Applied Radiation and Isotopes 141 (2018) 149–155

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

# Identification of weak peaks in X-ray fluorescence spectrum analysis based on the hybrid algorithm combining genetic and Levenberg Marquardt algorithm

Hua Du[a,b], Wuhui Chen[a,b], Qingjun Zhu[a,*], Songlin Liu[a], Jianbin Zhou[c]

[a] Institute of Plasma Physics, Chinese Academy of Sciences, Hefei, Anhui 230031, China
[b] University of Science and Technology of China, Hefei, Anhui 230027, China
[c] The College of Nuclear Technology and Automation Engineering, Chengdu University of Technology, Chengdu, Sichuan 610059, China

## HIGHLIGHTS

- A novel algorithm is developed to solve weak peaks in X-ray fluorescence analysis.
- The hybrid algorithm has higher accuracy, better stability and faster convergence.
- This is a promising method that can be used to determine heavy metals in other grains.

## ARTICLE INFO

*Keywords:*
Cadmium
Weak peak
Hybrid algorithm
Genetic algorithm
Levenberg-Marquardt algorithm

## ABSTRACT

Accurate measurement of cadmium content in rice is of utmost importance to determine if the inspected rice product is safe to people. X-ray fluorescence analysis is frequently used for multi-element analysis because it has characteristics of fast, accurate and nondestructive. However, due to the low content of cadmium in rice, its corresponding characteristics energy peak is relatively weak and is sensitive to the background information in the X-ray energy spectrum. Thus, it is very tough to obtain the accurate values of cadmium content by utilizing traditional X-ray fluorescence analysis. In this paper, the identification of weak peaks of cadmium is much improved by proposing a hybrid algorithm combining genetic algorithm (GA) and Levenberg-Marquardt algorithm (LM). The hybrid algorithm not only takes full advantages of GA and LM respectively but also inhibits their unwanted properties: poor local search ability of GA and locally convergent of LM. The proposed hybrid algorithm is employed to identify weak peaks in X-ray spectra of six contaminated rice samples with different contents of cadmium. Two comparative experiments are conducted to compare the performance between GA, LM and the proposed hybrid algorithm. One of the comparative experiments has the relative error varying with the number of calculations, which aims to verify the accuracy and stability. The results show that the hybrid algorithm is a better option in terms of accuracy and stability. Another comparative experiment of which the average relative error varies with the number of iterations is conducted to verify the computing efficiency. The experiments show that the hybrid algorithm exhibits a faster convergence rate. Two numerical experiments demonstrate that the proposed algorithm can well resolve the identification issue of the cadmium in the X-ray spectra and significantly improve the content measurement accuracy of cadmium in the quality evaluation experiment of rice products.

## 1. Introduction

The detection for heavy metal cadmium in rice has been listed as an important indicator of the national routine monitoring. Metal cadmium and its compounds can penetrate the body through the digestive and respiratory tract, and they will accumulate in kidneys and liver, eventually lead to the lesions of an immune system, nervous system and reproductive system (Williams and David, 1976; Nogawa et al., 1983; Watanabe et al., 2002; Simmons et al., 2005; Kobayashi et al., 2009).

The determination of cadmium content in rice has attracted great attention of many scholars. The graphite furnace atomic absorption spectrometry (GFAAS) (Holcombe and Borges, 2004; Fang et al., 1994)

* Corresponding author.
*E-mail address:* zhuqingjun@ipp.ac.cn (Q. Zhu).

https://doi.org/10.1016/j.apradiso.2018.07.009
Received 7 June 2017; Received in revised form 20 June 2018; Accepted 10 July 2018
Available online 26 July 2018
0969-8043/ 

was one of the most commonly used methods for measuring the cadmium in rice. However, the general heating time was too long, which affected the speed of analysis. Other analysis methods such as electrothermal vaporization atomic fluorescence spectrometry (XiaoDong et al., 2009), UV–vis spectrophotometry (Keawkim and Chuanuwatanakul, 2013), were also applied to analyze the cadmium in rice. But there are so many problems in the above methods, such as time-consuming, complex structure of detection instruments, harsh conditions, and high cost.

X-ray fluorescence analysis, with the characteristics of non-pollution and non-destructive, is a rapid, accurate and economical method for multi-element analysis (He et al., 1993; Ao et al., 1997; Sbarato and Sánchez, 2001; Myint et al., 2003; Revenko, 2002; Hall et al., 2010). The elements in solid, liquid, powder and even gas samples can be qualitatively and quantitatively analyzed by this technology (Sbarato and Sánchez, 2001; Revenko, 2002; Potts et al., 1984). It has become one of the most popular methods of spectral analysis in China. However, due to the low content of cadmium in rice, its corresponding characteristics energy peak is relatively weak and is sensitive to the background information. Meanwhile, most weak peaks cannot be correctly identified by the traditional spectral method in the process of X-ray fluorescence analysis. In many cases, identifying weak peaks accurately is a key technology in X-ray fluorescence analysis.

In this paper, a pioneer study is reported to identify the weak peaks in the X-ray fluorescence analysis. In order to improve the content measurement accuracy of cadmium in rice products, a hybrid algorithm combining genetic algorithm (GA) and Levenberg-Marquardt algorithm (LM) is developed to resolve the identification issue of cadmium in X-ray spectra.

## 2. Description of the algorithm

In the process of traditional X-ray fluorescence spectrum analysis, the peak's centroid position and peak's boundaries are firstly obtained by the peak detection algorithm, such as the first derivative method, the symmetric zero-area conversion method, the convolution method, and so on. Then the peak's area can be calculated by the total peak area method (TPA), Wasson method or Covell method. However, these algorithms are often used to solve strong peaks. For weak peaks, its corresponding characteristics energy peak is sensitive to the background information. Thus, it is very tough to identify some weak peaks by the traditional spectral methods.

In order to solve this kind of problem and to avoid the influence of the noise, the fitting method has been proposed in the spectrum analysis. Because the measured spectrum can be fitted against a fitting model expressed as a linear combination of full-energy-peaks from several individual nuclides. Therefore, the best parameters of the fitting model can be obtained by minimizing the difference between a measured spectrum and the fitted spectrum. Thus, some optimization algorithms are usually used to minimize the difference between the measured spectrum and the fitted spectrum.

### 2.1. Parametric model

The observed X-ray fluorescence spectrum can be approximately modeled as a linear combination of full-energy-peaks from several individual nuclides and be superimposed on a background (Meier, 2005; Ying-jie et al., 2016). Each peak can be simply modeled by a Gaussian curve, which consists of the amplitude $A_i$, the centroid position $p_i$ and the half width $\sigma_i$, so the energy spectrum can be expressed as:

$$\hat{f(X)} = \sum_{i=1}^{N} A_i e^{\frac{-(x-p_i)^2}{2\sigma_i^2}} + B(x) \tag{1}$$

where the independent variable $x$ is the number of channels of the spectrum, $\hat{f(X)}$ represents the estimated counts on the corresponding channel, $N$ is the number of Gauss peaks. $B$(x) stands for the function of the background, which is obtained by fitting in the form of Ying-jie et al. (2016):

$$B(x) = ax + b \tag{2}$$

When the estimated count $\hat{f(X)}$ on the corresponding channel is obtained, the corresponding error equation is acquired:

$$V = \hat{f(X)} - L \tag{3}$$

where $L$ is the count in channel $i$ of the measured spectrum, $V$ is the difference between the measured spectrum and estimated spectrum, then the sum of squares of residuals $R$ is:

$$R = V'V = (\hat{f(X)} - L)'(\hat{f(X)} - L) \tag{4}$$

It is a common computational optimization problem that to minimizes minimize $R$, The most common method for nonlinear least-squares minimization is the LM algorithm. However, the LM algorithm is locally convergent. The iterative divergence occurs when the initial guess is poor (Moré, 1978). In order to solve this kind of problem and to relax the constraints on initial guess, the GA is utilized to generate initial guess for LM algorithm because of its global optimization, strong adaptability, and strong robustness. Therefore, a hybrid algorithm combining GA and LM algorithm is proposed to improve its accuracy, stability and convergence speed.

### 2.2. Genetic algorithm

The genetic algorithm is probabilistic methods mimicking "real life", which is a stochastic optimization algorithm based on natural selection and genetic law with characters of global optimization, strong adaptability, strong robustness, and so on. It is widely used in many fields such as function optimization, nonlinear parameter estimation, pattern recognition, image processing and so on (Houck et al., 1995; Fleming and Fonseca, 1993; Freeman et al., 1999; Rennard, 2000; Li, 2006). But it has the weakness of premature and poor ability of local searching. It may wastes much time for local optimum value when the population is near the optimization.

The genetic algorithm is formed by a population of individuals of randomly chosen parameter values. Potential solutions are referred to as individuals and are encoded into binary strings which represent chromosomes. For our specific application, individuals represent the adjustable parameters of the amplitude, the centroid position, the half width and background coefficients. Each parameter can be forced to assume values inside a predefined range according to the model. Several operators inspired by the evolutionary biology, such as inheritance, mutation, selection and crossover, act on in the population of evolutionary. The process of parent selection, mating, crossover, and mutation through successive generations is called evolution. With the evolution of solutions, increasingly stronger solutions are generated. The parameter values that minimize $R$ are known as the ultimate solutions.

In the genetic algorithm, the probability of the individual genetic to the next group depends on the value of individual fitness. In our case the fitness function is:

$$fitiness = \frac{1}{\sum_i^N (\hat{f(X_i)} - L_i)^2} \tag{5}$$

The larger the fitness value of individual is, the smaller the difference between the measured spectrum and estimated spectrum is. The general step of the genetic algorithm as follows:

1. Initialize parameters.

a) Set the range of centroid position, amplitude, peak width and background coefficients.

b) Set *iter* = 0, where *iter* is the current number of generations.
c) Set *NIND* = 200 as the size of the population.
d) Set *MAXGEN* = 800 as the maximum generation.
e) Set *px* = 0.75 as crossover probability and pm = 0.001 as mutation probability.
f) Set *GGAP* = 0.95 as the generation gap.

2. Calculate the corresponding fitness value for each individual of the population.
3. Genetic Operators.

a) Select the higher fitness value of the individual, stochastic universal sampling is used to determine the probability of various individuals genetic to the next generation in population.
b) Generate new individuals, single-point crossover algorithm between pairs of individuals is employed with a probability of *px*.
c) Mutate the offsprings produced during crossover with probability *pm*.

4. Calculate the fitness value, and record the best individuals in the *iter* generation. *iter* = *iter* + 1.
5. If *iter* = *MAXGEN*, terminate the calculation, otherwise, go to 3.

### 2.3. Levenberg-Marquardt algorithm

The Levenberg-Marquardt (LM) algorithm is the most widely used optimization algorithm. It outperforms simple gradient descent and other conjugate gradient methods in a wide variety of problems. However, the LM algorithm is locally convergent, and the iterative divergence occurs when the initial guess is poor (Moré, 1978; Ranganathan, 2004; Transtrum and Sethna, 2012). In order to solve this kind of problem and to relax the constraints on initial guess, the GA is utilized to generate initial solutions for LM algorithm. At the end of the GA, the parameter estimation value $X_k$ is acquired which can be used as the preliminary solution of the LM algorithm. Then the first order approximation of $f(X)$ at $X_k$ is:

$$f(X_k + \Delta X) = L + V = f(X_k) + J(X_k)\cdot\Delta X \tag{6}$$

where $J(X_k)$ is the mapping value of the Jacobian matrix, so that

$$\Delta X = (J^T(X_k)J(X_k))^{-1}J^T(X_k)(L - f(X_k)) \tag{7}$$

Damping factor $\lambda^k$ is introduced to the process of iteration:

$$X^{k+1} = X^k + \Delta X = X^k + (J^T(X_k)J(X_k) + \lambda^k I)^{-1}J^T(X_k)(L - f(X_k)) \tag{8}$$

where $\lambda^k$ is any constant greater than zero. If the error goes down following an update, it implies that the measured value is close to the estimated value and $\lambda^k$ is reduced (usually by a factor of 10). On the other hand, if the error goes up, in order to follow the gradient more and so $\lambda^k$ is increased by the same factor. The general step of LM algorithm as follows:

1. Initialize parameters.

a) Set the number of iterations N = 1000.
b) Initialize the damping factor $\lambda^k$ = 0.01.
c) Set *iter* = 0, where *iter* is the number of iterations.

2. Calculate Jacobian matrix $J_k$, $\Delta X$, and $X'$ according to formula (7), (8).
3. Calculate $R'$ at the new parameter vector and evaluate the error $\Delta R = R' - R$.
   If $\Delta R > 0$, then increase $\lambda^k$ by a factor of 10, then go to step 3 and try an update again.
   If $\Delta R < 0$, then accept the step and decrease $\lambda^k$ by a factor of 10. *iter* = *iter* + 1.
4. If iter = *N*, terminate the calculation, otherwise, go to step 2.

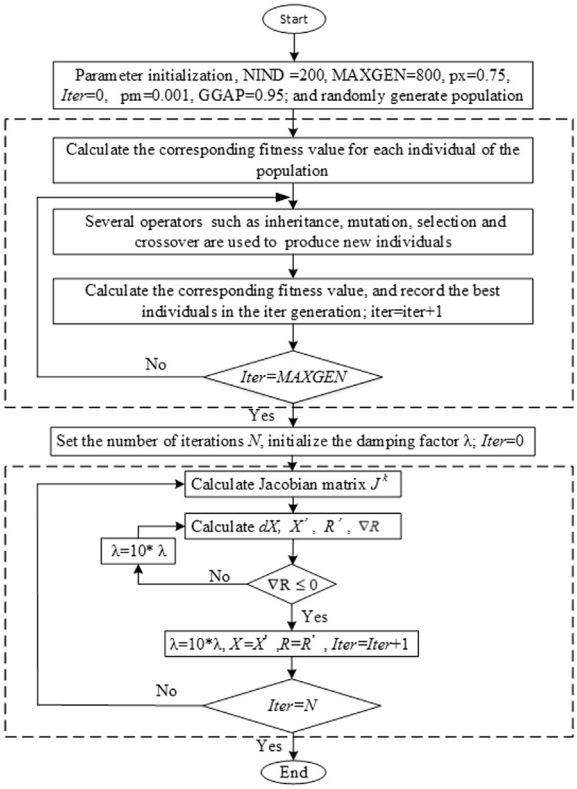


**Fig. 1.** Flow chart of hybrid algorithm.

### 2.4. Hybrid algorithm

The genetic algorithm has characters of global optimization, strong adaptability, and strong robustness, but it is poor in local search ability, which may wastes much time for local optimum value and the result of each calculation is unstable. The LM algorithm is the most widely used optimization algorithm, but it is locally convergent, the iterative divergence occurs when the initial guess is poor. In order to solve this kind of problem and to relax the constraints on initial guess, the GA is utilized to generate initial guess for LM algorithm. Therefore, a hybrid algorithm combining GA and LM algorithm is proposed to improve both its success rate and convergence speed. The hybrid algorithm takes full advantages of GA and LM respectively. The detailed process is shown in Fig. 1.

## 3. Experimental details

### 3.1. Apparatus

Measurements are performed with a CIT-3000SM EDXRF instrument (made by Sichuan New XianDa Technology and Control Co., Ltd.) with an energy resolution of 130 eV, and the energy range of recorded spectra from 1 to 40 keV. The instrument consists of high-voltage power, X-ray tube, SDD semiconductor detector, preamplifier, multichannel analyzer, vacuum system, recording and display. The schematic structure of the instrument is shown in the Fig. 2:

### 3.2. Sample

In this paper, six contaminated rice samples with different contents of cadmium (listed in Table 1) are prepared. Each rice sample has a mass weight of grams and a sequence from S1 to S6, measured for 300 s.

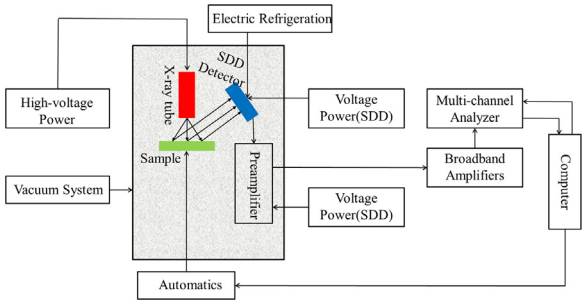


**Fig. 2.** Schematic structure of CIT-3000SM EDXRF instrument.

**Table 1**
Contents of cadmium in six contaminated rice sample (mg/kg).

| Rice sample | S1 | S2 | S3 | S4 | S5 | S6 |
|---|---|---|---|---|---|---|
| Cadmium content | 0.122 | 0.225 | 0.332 | 0.446 | 0.563 | 0.768 |

### 3.3. Measurement

Calibration measurements need to be taken before each measurement, and calibration is performed using calibration samples. Six contaminated rice samples with different contents of cadmium are measured by the CIT-3000SM EDXRF instrument. The spectrum of each standard sample is obtained, named and saved. Fig. 3 shows one of the standard rice sample's experimental X-ray fluorescence spectrum, in which the abscissa is the channel number and the ordinate is the count rate. The local amplification region in the diagram is the weak peak of cadmium determined by multiple experiments. The SNR value of the weak characteristics energy peak is less than 5. At the same time, it is easily influenced by the background information due to the low content of cadmium in rice as explained previously.

## 4. Results

The proposed hybrid algorithm is employed to identify weak peaks in X-ray spectra of six contaminated rice samples with different contents of cadmium. The comparative analyses in accuracy, stability and convergence speed between GA, LM and the hybrid algorithm is conducted to verify the identification performance of the proposed algorithm. All algorithms are implemented based on the MATLAB programming environment with a version of 2013. And the Genetic Algorithm Toolbox developed by the University of Sheffield was used in this paper (Chipperfield and Fleming, 1995).

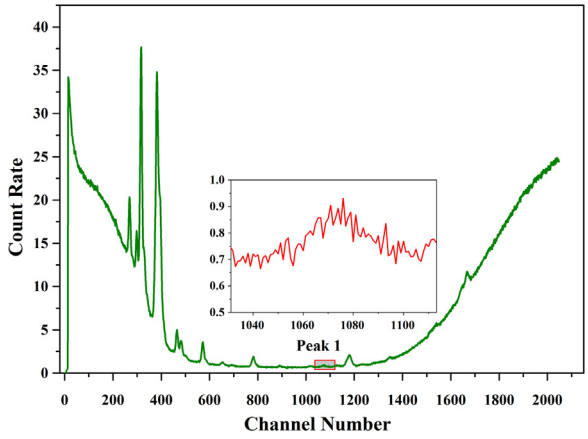


**Fig. 3.** Experimental X-ray fluorescence spectra.

**Table 2**
Comparison of average cadmium contents in six rice sample obtained by three different algorithms (mg/kg).

| Rice sample | S1 | S2 | S3 | S4 | S5 | S6 |
|---|---|---|---|---|---|---|
| Standard Value | 0.122 | 0.225 | 0.332 | 0.446 | 0.563 | 0.768 |
| Hybrid Algorithm | 0.113 | 0.178 | 0.346 | 0.383 | 0.528 | 0.809 |
| Relative Error | 4.22% | 17.89% | 8.11% | 10.98% | 2.86% | 3.63% |
| Standard Value | 0.122 | 0.225 | 0.332 | 0.446 | 0.563 | 0.768 |
| GA | 0.157 | 0.196 | 0.315 | 0.384 | 0.518 | 0.750 |
| Relative Error | 41.50% | 12.85% | 8.67% | 13.85% | 8.05% | 3.87% |
| Standard Value | 0.122 | 0.225 | 0.332 | 0.446 | 0.563 | 0.768 |
| LM | Divergence | Divergence | 0.348 | 0.307 | 0.528 | 0.809 |
| Relative Error | ∞ | ∞ | 4.71% | 31.28% | 6.26% | 5.38% |

### 4.1. Accuracy and stability assessment

Six contaminated rice samples with different contents of cadmium described in Section 3.2 are employed to quantify the performance of the hybrid algorithm. For each rice sample, the initial parameters $X$ consists of centroid position, amplitude, peak width and background coefficients are given firstly. After continuous iterations of the hybrid algorithm, the final parameters $X$ are obtained when the $R$ is the minimum. Two comparative experiments are conducted to verify the accuracy, stability and convergence speed of the proposed algorithm: the comparative analyses between GA, LM and the hybrid algorithm. Each spectrum was repeatedly calculated 20 times using GA, LM and the hybrid algorithm respectively (Table 2 and Fig. 4). In this paper, the accuracy of the algorithm is evaluated by relative error defined as:

$$\delta = \frac{\Delta}{L} = \left|\frac{E - L}{L}\right| \times 100\% \tag{9}$$

where, $\delta$ is the relative error, $E$ is the calculated content of cadmium in sample, and $L$ is the reference content of cadmium in the sample.

Table 2 shows the average contents of cadmium in six contaminated rice sample obtained by repeated calculation 20 times using GA, LM and the hybrid algorithm respectively. Comparison results show that iterative divergence occurs when the LM algorithm is used independently. That is because the LM algorithm is locally convergent, the iterative divergence occurs when the initial guess is poor. It can be found that the average relative error of cadmium calculated by the proposed hybrid algorithm is less than 10% (except S2). Hence, the hybrid algorithm exhibits a better accuracy rate comparing with the GA. It also shows that the hybrid algorithm has a better stability performance. As shown in Fig. 4, the relative error of cadmium in six contaminated rice samples varies with 20 repeated calculations. It is obvious that a consistent result can always be obtained for each calculation by the hybrid algorithm, while the result obtained by the GA has greater uncertainty, mainly due to the genetic algorithm has a poor local searching ability, and it is difficult to obtain a stable local optimum value. In fact, the LM algorithm is locally convergent, and it has a faster rate of convergence. However, in practical applications, we prefer to get a stable result at one time, rather than a result with a larger uncertainty. So, in terms of stability and accuracy performance, the hybrid algorithm is a better option.

### 4.2. Efficiency comparison

In addition to consider the accuracy and stability, another crucial factor to verify the performance of an algorithm is the computing efficiency, namely the computing time. Because in practical applications, it is preferred to get experimental results immediately. Therefore, a comparative verification of which the average relative error varies with the number of iterations is conducted between GA and hybrid algorithm. It can be found that the hybrid algorithm demonstrates a faster

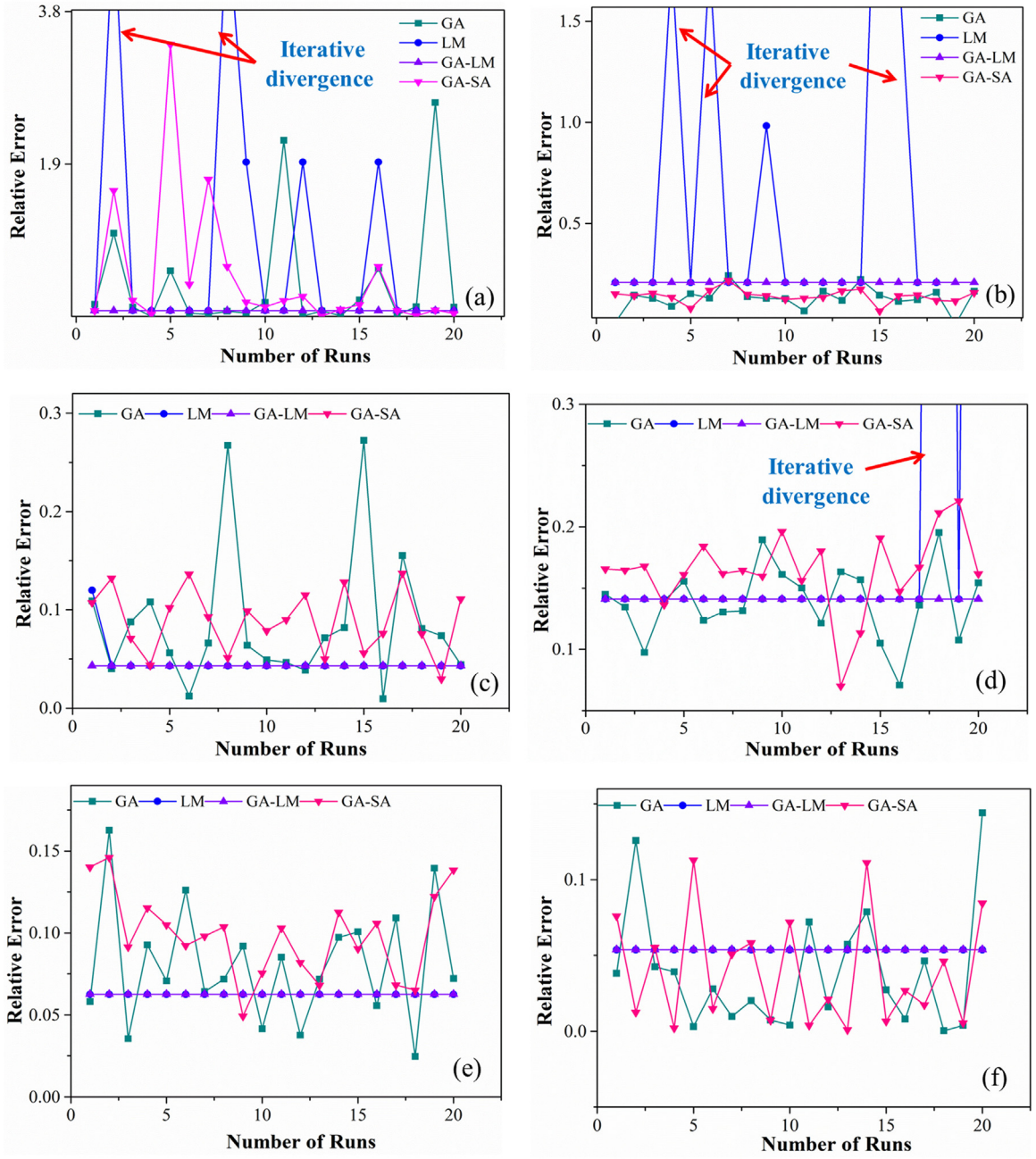


**Fig. 4.** The relative error of cadmium varies with the number of calculations in six contaminated rice samples calculated by GA, LM and the hybrid algorithm respectively. Rice sample with a cadmium content (a) 0.112 mg/kg (b) 0.225 mg/kg (c) 0.332 mg/kg (d) 0.446 mg/kg (e) 0.563 mg/kg (e) 0.768 mg/kg.

convergence rate compared with the GA. As shown in Fig. 5, the hybrid algorithm can reach a stable result after 800 iterations within 5.12 s and a consistent result can always be obtained for different iterations, while the GA need at least 3000 iterations with a time of 19.07 s to get a relative stable result with a smaller change, because the genetic algorithm wastes much time for local optimum value.

## 5. Discussions

The hybrid algorithm shows superiority in accuracy, stability and speed of convergence. However, there are several factors that may have a large influence on the calculation result, the most influential factors is the cadmium content in unit peak area of the standard sample. Therefore, in this experiment, in order to reduce the impact of statistical fluctuations on the experimental results as much as possible, the standard sample is firstly measured 10 times, and the spectrum for each measurement is obtained, named and saved. Then the average cadmium content in unit peak area is obtained by repeating calculation 20 times using GA, LM and hybrid algorithm respectively. Another important factor is the number of iterations. As discussed in Section 4.2, if the number of iterations is less than 500 times, the hybrid algorithm may not get a stable result or even lead to larger errors. It is worth noting that when the number of iterations is higher than 800 times, increasing the number of iterations does not improve the accuracy of the calculation. So in the actual calculation, 800 iterations are enough. Meanwhile, it is noted that the average relative error obtained by the GA decreases with the increase of the number of iterations, when the number of iteration is higher than 5000 times, the average relative error calculated by the GA is close to or smaller than the result calculated by the hybrid algorithm. Besides, a phenomenon can be observed

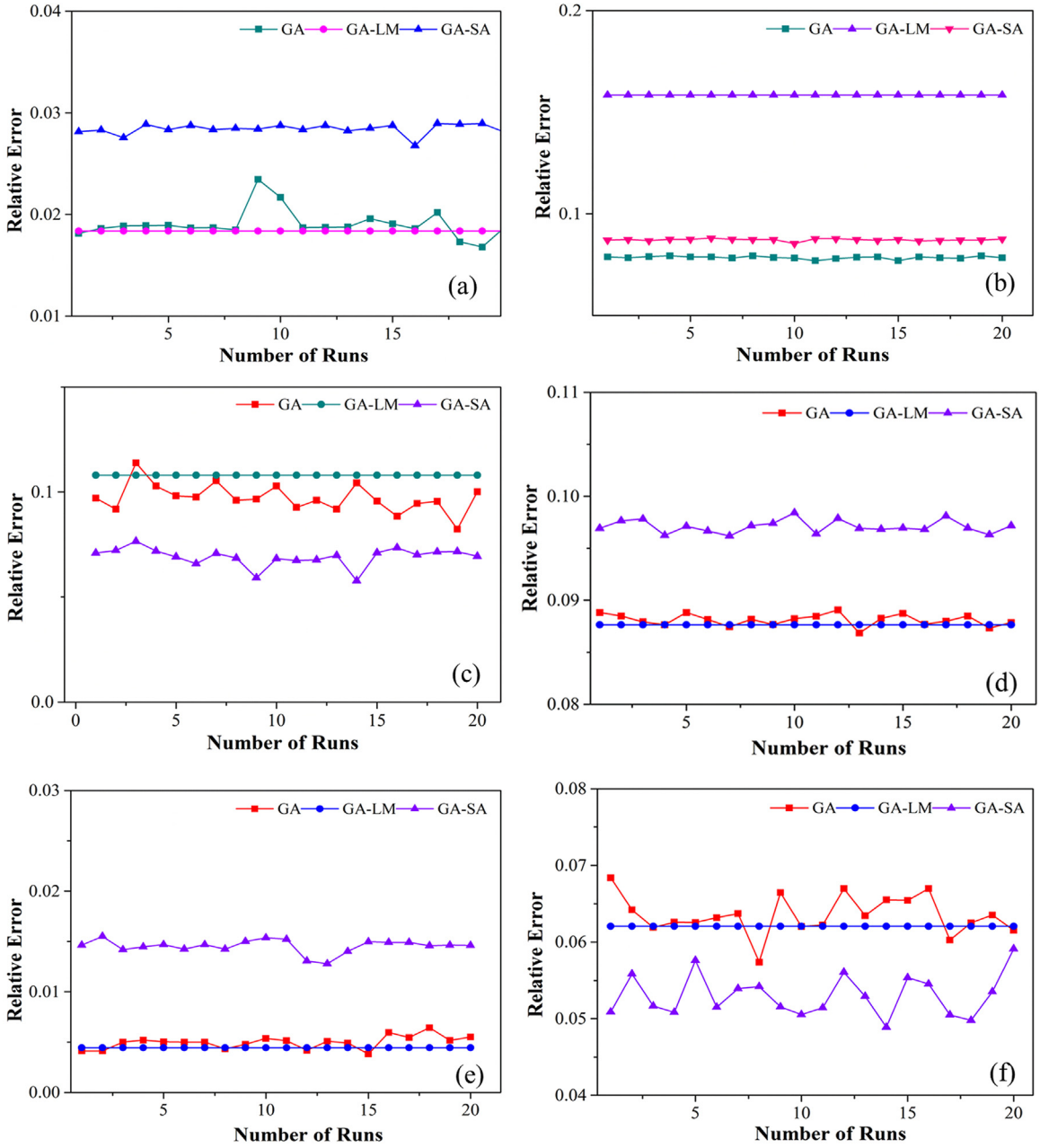


**Fig. 5.** The average relative error varies with the number of iterations in six contaminated rice samples calculated by GA, and the hybrid algorithm respectively. Rice sample with a cadmium content (a) 0.112 mg/kg (b) 0.225 mg/kg (c) 0.332 mg/kg (d) 0.446 mg/kg (e) 0.563 mg/kg (e) 0.768 mg/kg.

in Fig. 4, in some cases, the relative error calculated by the GA algorithm is smaller than that calculated by the hybrid algorithm, which means the local search ability of the LM algorithm is not the best. However, the accuracy of the hybrid algorithm has been greatly improved compared with that without using, which basically meets the error requirements.

## 6. Conclusions

In this paper, the identification of weak peaks of cadmium was much improved by proposing a hybrid algorithm combining the genetic algorithm and Levenberg-Marquardt algorithm. The proposed hybrid algorithm was employed to identify weak peaks in X-ray spectra of six contaminated rice samples with different contents of cadmium. Two comparative experiments were conducted to verify the identification performance of the proposed algorithm. Results showed that the hybrid algorithm has higher accuracy and better stability, because a consistent result can always be obtained for each calculation. Besides, results also showed that the hybrid algorithm exhibits excellent computing efficiency, because a stable result can be gained with a faster convergence rate. Two numerical experiments demonstrated that the proposed algorithm can well resolve the identification issue of cadmium in X-ray spectra and significantly improve the content measurement accuracy of cadmium in the quality evaluation experiment of rice products. It can also be used to determine the heavy metals in other grains, especially those whose content is very low with weak characteristic peaks.

## Acknowledgments

This work was supported by Research Foundation of ASIPP Grant no. DSJJ-14-GC05.

## References


Ao, Q., Lee, S.H., Gardner, R.P., 1997. Optimization of in vivo X-ray fluorescence analysis methods for bone lead by simulation with the Monte Carlo code CEARXRF. Appl. Radiat. Isot. Incl. Data Instrum. Methods Use Agric. Ind. Med. 48 (10–12), 1413–1423.

Chipperfield, A.J., Fleming, P.J., 1995. The MATLAB Genetic Algorithm Toolbox.

Fang, Z., Xu, S., Dong, L., Li, W., 1994. Determination of cadmium in biological materials by flame atomic absorption spectrometry with flow-injection on-line sorption preconcentration. Talanta 41 (12), 2165–2172.

Fleming, P.J., Fonseca, C.M., 1993. Genetic algorithms in control systems engineering. IFAC Proc. 26 (2), 605–612.

Freeman, D.W., Edwards, D.R., Bolon, A.E., 1999. Genetic algorithms – a new technique for solving the neutron spectrum unfolding problem. Nucl. Instrum. Methods Phys. Res. Sect. A: Accel. Spectrom. Detect. Assoc. Equip. 425 (3), 549–576.

Hall, E.T., Schweizer, F., Toller, P.A., 2010. X-ray fluorescence analysis of museum objects: a new instrument. Archaeometry 15 (1), 53–78.

He, T., Gardner, R.P., Verghese, K., 1993. The Monte Carlo—library least-squares approach for energy-dispersive x-ray fluorescence analysis. Appl. Radiat. Isot. 44 (s10–11), 1381–1388.

Holcombe, J.A., Borges, D.L.G., 2004. Graphite furnace atomic absorption spectrometry. Encycl. Anal. Chem. 52 (1), 167–176.

Houck, C.R., Joines, J., Kay, M.G., 1995. A genetic algorithm for function optimization: a Matlab implementation. NCSU-IE TR 95 (09). https://www.researchgate.net/publication/2386612.

Keawkim, Chuanuwatanakul, Suchada, 2013. Determination of lead and cadmium in rice samples by sequential injection/anodic stripping voltammetry using a bismuth film/crown ether/Nafion modified screen-printed carbon electrode. Food Control 31 (1), 14–21.

Kobayashi, E., Suwazono, Y., Dochi, M., Honda, R., Kido, T., 2009. Influence of consumption of cadmium-polluted rice or Jinzu River water on occurrence of renal tubular dysfunction and/or Itai-itai disease. Biol. Trace Elem. Res. 127 (3), 257–268.

Li, X., 2006. An introduction to mixed genetic algorithm for solving multi-dimension package problem. Comput. Dev. Appl.

Meier, R.J., 2005. On art and science in curve-fitting vibrational spectra. Vib. Spectrosc. 39 (2), 266–269.

Moré, J.J., 1978. The Levenberg-Marquardt algorithm: implementation and theory. In: Watson, G.A. (Ed.), Numerical Analysis. Springer, pp. 105–116. https://doi.org/10.1007/BFb0067700.

Myint, U., Tölgyessy, J., Kristiansen, K., Myint, U., Tölgyessy, J., Kristiansen, K., 2003. X-ray fluorescence analysis. Anal. Chem. 56 (9), 1099.

Nogawa, K., Yamada, Y., Honda, R., Ishizaki, M., Tsuritani, I., Kawano, S., et al., 1983. The relationship between itai-itai disease among inhabitants of the Jinzu River basin and cadmium in rice. Toxicol. Lett. 17 (3), 263–266.

Potts, P.J., Webb, P.C., Watson, J.S., 1984. Energy-dispersive x-ray fluorescence analysis of silicate rocks for major and trace elements. X-ray Spectrom. 13 (1), 2–15.

Ranganathan, A., 2004. The levenberg-marquardt algorithm. Tutor. LM Algorithm 11 (1), 101–110.

Rennard J., 2000. Genetic algorithm viewer: Demonstration of a genetic algorithm. Ph. D. May 2000 Goldberg D, idem.

Revenko, A.G., 2002. X-ray fluorescence analysis of rocks, soils and sediments. X-ray Spectrom. 31 (3), 264–273.

Sbarato, V.M., Sánchez, H.J., 2001. Analysis of arsenic pollution in groundwater aquifers by X-ray fluorescence. Appl. Radiat. Isot. Incl. Data Instrum. Methods Use Agric. Ind. Med. 54 (5), 737–740.

Simmons, R.W., Pongsakul, P., Saiyasitpanich, D., Klinphoklap, S., 2005. Elevated levels of cadmium and zinc in paddy soils and elevated levels of cadmium in rice grain downstream of a zinc mineralized area in Thailand: implications for public health. Environ. Geochem. Health 27 (5–6), 501–511.

Transtrum, M.K., Sethna, J.P., 2012. Improvements to the Levenberg-Marquardt algorithm for nonlinear least-squares minimization. arXiv preprint arXiv:1201.5885.

Watanabe, Y., Kobayashi, E., Okubo, Y., Suwazono, Y., Kido, T., Nogawa, K., 2002. Relationship between cadmium concentration in rice and renal dysfunction in individual subjects of the Jinzu River basin determined using a logistic regression analysis. Toxicology 172 (2), 93–101.

Williams, C.H., David, D.J., 1976. The accumulation in soil of cadmium residues from phosphate fertilizers and their effect on the cadmium content of plants. Soil Sci. 121 (2).

XiaoDong, W., Peng, W., Li, C., XianDeng, H., 2009. Determination of cadmium in rice and water by tungsten coil electrothermal vaporization-atomic fluorescence spectrometry and tungsten coil electrothermal atomic absorption spectrometry after cloud point extraction. Anal. Chim. Acta 650 (1), 33–38.

Ying-jie, Ma, et al., 2016. Study on the high speed and precision Gaussian function fitting algorithm for nuclear single spectral peak. Spectrosc. Spectr. Anal. 36 (8), 2373–2377.