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# Rapid analysis of multicomponent pesticide mixture by GC–MS with the aid of chemometric resolution

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ABSTRACT

Applications of hyphenated chromatographic techniques, especially GC–MS technique, have been reported in chemical, biological, environmental, agricultural and medical analysis. The complexity of the samples in these fields is still an obstacle for the technique to be practical and the overlapping of the multicomponent signals induces chemometric methods widely employed. In this work, taking the rapid analysis of pesticide mixture as an example, a chemometric approach was proposed for resolution of multicomponent overlapping GC–MS signal. In the method, a mass spectral library of pesticides was organized at first, then target factor analysis (TFA) was employed for testing the existence of a specific pesticide in the multicomponent overlapping GC–MS signal, and finally the chromatographic information of the pesticide was extracted by a non-negative immune algorithm (IA). A GC–MS signal of a 40-component pesticide mixture eluted within 9 min was analyzed by the method. It was found that the mass spectra and chromatographic profiles of almost all the pesticides can be obtained.



## 1. Introduction

Hyphenated chromatographic techniques, such as gas chromatography–mass spectrometry (GC–MS), high-performance liquid chromatography with diode array detector (HPLC-DAD) and liquid chromatography–mass spectrometry (LC–MS), etc. have been proved to be powerful methods for both qualitative identification and quantitative analysis. These techniques are, therefore, widely employed for analysis of complex components in various fields, e.g. in the analysis of biological, metabolomic [1,2], environmental [3,4], agricultural [5] and medical [6] samples. However, the complexity of the analytical signals, especially the overlapping of the responses by different components, and the huge amount of data produced by hyphenated instruments are still obstacles to qualitative identification and quantitative analysis. In most cases, the signals of compounds of interest are overlapped with the signals of the complex matrix or coexistent components, making the detection very hard and even impossible. Moreover, overlapping is also a problem to affect the efficiency of the techniques. Although lots of experimental efforts have been made to improve the throughput of these hyphenated chromatographic techniques [7–9], it is still an important task to develop effective methods for high-throughput analysis of complex systems.

Chemometrics has provided an alternative way for improving the efficiency of hyphenated chromatographic techniques. Chemometric methods can be of great help for extracting hidden information from the multicomponent overlapping signals. Factor analysis (FA) techniques have been widely used for analysis of overlapping signals in complex systems [10] like traditional Chinese herbal medicine [11] and metabolomic samples [12]. As well-known FA-based methods, evolving factor analysis (EFA) [13], window factor analysis (WFA) [14], and heuristic evolving latent projections (HELP) [15,16] have been widely employed to study the evolving processes such as chemical reactions or elution in chromatography. Rank annihilation factor analysis (RAFA) [17] provided an efficient tool for quantitative analysis of gray systems, and target factor analysis (TFA) [18,19] and iterative target transformation factor analysis (ITTFA) [20] can be used for qualitative and quantitative aims simultaneously. Methods based on least squares like multivariate curve resolution—alternating least squares (MCR-ALS) [21,22] and immune algorithm (IA) [23] have also been successfully employed for resolution of multicomponent complex systems [24–27]. Although both MCR-ALS and IA are based on curve-fitting strategy, the two techniques work differently. IA directly extracts the contribution of each component to the total signal, instead of trying to fit the total signal under the constraint of least squared error. Furthermore, IA extracts the information of each component independently and simultaneously, and thus can avoid the influence of noise and background. On the other hand, concentration obtained by IA method is an absolute value, instead of a relative one. In addition, as a convolution and deconvolution technique,

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wavelet transform (WT) can also be helpful for resolution of overlapping chromatographic signals [28–30]. With these chemometric methods, time-consuming sample pre-treatment for concentration and purification can be saved, and the optimization of experimental conditions can be simplified.

In our previous works, IA was engaged for resolution of the overlapping signals [23,31]. The basic IA has a strong ability for resolution of the overlapping analytical signals, but the spectra of all components must be provided. Due to the complexity of real systems, it is difficult to obtain the mass spectrum of each component. Thus, independent component analysis (ICA) was employed for extraction of mass spectra from GC–MS signal [32]. With the help of ICA, it is no longer necessary to provide the spectra of pure components. Yet, when the spectra of the components are also overlapping, the negative values will appear in the extracted spectra and the resolved chromatograms are also distorted [33,34]. On the other hand, when the number of the provided spectra is less than the real number of the components, the resolved chromatographic profiles are not correct. Therefore, efforts on the improvement of ICA were made [35–38] and a non-negative immune algorithm (non-negative IA) was developed for the problems [39]. In non-negative IA, a negative correction was proposed. These efforts have been proved to be applicable to extract spectral and chromatographic information from overlapping signals [40]. Nevertheless, in most of real applications, it is generally expected to obtain only the information of some specific components, instead of all the components. Thus, it is still a great challenge to develop a method for extracting the information of specific components from a multicomponent overlapping signal.

In this paper, for the aim of extracting only the information of compounds of interest, an approach based on IA and TFA [18,19] was proposed for resolution of multicomponent overlapping GC–MS signal. At first, a mass spectral library of the compounds of interest was organized for providing mass spectra of the possible components. Then, in stead of extracting the pure spectra of the components from the measured signal by WICA as in Ref. [39], TFA was employed for testing the existence of a specific component in the measured GC–MS signal. Once the component is detected, the chromatographic information of the component was extracted by non-negative IA. A GC–MS signal of a 40-component pesticide mixture eluted within 9 min was investigated by the proposed approach with a mass spectral library of 300 possible pesticides. The results show that both the mass spectra and chromatographic profiles of the pesticides can be obtained. The method may be promising for detection of a specific component in a complex sample.

## 2. Algorithm and calculations

A measured GC–MS signal can be represented as an $m \times n$ two-way data matrix, where $m$ and $n$ are the number of retention time and $m/z$ channels. Therefore, each column is a chromatogram for an $m/z$ channel, whereas each row is a mass spectrum at a retention time. For a multicomponent sample, the measured signal is a linear combination of the signals of the components. For the signals of overlapping, the mass spectrum at a retention time can be described as:

$$V = \sum_{i=1}^{d} V_i = \sum_{i=1}^{d} c_i V_{0i} \tag{1}$$

where $V_i$, $V_{0i}$, and $c_i$ are the mass spectral response, standard spectrum and concentration of the $i$th component at a retention time, respectively. $d$ is the number of components in the signal. When $V$ and all $V_{0i}$ are given, the calculation of basic IA can be summarized as the following iteration:

$$dc^{(k)} = \langle (V - V_F^{(k-1)}),\ T \rangle \tag{2}$$

$$c^{(k)} = c^{(k-1)} + dc^{(k)} \tag{3}$$

$$V_F^{(k)} = \sum_{i=1}^{d} c_i^{(k)} V_{0i} \tag{4}$$

where $k$ is the number of iterations, $T$ is the normalized standard spectra, $V_F$ represents the resolved information, and $V - V_F$ means the residue. The operator $\langle , \rangle$ expresses the inner product or projection. Therefore, $dc$ is the relative concentrations of the components in the current residue, and $c$ is the concentrations in the signal $V$. The iteration will stop until $dc$ approaches zero, which means that the information of the components has been completely subtracted. Clearly, after the iterations, $V_F$ will be the information of the components in the signal $V$ and $c$ will be the concentrations of the components at a retention time. In the algorithm, each retention time row is calculated independently. Thus, connecting the concentrations of every component obtained at all retention time will form the chromatographic profiles of the components.

From the theory of IA, it is clear that the standard spectra, $V_{0i}$, of all the components must be correctly provided and subtracted simultaneously. Therefore, ICA was adopted to extract the spectral information from the measured GC–MS data matrix [35–38] and a non-negative IA was developed to subtract the information of a specific component [39]. However, there are still limitations for these techniques in real applications. In this work, therefore, in order to improve the efficiency of resolution, a mass spectral library was used for providing the possible components in the measured signal, instead of extracting the information by ICA, and TFA was employed for testing the existence of the component. If TFA gives a positive result, non-negative IA was adopted for the resolution. Therefore, the calculations of the method can be summarized as three steps:

(1) A mass spectral library of the possible components was organized. In this study, because the analysis of pesticides was taken as an example, a library containing 300 pesticide compounds was established using the NIST05 MS database and NIST mass search 2.0 program. Normalized spectra were used in the library.
(2) TFA was performed by taking the mass spectrum of a compound in the library as a test vector to test the existence of the compound in the measured GC–MS signal. In the calculation, the rank was estimated by the cumulative variance. 99% was used as the criterion for ensuring the rank not less than the real component number, because almost no effect can be found when the rank is slightly larger than the number of components. However, if the rank was less than the number, some components in lower response cannot be identified by TFA. Moreover, normalization was performed to keep the consistency and comparability of the projected mass spectrum with the ones in the library. Furthermore, instead of the criteria defined in literatures, the correlation coefficient between the projected mass spectrum and the test vector was adopted for the judgement of the existence. When the correlation coefficient exceeds 0.8, TFA gives a positive answer.
(3) Once a target component is approved, the projected mass spectrum of the component is employed for computing the chromatographic profile of the component by using non-negative IA. Otherwise, step (2) will be repeated for the next compound in the library and the iteration will not stop until all the compounds are tested.

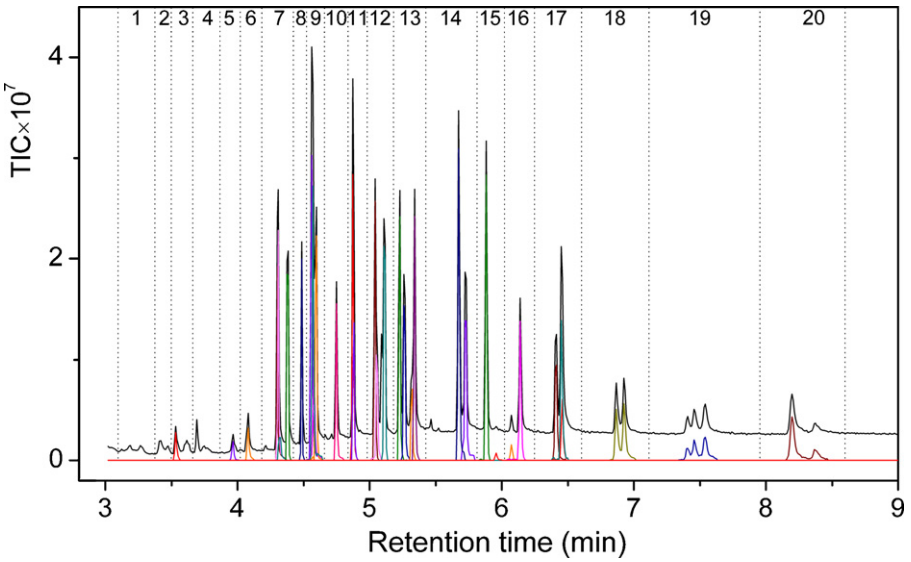


**Fig. 1.** Total ion chromatogram (TIC) of the mixed pesticides sample denoted as solid line and the resolved results as dot lines. Division of the whole chromatogram is shown by the vertical dot lines.

## 3. Experimental

All chemicals are of analytical reagent grade. The mixed solution containing 40 pesticides (10 ppm) in acetone was provided by China import and export commodity inspection technology institute, and stored at 4 °C in darkness. Thermo GC–MS system (USA, Thermo Fisher Scientific) consisting of a Trace gas chromatograph with weak polar capillary column, CP-Sil8CB (USA, VARIAN, 30 m long, 0.32 mm i.d., and 0.25 μm film thickness) and a Polaris Q mass spectrometry with an electron impact ionization source (EI) was employed.

In the experiment, the electron impact ionization was tuned at 70 eV and helium (BOC, 99.999%) was used as carrier gas with an average linear velocity of 1.0 mL $min^{-1}$. The pesticides solution was analyzed with the following oven temperature program: set the initial temperature at 50 °C with 1 min, then, increased to 300 °C at a rate of 100 °C $min^{-1}$, hold 6 min, and the temperature of the GC injector was 280 °C. The mass spectrometer was operated with a transfer line temperature of 280 °C, ion source 200 °C, mass range from 50 to 650 amu and scan event time 0.58 s. All pesticides were eluted within 9 min under this condition. The total ion chromatogram (TIC) of mixture is shown in Fig. 1 as the solid line. It can be observed that there are just several group of peaks in which the chromatographic profiles of 40 pesticides and impurities are embedded.

It should be noted that, for simplicity, the whole chromatogram was divided into several regions along the retention time as shown in Fig. 1 by the vertical dot lines. For each testing compound, TFA was run separately over different regions. For most cases, the test vector can be matched correctly with the correlation coefficient

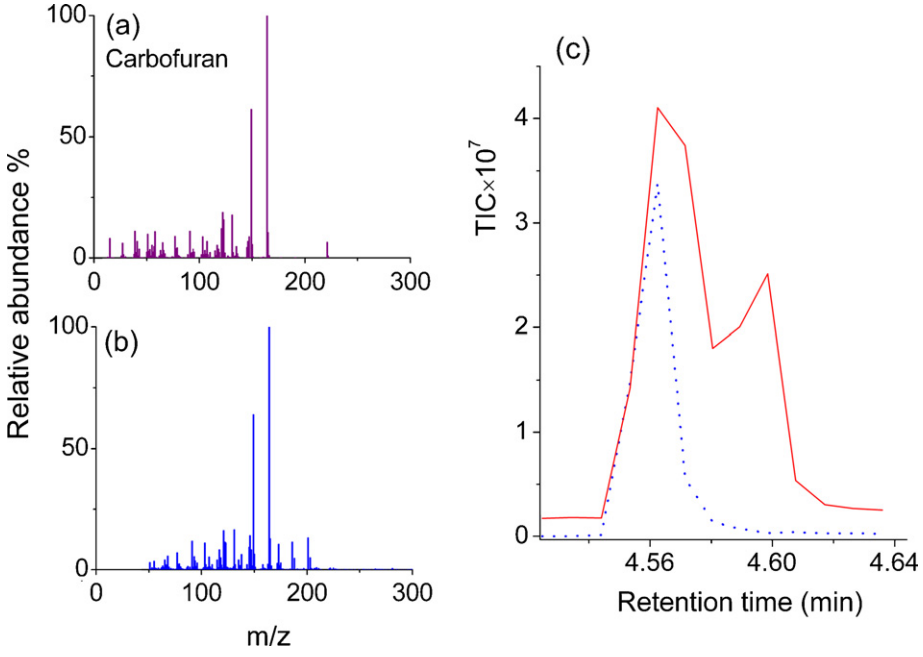


**Fig. 2.** Mass spectra of carbofuran obtained from mass spectral library (a) and TFA (b), and the resolved result obtained by non-negative IA (c), in which solid line represents the measured TIC, and dot line denotes the resolved chromatographic profile of carbofuran.

criterion, but one region may match two or three test vectors of isomeric compounds with similar mass spectra. In the later situation, the result must be approved manually with the elution sequence of components along retention time. Therefore, a well separated chromatogram of the sample was also measured under the optimized temperature program. In the experimental condition, the 40 pesticides are separated within 35 min.

## 4. Results and discussion

### 4.1. Identification of the components in the measured GC–MS signal

As described in the calculation steps above, the first task is to identify the existence of a candidate compound in the measured GC–MS signal, i.e., performing TFA with the mass spectra of the compound in the library as a test vector over each retention time region. Taking carbofuran as an example, it was found the component is located in the region of 4.52–4.64 min. Fig. 2(a) and (b) shows the test vector (from mass spectral library) and projected (or accepted) vector, respectively. Although apparent difference can be seen between the two spectra, the correlation coefficient between the two vectors is found to be 0.96, and the match ratio of the projected vector given by the NIST mass search program with the NIST05 MS database is 869, which evaluates the similarity (in thousandths) between the mass spectrum obtained and the one from the NIST mass library by the automated mass spectral deconvolution and identification system (AMDIS).

After the 300 candidate compounds were tested by TFA, 31 candidates were identified in the overlapping GC–MS signal of the pesticide mixture, except for the three groups of isomeric compounds permethrin, cypermethrin and fenvalerate, having 2, 4, and 2 isomers, respectively. It is apparent that the reason for TFA not able to identify the mass spectra of the isomers is the similarity between them. Therefore, the elution order in the separated chromatogram was used for identification of these isomeric components. However, because the mass spectra of cypermethrin-3 and cypermethrin-4 are too similar and the retention times of the two isomers are too close, only one isomer was identified. Besides, simazine was not detected due to the too fast speed of the temperature program. The identified results and their match ratios with the spectra in the NIST05 MS database are listed in Table 1. The components identified manually are marked with an asterisk. It can be found that all the match ratios are above 750, indicating the identification is reliable. Furthermore, compared the match ratio with the results in Ref. [39], it can be found that the mass spectra obtained by TFA are even better than that obtained by ICA.

**Table 1**
Identification results of the components in the measured GC–MS signal.

| Retention time (min) | Compound | Correlation coefficient | Match ratio (‰) |
|---|---|---|---|
| 3.53 | Methamidophos | 0.84 | 805 |
| 3.97 | Acephate | 0.82 | 877 |
| 4.08 | Trichlorfon | 0.81 | 751 |
| 4.30 | BPMC | 0.91 | 855 |
| 4.31 | Propoxur | 0.86 | 781 |
| 4.32 | Omethoate | 0.88 | 818 |
| 4.38 | Trifluralin | 0.89 | 898 |
| 4.49 | Phorate | 0.87 | 853 |
| 4.56 | Carbofuran | 0.96 | 869 |
| 4.57 | Atrazine | 0.88 | 845 |
| 4.58 | Dimethoate | 0.89 | 815 |
| 4.60 | Hexachlorobenzen | 0.97 | 922 |
| –[a] | Simazine | – | – |
| 4.75 | Pirimicard | 0.91 | 859 |
| 4.87 | Prometryn | 0.81 | 848 |
| 4.88 | Parathion-methyl | 0.90 | 841 |
| 5.04 | Chlorpyrifos | 0.81 | 854 |
| 5.05 | Triadimefon | 0.80 | 813 |
| 5.11 | Aldrin | 0.81 | 890 |
| 5.23 | Quinalphos | 0.85 | 868 |
| 5.26 | Procymidone | 0.83 | 919 |
| 5.32 | Methidathion | 0.89 | 822 |
| 5.34 | Fenamiphos | 0.81 | 841 |
| 5.67 | 4,4'-DDD | 0.99 | 892 |
| 5.73 | β-Endosulfan | 0.90 | 883 |
| 5.88 | 4,4′-DDT | 0.99 | 891 |
| 5.96 | Dicofol | 0.89 | 848 |
| 6.07 | Captafol | 0.87 | 793 |
| 6.14 | Fenpropathrin | 0.89 | 859 |
| 6.41 | Tetradifon | 0.95 | 883 |
| 6.45 | Phosalone | 0.89 | 921 |
| 6.46 | Amitraz | 0.94 | 920 |
| 6.87[a] | Permethrin-2 | 0.97 | 849 |
| 6.92[a] | Permethrin-1 | 0.98 | 906 |
| 7.41[a] | Cypermethrin-1 | 0.83 | 844 |
| 7.46[a] | Cypermethrin-2 | 0.91 | 836 |
| 7.54[a] | Cypermethrin-3 | 0.91 | 832 |
| –[a] | Cypermethrin-4 | – | – |
| 8.20[a] | Fenvalerate-1 | 0.81 | 876 |
| 8.37[a] | Fenvalerate-2 | 0.88 | 858 |

[a] The components identified manually. The two components without retention time were not identified.

### 4.2. Resolution of the chromatographic profiles

Once a candidate compound is identified, the chromatographic profile of the component can be calculated by using non-negative IA. Fig. 2(c) shows the result obtained for carbofuran, in which the solid line represents the measured TIC and the dot line illustrates the extracted information by non-negative IA with the projected mass spectrum of the compound. Due to the sparseness of the data points caused by the fast elution, the chromatogram looks not so continuous but it is reasonable. Therefore, the information of a specific component can be extracted by the method, rather than all the components in the overlapping signal.

For further investigation of the results, Fig. 3 shows the mass spectra and the chromatographic profiles of all the components in the overlapping signal. In the figure, the four chromatographic profiles were plotted as dot lines and the residual was plotted as dash line. It can be seen that all the chromatographic profiles are reasonable and the residue fits the baseline well except for the small peak at 4.5625 min. Similarly, Fig. 4 shows the projected mass spectrum and chromatographic profiles for the retention time region 5.00–5.15 min. It is clear that besides the information of three identified components, there is still information of a component in the residue. This clearly means that the mass spectrum of the component does not match any one in the library. In fact, the component is an impurity identified as p-dichlorobenzophenone according to the residual signal, which may be generated from the deterioration of the mixed solution. Therefore, only the specific components are extracted by the method, rather than all the components contained in the measured signal. Thus, different from the previous work in Ref. [39], in which the information of all components was extracted, the method can be used for analyzing only the components of interest in a mixture regardless of the impurities or unconcerned components. It may be more practical for identifying a specific component in a complex mixture.

All the resolved chromatographic profiles are shown in Fig. 1 as the lines in different color. From the figure, it can be seen that except for cypermethrin-4 and simazine, the other 38 pesticides in the mixture were successfully identified and resolved. It is worthy of note that the peaks in the three groups of isomers were not resolved due to the similarity of their spectra.

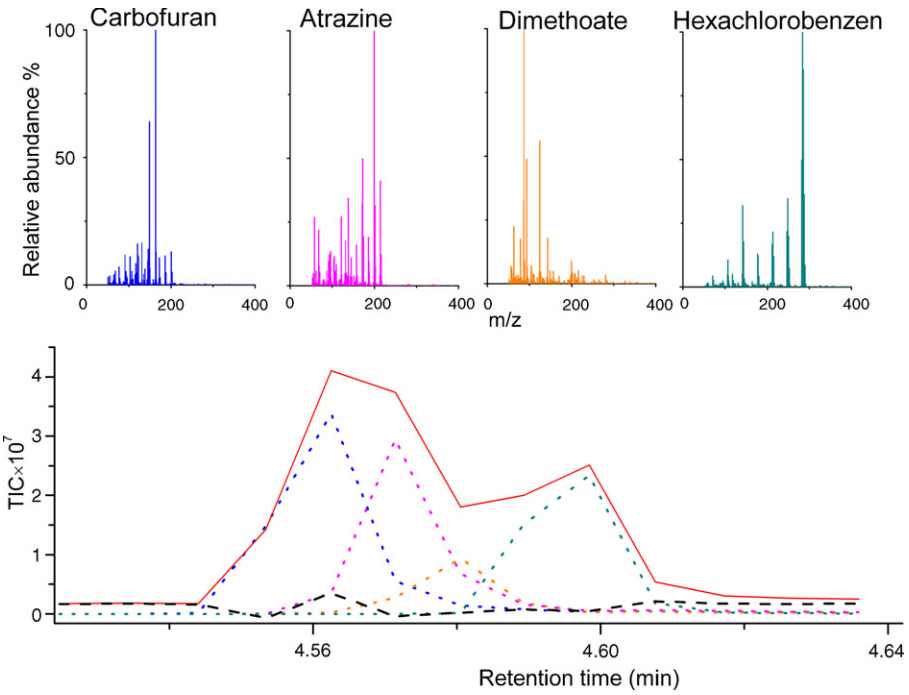


**Fig. 3.** Identified mass spectra and the resolved chromatographic profiles obtained by the proposed approach for the region of 4.52–4.64 min. Solid line represents the measured TIC, dot lines express the resolved chromatographic profiles and dash line denotes the residual.

### 4.3. Evaluation of the proposed method

To further evaluate the efficiency of the proposed method, the TIC profiles between 4.52 and 4.64 min is taken as an example. The mass spectra of carbofuran, atrazine, dimethoate, and hexachlorobenzen obtained from the library, as shown in the top of Fig. 5, are directly used, instead of the projected mass spectra by TFA, for extraction of the chromatographic profiles in the calculation of non-negative IA. The resolved results are shown in the bottom of Fig. 5. Comparing the chromatograms in Figs. 3 and 5, it can be seen that the residue in Fig. 3 fits the baseline better than that in Fig. 5, although there is also an obvious small peak at 4.5625 min in Fig. 3. Quantitatively, the proportion of the residue to the TIC is 3.53% in Fig. 3 but 9.21% in Fig. 5. To further analyze the small peak

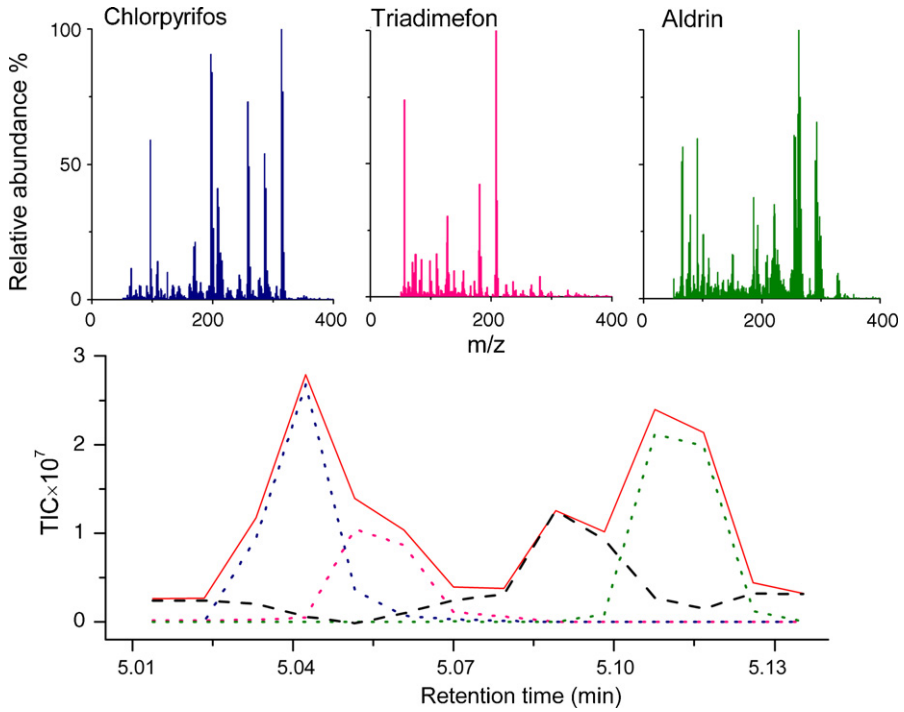


**Fig. 4.** Identified mass spectra and the resolved chromatographic profiles obtained by the proposed approach for the region of 5.00–5.15 min. Solid line represents the measured TIC, dot lines express the resolved chromatographic profiles and dash line denotes the residual.

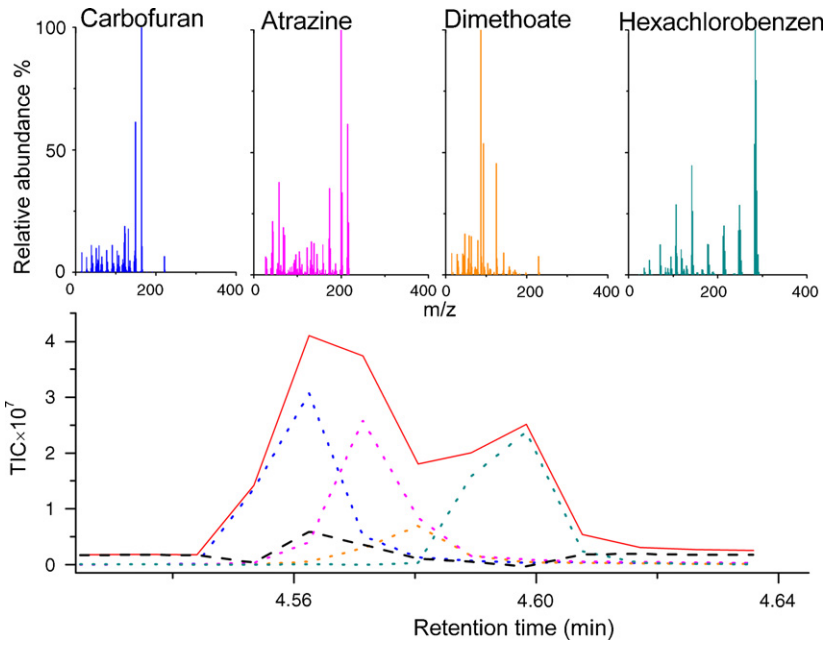


**Fig. 5.** Mass spectra from mass spectral library and the chromatographic profiles resolved by non-negative IA for the region of 4.52–4.64 min.

in the residue in Figs. 3 and 5, the mass spectrum was identified as atrazine, which is one of the four components. However, inconsistence between the mass spectrum and the library one can be found. It indicates that the mass spectral information was not completely extracted because of the inconsistence. Therefore, it can be concluded that the resolved chromatographic information in Fig. 3 is more reasonable, and the projected mass spectra by TFA are more similar to the spectra of the components in the measured GC–MS signal. Therefore, the extracted mass spectra from the measured signal may be more suitable for identification of the components than the spectra in databases because experimental condition may induce a slight change of the mass spectra.

## 5. Conclusion

Rapid analysis of pesticides by GC–MS was performed with the aid of TFA and non-negative IA. TFA was proved to be an efficient tool to test the existence of a specific component in an overlapping GC–MS signal. With a mass spectral library, rapid identification of pesticides in a mixture was achieved by a GC–MS measurement with very fast temperature program. In addition, non-negative IA is demonstrated to be workable for extracting the chromatographic information of specific component separately rather than all the components simultaneously. With the proposed approach, 38 pesticides are identified in the measured overlapping GC–MS signal of a 40 components eluted within 9 min, and the corresponding chromatographic profiles are extracted. Furthermore, the extracted mass spectra from measured signal are considered to be more suitable for identification of the components than that in databases because the former ones can reflect a slight change produced in experiment. Therefore, the combination of TFA and non-negative IA may be a practical alternative for identification of the components and resolution of the chromatographic profiles from multicomponent overlapping GC–MS signals.

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