Communication

Ant Colony Algorithm and Optimization of Test Conditions in Analytical Chemistry

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The research for the new algorithm is in the forward position and an issue of general interest in chemometrics all along. A novel chemometrics method, Chemical Ant Colony Algorithm, has first been developed. In this paper, the basic principle, the evaluation function, and the parameter choice were discussed. This method has been successfully applied to the fitting of non-linear multivariate function and the optimization of test conditions in chrome-azure-S-Al spctrophotometric system. The sum of residual square of the results is 0.0009, which has reached a good convergence result.

Keywords Ant Colony Algorithm, optimization, fitting, CASAl, photometry

In Chemometrics, the biominetic algorithm has showed obvious superiority. Recently, a new biominetic algorithm, Ant Colony Algorithm (ACA) has been proposed by Dorigo *et al*.[1] There are many advantages in this method, such as intelligent search, global optimization, robustness, distributed computation and combination easy with other heuristics method and so on. It provided a new way solving complex combinatorial optimization problems. At present, ACA has been applied to Traveling Salesman Problem,[2] Quadratic Assignment Problem,[3] Network Routing,[4] Vehicle Routing,[5] Graph Coloring[6] *etc*.[7,8] Especially after the coming-out of robot programmed with ACA,[8] the Ant Colony Algorithm has more attracted attention of scientists. However, the report about application of ACA method in chemistry and chemical engineering has not been found still. Therefore, Chemical Ant Colony Algorithm (CACA) is first put forward in this paper, and successfully applied to the fitting of non-linear multivariate function and the optimization of test conditions in analytical chemistry about photometric system of chrome-azure-S with aluminum.

Ant Colony Algorithm is a biominetic algorithm based on ant colony behavior. Real ants are capable of finding the shortest path from ant nest to a food source, because, while walking, ants deposit pheromone on the ground, and follow pheromone previously deposited by other ants. Fig. 1 shows the process that ants exploit pheromone to find the shortest path between two points.

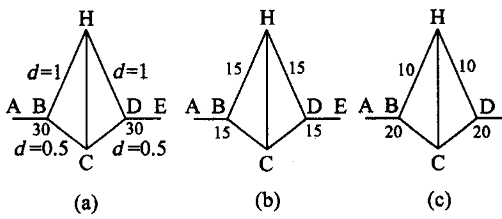

Fig. 1 Diagram of ACA principle.

In Fig. 1, the point A is a nest, the point E is a food source, the point B or the point D is a path-crotch, the line HC is a obstruction, and d is the distance between two points. Because of barrier HC, the ants, which come out of the nest A or go back from the food source E, can reach their destinations only via H or C. Suppose all ants go there and back between A and E at a speed of 1 unit length per unit time, and there are 30 ants per unit time from A and E to E and A to decide whether to turn left or right at B and D (Fig. 1a), respectively. At first, they choose randomly (15 left and 15 right separately, Fig. 1b) for there are not any pheromones on the ways. After 1 unit time, 30 ants have passed through the shorter path BCD and deposit pheromone on the ground, while only 15 ants have done through the longer path BHD (length double BCD). Therefore, the amount of pheromone on BCD is two times as much as on BHD. Then, there again are 30 ants to choose path at B. and D respectively. Since the amount of pheromone on BCD is different from BHD, the path choice of the ants is influenced by it and is roughly proportional to it. So, about 20 ants turn to direction C and the other 10 ants turn to H (Fig. 1c), and the outcome is that more pheromone deposits on shorter path BCD. As time goes on and the process repeats, the

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pheromone amount of the shorter path accumulates faster, and more and more ants choose this path. With the above positive feedback effect, very soon, all ants will choose the shorter path.

In analytic chemistry, the researchers always hope to find out the best experiment conditions with the least numbers of experiments. This aim can be achieved by the ant optimization method, with which the non-linear multivariate function can be precisely fitted through the test data of the uniform design.

Chrome-azure-S (CAS) is a kind of coordination chromogenic reagent, and can react with aluminum (Al) to form color complex CAS-Al. The absorbance of CAS-Al is proportional to the Al concentration, so this chromogenic system can be used for spectrophotometric determination of Al. Usually, the chromogenic reaction is influenced by many factors (such as chromogenic reagent concentration, assistant concentration, reaction acidity, reaction time, *etc*.), and the relationship between the absorbance and those factors is not linear. In this paper, the non-linear-relationship between the CAS-Al absorbance and the chief affecting factors (CAS concentration, NaAc concentration and pH) has been fitted by ACA method.

In CAS-Al color system, the non-linear relationship between the absorbance ($\hat{A}$) and affecting factors (x) can be expressed by a multivariate function. The effect of the x terms over cubic is usually very small, so the following quadratic regression equation model is chosen.

$$\hat{A} = a_0 + \sum_{i=1}^{m} a_i x_i + \sum_{i<j}^{m} a_{ij} x_i x_j + \sum_{j=1}^{m} a_j x_j^2 + e \qquad (1)$$

where a is the fitting coefficient, e is the fitting error, $\hat{A}$ and A are the estimate value and the measure value of the absorbance respectively, m is the numbers of the affecting factors, i and j are the ordinal number of the factors. While fitting Eq. (1), e^2 ($= |A - \hat{A}|^2$) is used for the evaluation function. Therefore, the fitting issue of the non-linear multivariate function will turn into an optimization issue of the function e^2.

In the process of optimization through ACA method, the different combinations of a values are used for the paths. The qualities of the paths are evaluated by e^2, and the evaluation results of every time will be recorded in certain form (such as $\Delta\tau$) as pheromone. The pheromone may gradually add and evaporate, so the parameter ρ is used to adjust the volatility of the pheromone. The ratio of the total pheromone on certain path to all paths is used for selection probability (P_i) to guide the search for the optimum path. Moving in cycles, till the best path (fitting coefficient) be found, and the Eq. (1) will be fitted. The adjust formula of pheromones is as follows:

$$Pheromone(i) \leftarrow \rho \cdot Pheromone(i) + \Delta\tau \qquad (2)$$

$$\Delta\tau = Q/g \qquad (3)$$

$$g = \Sigma e_i^2 \qquad (4)$$

where $\Delta\tau$ is the *Pheromone* added in this cycles, $(1-\rho)$ is the evaporation rate of *Pheromone* ($0 < \rho < 1$, and Q is a positive parameter.

The probability (P_i) selecting certain path, among those paths that have not been chosen, can be expressed as Eq. (5):

$$P_i = \begin{cases} \dfrac{Pheromone(i)}{\Sigma Pheromone(u)} & \text{if } i, u \in J_x(p) \\ 0 & \text{otherwise} \end{cases} \qquad (5)$$

where $J_x(p)$ is the set of paths used for choice.

In CAS-Al color system, the main affecting factors of the absorbance are CAS concentration (x_1), solution pH (x_2) and NaAc concentration (x_3). According to the uniform design theory invented by Fang,[9] the design of three factors and six levels[10] is listed in Table 1.

Table 1 List of factors and levels

Factor	Level					
	1	2	3	4	5	6
x_1 [(CAS (%)]	0.05	0.10	0.15	0.20	0.25	0.30
x_2 (pH)	3.00	3.50	4.00	4.50	5.00	5.50
x_3 [NaAc (g/mL)]	0.50	1.00	1.50	2.00	2.50	3.00

On the basis of Table 1, the experiment data have been determined, and the Eq. (1) will be fitted with the data.

Evaluation function is a standard to judge individual quality and colony optimization. A suitable evaluation function can not only speed algorithm convergence up, but also improve the precision of calculation. Generally, evaluation function may take absolute error, relative error, mean square deviation and so on. Tests show that sum residual square ($r_{sum} = \Sigma|A - \hat{A}|^2$) is the best choice for the Chemical Ant Colony Algorithm (CACA).

The ρ value is a parameter adjusting the renewal rate of pheromone. In ant colony optimum process, the choice of ρ value is very important. If ρ value is too small or too big, it will influence the calculating results. Tests indicate that the suitable ρ values are in the range of 0.3—0.8, and 0.6 is elected in this paper.

According to the above CACA principle, the CACA program was worked out with C language, and the Eq. (1) was fitted by the program with a P-III computer in 15 min. The fitting results of Eq. (1) by ACA and other methods [Genetic Algorithm (GA), Least Squares (LS)] are shown in Table 2.

From Table 2, it can be seen that r_{sum} with ACA method is less, 0.0009, which indicates the ACA's success in analytical chemistry.

Ant Colony Algorithm (ACA) is a novel, global optimizing biominetic algorithm. Research indicates that it can excellently solve the optimization problem in analytical chemistry, such as the optimizations of the test conditions in optical analysis, electric analysis, chromatographic analysis, and so on. The method is easy to find better solutions by positive feedback. After being revised, it will be able to be applied to the multivariate calibration for analytical systems, and even to the other fields of chemistry and chemical engineering.

Table 2 Fitting results of quadratic regression equation

Parameter	ACA	GA	LS
a_0	-0.0136	0.108344	0.14166
a_1	1.224	0.6875	1.366
a_2	0.01958	0.0000	0.272497
a_3	-0.06486	-0.072266	0.016382
a_4	-0.07562	0.0000	-0.030544
a_5	-0.01477	-0.03125	0.019393
a_6	0.03230	0.019531	0.014257
a_7	-1.863	-1.2500	-3.0407901
a_8	-0.002684	0.0000	-0.029685
a_9	-0.0235	-0.001953	-0.023412
r_{sum}	0.0009	0.003165	0.0211463

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