Back Propagation Artificial Neural Network Modeling and Migration Analysis of Siloxane D5 Migration from Selected Food Contact Materials

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Abstract. The detection and quantification of environmental pollution compounds migration in food contact silicone rubber materials remains a prospective issue to be solved in the consideration of toxicology and safety assessment. In this study, an artificial neural network (ANN) model was established to predict migration property of non-target compound decamethylcyclopentasiloxane (D5) molecule in food contact silicone rubber. The average prediction accuracy of the model was 99.8%. The analysis of ANN indicates that high temperature condition accelerates the migration of D5 from silicone rubber into two typical food simulants, namely H2O and acetic acid. The migration of D5 is more apparent when the silicone rubber is in contact with acetic acid. The combination of experiment and simulation analysis of D5 migration indicates that high temperature and acetic acid food simulant environment threaten the safety of food contact silicone rubber. These fundamental studies can provide a comprehensive understanding of the migration of cyclic organosiloxane oligomer from silicone rubber and guidance for the safety evaluation and early warning mechanisms.

1. Introduction
Because of excellent elasticity, anti-fouling ability and chemical inertness, silicon rubber is widely used in the field of food materials. Silicon rubber products are supposed to be cheaper and user friendly alternatives to traditional metal products and have achieved a quite significant market share nowadays. According to Regulation 1935/2004/EC, food contact materials are required to be inert to preclude a large number of environmental pollution compounds being transferred to food, which endangers human health [1, 2]. However, the application environment of silicone rubber product is complex and depolymerization substances can migrate into food. The scientific reports emit some concern and suggest that proper usage of the silicone rubber products should restrict migration into different foodstuffs [3]. Additionally, the environment in which food comes into contact is highly determining parameters for the migration [4]. For example, Leda et al. [5] pointed out that different environments affect the amount of migration in PVC gaskets. Goulas et al. [6] found that when food
packaging materials are in contact with oil, the material structure changes with the change of temperature and time. Migrants have become the subject to control and regulation in the food industry [7]. Therefore, it is significantly important to study effect of different environments on the migration of depolymerization substance.

It is commonly known that the study on environmental pollution compounds in food contact products is crucial for safety evaluation. Some efficient methods allow for the analysis of environmental pollution compounds in food contact materials. For example, gas chromatography-mass spectrometry (GC-MS) is widely applied for analyzing migrants in food contact materials because of its environment-friendly performance [8]. Linssen et al. [9] used the headspace sampling combined with GC-MS to study the migrants in rubber rings. Bouma et al. [10] used the GC-MS to analyze migrants in natural rubber products. However, recent researches on migrants in silicone rubber products are rare. Lund et al. [11] used the GC-MS to analyze the volatile compounds in silicone rubber products. Their results indicated that cyclic organosiloxane oligomers are main migrants. Decamethylcyclopentasiloxane (D5) is a cyclic volatile methyl siloxane (cVMS) commonly found in commercially available products [12]. In addition, cVMS, such as D4, D5 and D6, have been identified as environmental contaminants because of their persistent properties [13]. Therefore, migration research and safety evaluation of cyclic organosiloxane oligomers when silicone rubber is in contact with different simulated food liquids would become the key of future research work.

At present, there is growing pressure within the food industry to improve the measurement of food quality. Elskens et al. [14] presented three kinds of regression methods for predicting the migration from silicone moulds and confirmed that multivariate modelling can be adapted to assess the migration from silicone moulds. Because of heuristic ability to study complex relationships, artificial neural network (ANN) recently has widely applied in scientific applications [15]. Normandin et al. [16] compared equation of state (EOS) and ANN and indicted that ANNs showed higher accuracy than EOS. Wang et al. [17] adapted ANN to study the physical properties of diene rubber and their results indicated that ANN was powerful for service life prediction. Wu et al. [18] adopted ANN technology to predict the fatigue life of natural rubber product. In this study, ANN was proposed innovatively to quantitatively predict and explain the impact of complex usage environments on migration of silicone rubber.

Based on the aforementioned researches, an ANN was proposed to predict the siloxane oligomers migration of silicone rubber in different simulated food liquids. This study is intended to proposing an ANN model to investigate and predict service life of food contact silicone rubber. The combination of experimental and theoretical studies is helpful to understand the connections between macroscopic migration behavior and microscopic migration mechanism of food contact silicon rubber.

2. Computational Details

2.1 ANN Modeling

Becuse no first principle model is available for migration study, we adopt the framework of back propagation (BP) ANN. A commonly feed-forward structure is shown in Figure 1. BP is a single-hidden-layer feed-forward neural network trained by error back propagation algorithm. One neural unit (also called node) collects information provided by other neural units to which it is connected through weighted connections, working as synapses. The value of synaptic weights is trained by reducing the error between the target and the ANN output. A BP model with multiple input and single output could be showed as follows:

\[
\text{output}_{j,k} = f \left[ \sum_{i=1}^{n} (W_{j-1,i} \cdot \text{input}_{j-1,i}) \cdot \theta_{j,i} \right]
\]  

(1)

where input \(j-1,i\) is the \(i\)th input variable from the \((j-1)\)th layer, \(W_{j,i}\) is the weights on input \(j-1,i\), \(\theta_{j,i}\) is the \(i\)th threshold in the \(j\)th layer, \(f\) is an activation function, and output \(j,k\) is the \(k\)th output unit in the \(j\)th layer.
Three service conditions (types of food simulation fluid, temperature, and time) are taken as input variables, and the migration value of D5 is the output variable; therefore, the ANN with a three-dimensional input and a one-dimensional output is proposed.

![Figure 1. Structure of artificial neural network](image)

3. Experimental Section

3.1 Materials and Sample
Silicone moulds provided by Dongjue silicone co., LTD (Nanjing, China) were used to migration tests. The structure of the silicone moulds is dimethyl silicone rubber. D5 and internal standard n-dodecane (>99.5%) were purchased from Aladdin (Shanghai, China). The food simulation liquids used were H₂O and acetic acid from Merck (Darmstadt, Germany).

3.2 GC-MS Analysis
A Trace 1310 GC combined with a capillary column TR-1MS (30 m × 0.25 mm i. d. × 0.25 mm film thickness) and an ISQ mass selective detector (Thermo Fisher, America) was adopted. The scanning ranged from 45 aum to 900 aum. Thermo Xcalibur software was adopted to collect and process data. The migration of D5 from the migration product of silicone rubber in different simulated liquids was measured by GC-MS at different temperatures. According to the European Union regulations, two types of food simulation liquid, H₂O and acetic acid were selected to carry out the migration experiment.

4. Results and Discussion

4.1. ANN Analysis
Based on the migration experiments in section 3.2, the BP model is constructed. With the temperature, time, and food simulation liquid type as the input of ANN, and the migration of D5 as the output of ANN. Based on the network training error, the number of centers in hidden layer nodes are calculated. Two performance functions mean squared error and mean squared error with regularization, were adopted to train the BP. The gradient descent weight learning function and bias function and gradient descent with momentum weight and bais learning function were adapted to train the BP. BFGS quasi-Newton backpropagation training function and conjugate gradient backpropagation with Polka-Ribiére updates training function were adopted to train the BP. The epoch number and error goal parameter were set at 1000 and 0.01, respectively. The total 170 samples are equally divided into training data set
and predicting data set. The hidden layer neuron parameter, determined by the sample size, is the most important turning parameter of BP. Training results of the BP with 300 hidden layer neurons, were shown in Figure 2. The curve was the convergence curve of the ANN global error, the straight line represented error goal (0.001). It can be seen that when the number of hidden layer neurons was 180, the network global error was 0.000396, less than error goal (0.001) only after 1000 iterations.

![Figure 2. Trained MSE of BP with respect to epochs](image)

Figure 2. Trained MSE of BP with respect to epochs

Figure 3 shows parameter changes in the process of artificial neural network training state. The training results indicate that the gradient and Mu were less than error goal only after 1000 iterations.

![Figure 3. Parameter variation during neural network training with respect to epochs](image)

Figure 3. Parameter variation during neural network training with respect to epochs

Figure 4 compares the predicted and experimental migration values of D5. The multiple correlation coefficient (MCC) between the predicted and experimental migration values were studied. The MCC results show that the proposed BP model can be adopted to predict the migration value of D5 with a high accuracy of 0.998. There is a difference of 0.00014 between the predicted migration values by ANN and that measured by experiment. The proposed BP ANN can be adopted to model and predict the migration value of D5 in silicone rubber under different simulated food liquids and temperatures.
Figure 4. Comparison between the predicted and experimental migration values of D5

4.2 Migration Prediction

Figure 5 shows the predicted evolutions of migration values of D5 vs migration temperature and time. The experimental migration values under different migration conditions are listed in Figure 5. The experimental and predicted values agree well with each other. The migration values of D5 increase obviously with time in the first 100 minutes, which indicates that the effect of food simulation liquid are more prominent at the beginning. The migration values of D5 increase with temperature, suggesting that high temperature favor the diffusion of D5 molecules. More interestingly, by comparing the migration values of D5 molecules when silicone rubber is exposed to different simulated liquids, it is found that in two food simulation fluids, acetic acid simulated liquid favors the migration behavior of D5. Nelson et al. assessed the toxicity of polymeric food-contact substances, their study indicated that the migration value of cyclic siloxanes can be adapted to judge the failure of food materials. Elskens et al. [16] applied multivariate model to forecast the migration values from silicon moulds. Therefore, the established BP can be used to predict the failure time of silicone rubber. It can be asserted that when the silicone rubber comes into contact with acetic acid, the material is prone to failure.
5. Conclusions
This study analysed the migration of environmental contaminant D5 molecules from silicone rubber into food simulants, concentrating on the environment effects on the migration property and mechanism of different temperatures, exposure times, and food simulants. A back-propagation artificial neural network model consisting temperature, time, and food simulant type was proposed to predict the migration property. The BP indicated that the migration value of D5 increases with the increase of temperature. Moreover, the model shows an interesting finding that the migration of D5 is remarkable when the silicone rubber comes into contact with acetic acid. The two simulants investigated follows the order: acetic acid > H₂O. The results confirmed that high temperature and acetic acid environment easily lead to the failure of the material.

Our study shows that the established ANN can be adopted to predict the migration of environmental contaminants. Furthermore, the methodology and data presented here will allow the relevant regulatory bodies to predict the environmental contaminant contents of foodstuffs, from which a risk assessment and the appropriate standards can be derived to ensure food safety and protect public health.

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7. References
[1] Feng, D, Yang, H, Qi, D and Li, Z 2016 Extraction, confirmation, and screening of non-target compounds in silicone rubber teats by purge-and-trap and SPME combined with GC-MS Polymer Testing 56 91-8
[2] Regulation 1935/2004/EC of the European parliament and of the council of 27 October 2004 Official Journal of the European Union C Series 338 4-17
[3] Kręgiel, D 2014 Advances in biofilm control for food and beverage industry using organo-silane technology: a review Food Control 40(1) 32-40
[4] Helling, R, Kutschbach, K and Simat, T. J 2010 Migration behaviour of silicone moulds in contact with different foodstuffs Food Additives & Contaminants Part A Chemistry Analysis Control Exposure & Risk Assessment 27(3) 396-405
[5] Leda, C, Joyce, B. P, Paulo, A. C, Mary, A. F. P, Vanessa, A. A and Rafaela, R 2014 Migration of conventional and new plasticizers from PVC films into food simulants: a comparative study Food Control 44 118-29
[6] Goulas, A. E, Salpea, E and Kontominas, M. G 2008 Di(2-ethylhexyl) adipate migration from
PVC cling film into packaged sea bream (Sparus aurata) and rainbow trout (Oncorhynchus mykiss) fillets: kinetic study and control of compliance with EU specifications European Food Research and Technology 226 915-23

[7] Fankhauser-Noti, A and Grob, K 2006 Migration of plasticizers from PVC gaskets of lids for glass jars into oily foods: amount of gasket material in food contact, proportion of plasticizer migrating into food and compliance testing by simulation. Trends in Food Science & Technology 17(3) 105-12

[8] Reid, L. M, O'Donnell, C. P and Downey, G 2006 Recent technological advances for the determination of food authenticity Trends in Food Science & Technology 17(7) 344-53

[9] Harry S. Hertz., Ronald A. Hites and Klaus. Biemann 1971 Identification of mass spectra by computer-searching a file of known spectra Anal. Chem 43(6) 681–90.

[10] Bouma, K and Schothorst, R. C 2003 Identification of extractable substances from rubber nettin

[11] Forrest, M, Holding, S and Howells, D 2006 The use of two-dimensional GC-MS for the identification and quantification of low molecular weight compounds from high performance elastomers Polymer Testing 25(1) 63-74

[12] Lund, K. H and Petersen, J. H 2002 Safety of food contact silicone rubber: liberation of volatile compounds from soothers and teats European Food Research & Technology 214(5) 429-34

[13] Velicogna, J, Ritchie, E, Príncez, J, Lessard, M. E and Scroggins, R 2012 Ecotoxicity of siloxane d5 in soil Chemosphere 87(1) 77-83

[14] Alaee, M, Wang, D. G and Gouin, T 2013 Cyclic volatile methyl siloxanes in the environment Chemosphere 93(5) 709-10

[15] Hess, B, Kutzner, C, David, V. D. S and Lindahl, E 2008 Gromacs 4: algorithms for highly efficient, load-balanced, and scalable molecular simulation Journal of Chemical Theory and Computation 4(3) 435-47

[16] Ziegel, E. R 2003 The elements of statistical learning Technometrics 45(3) 2

[17] Normandin, A, Grandjean, B. P. A and Thibault, J 1993 PVT data analysis using neural network models. Industrial & Engineering Chemistry Research 32(5) 970-75

[18] Wang, X. J, Zhao, X. Y, Li, Q. G, Chan, T. W and Wu, S. Z 2016 Artificial neural network modeling and mechanism study for relaxation of deformed rubber Industrial & Engineering Chemistry Research 55(14) 4059-70