracted from 250 ml water sample, was concentrated to 2 ml in *n*-hexane by nitrogen blowdown technique. No clean-up was required as no interferences were observed during analysis. Spike certain volume of I.S. stock standard solution to each sample extract to obtain PCNB concentration of 100 ng/ml .

Spiked water samples, used for calculating recovery rates of sample pretreatment method, were prepared by spiking three different levels of HCH standards (8 ng/l , 60 ng/l and 160 ng/l for α -HCH, β -HCH and lindane; 6 ng/l , 30 ng/l and 80 ng/l for δ -HCH) into water sample blank. Spiked water samples, used for validat-

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