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A New Algorithm for Quantitative Conversion of Non-sinusoidal Image Charge or Current Signal from Planar Electrostatic Ion Trap

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Abstract: Mass resolution of Foureir transform mass spectrometer (FTMS) highly depends on the acquisition time of image charge/current signal. In order to achieve higher resolution with a shorter transient time, apart from increasing the field strength of the analyzer, the high order harmonics in the image charge signal may also be exploited. The image charge or current signal obtained from the planar electrostatic ion trap has a non-sinusoidal waveform which contains many high-order harmonic components. However, presence of high harmonics increases the complexity of spectral analysis, such as identification of a peak for its correct harmonic order, and avoiding quantitation error due to the peak overlapping from different harmonic groups. A new quantitative algorithm consists of a scoring-based peak classification and the least square fitting (SC-LSF), which has been developed to convert image charge or current signal to mass spectrum. The scoring process will go through all the peaks identified above the noise background, for assumptions that the peak belongs to a certain harmonic order. The score will go up when a relevant lower harmonic peak is confirmed. The harmonic order which achieves the highest score, is assigned to the peak so its fundamental frequency can be determined. Through the SC tests, the candidates of all fundamental frequencies are found for all possible m/z of ions. The basis signals for all possible m/z are constructed using the identified fundamental frequencies and are brought to the LSF to determine the intensities of each species. The SC-LSF algorithm was tested using simulated signal from a mixture of 48 different m/z ions. Different levels of artificial noise were added to the signal to challenge the algorithm. The results show a wide range of mass and ion numbers in the sample mixture can be accurately returned through the SC-LSF algorithm even if the transient signal is under high noise condition. LSF in frequency domain is more efficient than in time domain because a subset of frequency points may be selected, so the amount of calculation is massively reduced. In addition, the test proves that good quantitation can be achieved only when LSF is carried out using data in complex number, while fitting with magnitude data results in large errors for ions in the closed mass group. This is because those closed mass peaks are overlapping at certain low-order harmonics and the amplitudes of a FFT spectrum are not addable, thus leading to the fitting errors.

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一种平面静电离子阱非正弦镜像电荷/电流信号的定量转换新算法

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摘要：傅里叶变换质谱（FTMS）的质量分辨率取决于镜像电荷/电流的采集时间。为了在较短的时间内获得较高的分辨率，除增加分析器场强外，还可以利用镜像电荷信号中的高次谐波。平面静电离子阱获得的镜像电荷信号具有非正弦波形，其中包含许多高次谐波成分，增加了频谱分析的复杂程度，例如，难以辨认 1 个谱峰的谐波次数，以及当不同次的谐波发生重叠时出现定量困难。为了将多质荷比离子的镜像电荷信号转换成质谱，本文开发了一种新的定量算法，包含谱峰评分分类（SC）和最小二乘法拟合（LSF）。通过评分可以确定每个峰属于哪一次谐波，从而确定其对应的基频。打分算法列出所有候选离子的基频，并使用确定的基频构建所有基信号，然后用其对原频谱进行 LSF，以确定每种质荷比离子的数量。使用 48 种不同质荷比离子的仿真镜像电荷信号对 SC-LSF 算法进行测试。结果表明，该方法允许较宽的质量范围，即使在高噪声条件下，通过 SC-LSF 算法也能准确得到各种不同质荷比离子的数量。因为频谱中通常存在大量的空白频点，可以选择 1 个频点子集进行 LSF，这相对于时域中的 LSF，能够大大减少计算量，提高效率和准确度。此外，只有使用复数频谱数据进行 LSF 时才能获得良好的定量效果，而使用幅值数据则会对质荷比接近的离子定量造成较大的误差，这是因为质荷比接近的离子信号的低次谐波峰未能彻底分解，而复数的幅值不具有可加性，从而造成拟合的错误。

关键词：镜像电荷；傅里叶变换质谱（FTMS）；定量算法；谱峰评分分类（SC）；最小二乘法拟合（LSF）

1　Introduction

Fourier transform mass spectrometry (FTMS) has been increasingly adopted in applications demanding very high mass resolution and high mass accuracy[1]. Activities seeking higher mass resolution never stops. In addition to improve the trapping field, including magnetic field generated by super conductor coil in the Fourier transform ion cyclotron resonance (FTICR)[2] and electrostatic field in the Orbitrap[3], there are also other approaches to push the limit of mass resolving power. One of the effective approaches is to exploit the improvement of high-order harmonics in the image charge/current signals, for example, by dividing the pickup electrodes in the ICR cell[4-6] or the electrostatic orbital trapping cell[7-8]. Another successful method is related to the design of electrostatic ion trap, such as the electrostatic linear ion trap (ELIT)[9-10] and the planar electrostatic ion trap (PEIT or OFA)[11-13], where the image charge signals are in periodical pulsed waveform. The non-sinusoidal pulsed signal gives rise to multiple high-order harmonics in frequency spectrum, which helps to achieve high mass resolution with shorter acquisition time[12].

However, the non-sinusoidal image charge signal also causes problems. Multiple harmonics often make the spectrum complicated with overlapping peaks from different harmonics. It is difficult to convert the frequency of a peak to its mass-to-charge ratio (m/z) if its harmonic order is not correctly identified, and for those merged peaks from different harmonic orders, the quantification of each component is almost impossible using current available FT algorithms.

To convert image charge signal in the form of periodic impulses obtained in ELIT, Greenwood et al[14] utilized a comb-sampling method where the frequency coefficients were determined using the integration of dot product between the time domain transient signal and an artificial comb signal of varying frequency. However, this method requires picking up image charge signals at several different locations simultaneously to suppress various harmonic and subharmonics. Ding et al[15] proposed a method following the fast Fourier transform (FFT) to determine the harmonic order of a peak according to the phase at the peak apex, thus realizing harmonic peak classification. However, it is difficult to calculate phase at the apex when there are two or more peaks really overlapped. Sun et al[16-17] tried to use the orthogonal projection to achieve conversion from discrete image charge/current signal to mass spectral data. However, high density of m/z points must be used for the whole spectrum where high mass resolution and high mass accuracy are involved, resulting in a huge amount of computing time, and sometimes accuracy loss due to accumulated errors.

The least square fit (LSF) is used in FTMS to improve the peak shapes after the signal is already transformed to frequency domain. Aushev et al[18] pointed out that the peak-shape fitting in the frequency domain might imply a reduced performance due to non-linear spectral interference effects, so instead, they applied the LSF to the time domain signal, and proved that the LSF could provide the amplitude, frequency and phase information for the harmonic signal components with shorter time duration and obtain a better resolution than FFT. However, this work used only 24 ms short time domain signal and demonstrated up to 5 frequency components in the test. Image charge/current signal normally contains large noise, so fitting with only a short time signal can produce large error, while fitting with the whole time domain signal by larger number of frequency components will face a huge calculation time. In fact, according to the linear additivity of FT, LSF can be done in either time domain or frequency domain signals without so-called nonlinear spectral interference, providing the complex form of the frequency spectrum is preserved after the FFT. In this paper, a quantitative algorithm consisting of a scoring-based peak classification and the least square fitting (SC-LSF) was presented to convert an image charge/current signal to mass spectrum for a mixture of multiple m/z ions. LSF was performed in frequency domain with multiple basis signals with their fundamental frequencies derived by a scoring test. The SC-LSF algorithm gives an accurate quantitation for all the m/z ions.

2 Method

2.1 Working principle

The structure and working principle of PEIT have been reported previously[12-13]. The PEIT has a pair of rotationally symmetrical electrode sets which sandwich an ion trapping space. After ions are injected into the trapping space, they fly in the space with hypocycloid type trajectories, and each passes the vicinity of center pickup electrode and induces a so-called image charge repeatedly. The center pickup electrode outputs the image charge/current signal in a pulsed waveform with a certain frequency for each ion group with the same m/z, or a combination of multiple pulsed signals with different frequencies when different m/z ions are flying together. Such image charge/current signal is amplified and acquired digitally *via* the analog-to-digital converter, and recorded as transient data. Ion motion in a tuned PEIT preserves isochronous property, which means the frequency of the image charge/current signal is only dependent on ions' m/z, independent on initial position and energy of injection, that is:

$$f = A\left(\frac{m}{z}\right)^{-\frac{1}{2}} \tag{1}$$

where A is a constant determined by the size and structure of the electrodes, and the voltages applied to electrodes. The signal formed by each ion is a periodical signal with a fixed frequency related to its *m*/*z*, so the mass spectrum[12] can be obtained using FFT and a conversion from frequency axis to mass axis using eq (1). However, a non-sinusoidal periodic signal is composed of multiple harmonic frequency components, each with properties such as frequency, amplitude, and phase. The frequency of these wave components is *N* times the fundamental frequency of the periodic signal (*N*=1,2,3......), so they are called fundamental frequency component and high-order harmonic components, respectively. The existence of higher harmonic components in the frequency domain provides more information and allows higher mass resolution, although, making the spectrum more complicated. The main difficulties in the spectrum conversion where the image charge/current signal in non-sinusoidal waveform are produced by ions of numerous *m*/*z* include:

1) For a wide *m*/*z* range, the frequency range of different harmonics will overlap. For example, when the ratio of the largest ion mass to the smallest one ($m_{\max}/m_{\min}$) exceeds 1.4, the 5th and 6th harmonics will overlap, making it difficult to classify.

2) Although the high-order harmonics gives higher resolution, their peak intensities can become so low that the sensitivity of quantitation is not sufficient. It is best to make full use of all harmonic components in the frequency spectrum for quantification, so as to improve both sensitivity and dynamic range.

3) One of the harmonic peaks of a certain *m*/*z* may coincidentally merge with a different harmonic peak of another *m*/*z*. In this case, both mass prediction and quantification for the two masses are impossible.

Smirnov et al[19] disclosed a method to classify harmonic peaks and find the fundamental peaks with a scoring algorithm. This method, though often gives false positive mass species due to the noise and interference in the signal, can largely reduce candidates number before fitting. Following this approach, our quantitative spectral analysis for the image charge/current signal generated from ions of numerous masses takes two steps. The first step is to classify the various spectral peaks using a scoring test, so as to find a list of possible fundamental frequencies which may include some extra false positive species. In the second step, the LSF with the multiple basis functions constructed upon the found fundamental frequencies to the original signal in frequency domain is carried out to determine the intensity of each basis function.

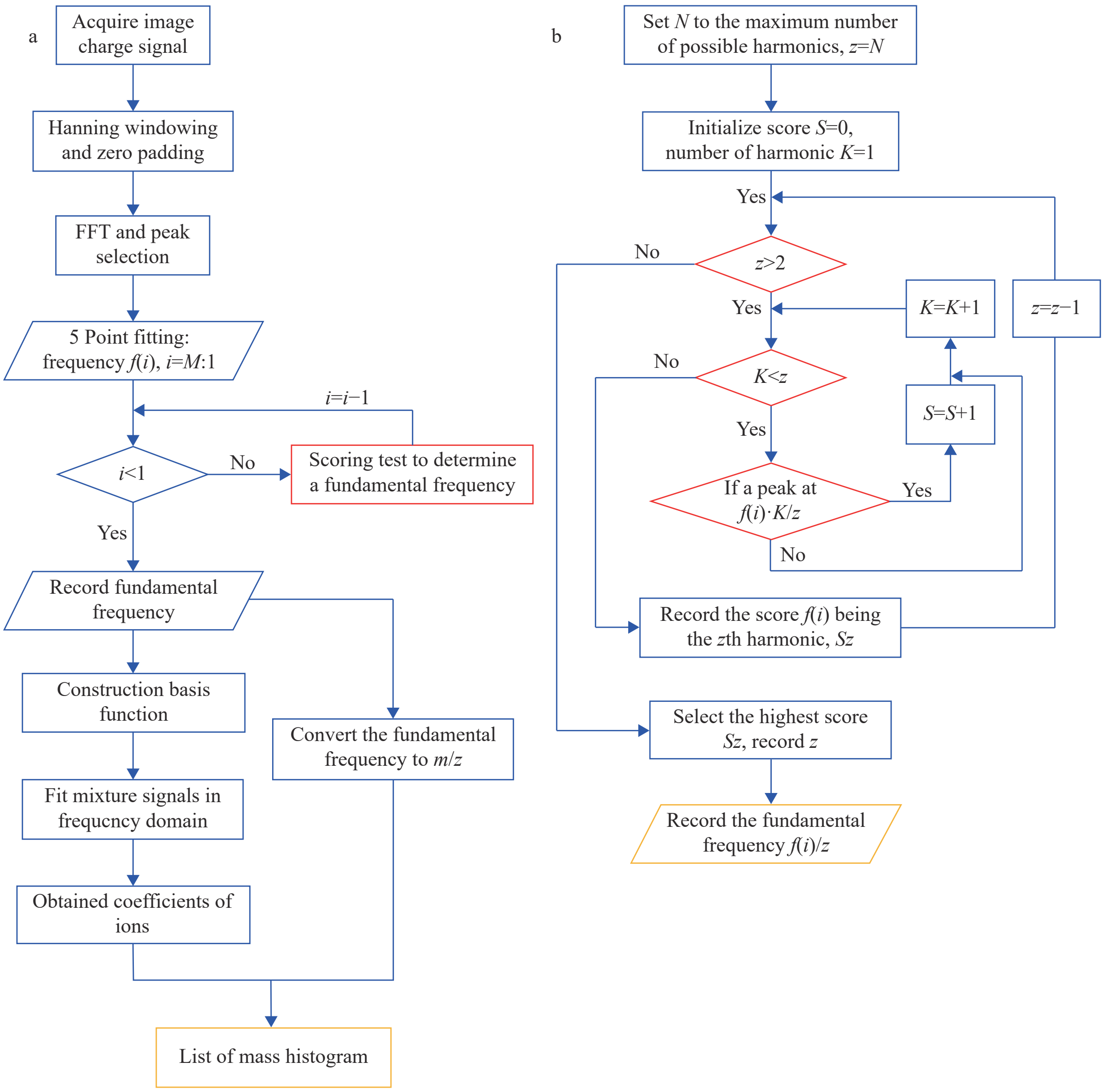
2.2　SC-LSF algorithm

The combined flow chart for converting the image charge/current signal to mass spectrum is shown in Fig.1a. Firstly, the time domain image charge/current signal is acquired, and FFT is used to transfer it to a frequency spectrum. A fundamental frequency range $f_{\min}$-$f_{\max}$ is defined according to the mass range of study by using eq (1). Then the high-frequency end is set as the 10 times of the fundamental frequency of the lowest *m*/*z*, and the low-frequency end is set as the fundamental frequency of the highest *m*/*z*, assuming that harmonics up to 10th order is usable. Peaks between the high and low frequency ends with heights above a preset noise threshold are identified. All the peaks are tested from the high-frequency end to the low-frequency end, and their harmonic order is determined according to the score tests.

Scoring test is used to identify the harmonic order of each peak in the frequency spectrum and calculate its candidate fundamental frequency. For one *m*/*z* of ions, the image charge signal contains the fundamental frequency and multiple high-order harmonic components. The frequency of the *z*th order harmonic component is *z* times its fundamental frequency f_{b}.

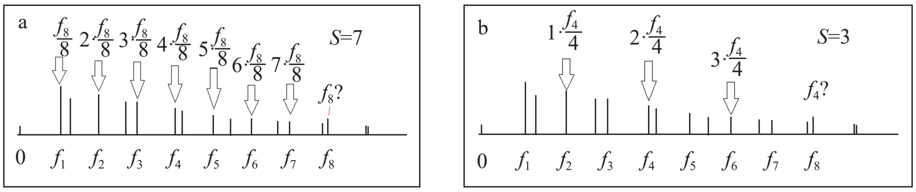
$$f_z = zf_{\mathrm{b}} \tag{2}$$

As shown in the Fig.1b and Fig.2, we judge whether a peak at f_i is the *z*th harmonic by searching if there are also peaks at $f_K = Kf_i/z$ in the spectrum, where K=1, 2…z−2, z−1. One is added to the score *S* when one lower harmonic *K* is confirmed in its right position. Different number of *z* will be tried and the one both gains the highest score and the “score≥2”



P.S. a. overall conversion algorithm; b. SC step to determine fundamental frequencies

Fig. 1　Flowchart of SC-LSF algorithm



P.S. a. assumes it is 8^{th} harmonic peak and found subsequent 7 harmonics, so the score of 7 is obtained; b. assumes it is the 4^{th} harmonic peak and only score of 3 is obtained; assuming the red peak with other harmonic order would probably gain even low score, so it is elected as f_8

Fig. 2　Illustration of the scoring test to the “red peak” among other unknown peaks

will be elected as the correct harmonic number.

From the high-frequency end to low-frequency end, all peaks are tested and assigned with the highest scored harmonic number z. The fundamental frequencies f_b is then calculated using eq (2). In fact, f_b can be obtained from the tests of different peaks, but we normally use the one with the highest possible harmonic order so as to achieve the highest frequency accuracy. The m/z associated with each fundamental frequency is also calculated. After the candidate fundamental frequencies are determined, the intensity of ion components can be calculated using LSF.

Firstly, through a calibration procedure, which can be either by experiment or simulation, we can get the image charge/current signal $S_c(t)$ for single ion of a series of m/z, and extract phase-mass relation. Then, the image charge/current signal of any given mass m_i can be extrapolated using

$$S_i(t) = S_c\left[\sqrt{\frac{m_c}{m_i}}(t-t_i)\right] \tag{3}$$

where m_c is the calibration mass assuming single charge species is used, and t_i is mass dependent phase delay for m_i. Each signal in discrete form which has the same time step as the mixture signal is formed and transformed to its frequency domain spectrum. Let's assume for one of the m_i or fundamental frequencies f_i, its frequency domain discrete spectrum signal is represented as

$$\boldsymbol{X_i} = (X_{1i}, X_{2i}, X_{3i} \cdots X_{mi})^T \tag{4}$$

Our acquired mixture signal in frequency domain is

$$\boldsymbol{Y} = (Y_1, Y_2, Y_3 \cdots Y_m)^T \tag{5}$$

To fit $\boldsymbol{Y}$ with multiple $\boldsymbol{X}_i$, the data points for $\boldsymbol{X}_i$ and $\boldsymbol{Y}$ in eq (4) and (5) may not take all the consecutive discrete points in the spectrum, rather, they can be selected as subsets of data only to cover those points with significant spectral values. Here the multiple linear regression model[20] can be written as:

$$\boldsymbol{Y} = \beta_1\boldsymbol{X}_1 + \beta_2\boldsymbol{X}_2 + \cdots + \beta_n\boldsymbol{X}_n + \boldsymbol{\varepsilon} \tag{6}$$

Where β_i (i=1-n) are the ion numbers for the fundamental frequencies f_i, which are determined by the LSF. The formula (6) can be written in form of matrix as:

$$\boldsymbol{Y} = \boldsymbol{X\beta} + \boldsymbol{\varepsilon} \tag{7}$$

To minimize the error $\boldsymbol{\varepsilon}$, the derivative of the function:

$\min\|\boldsymbol{X\beta} - \boldsymbol{Y}\|_2^2 = (\boldsymbol{X\beta} - \boldsymbol{Y})^T(\boldsymbol{X\beta} - \boldsymbol{Y}) = \boldsymbol{\beta}^T\boldsymbol{X}^T\boldsymbol{X\beta} - 2\boldsymbol{\beta}^T\boldsymbol{X}^T\boldsymbol{Y} + \boldsymbol{Y}^T\boldsymbol{Y}$ needs to be zero, so we finally have:

$$\boldsymbol{\beta} = \left(\boldsymbol{X}^T\boldsymbol{X}\right)^{-1}\boldsymbol{X}^T\boldsymbol{Y} \tag{8}$$

From this solution, the best estimated ion numbers ($\beta_1, \beta_2 \cdots$) for all found fundamental frequencies are given. These fitting coefficients with their respective m/z will be the representation of the spectrum intensities (ion number), so a mass spectral histogram is generated. The SC-LSF method should be much more reliable to determine the quantity of ions at each m/z than a method that only use the peak height of one harmonic component, because it fits the peak intensities at all detected harmonic peaks thus reduces the statistic error.

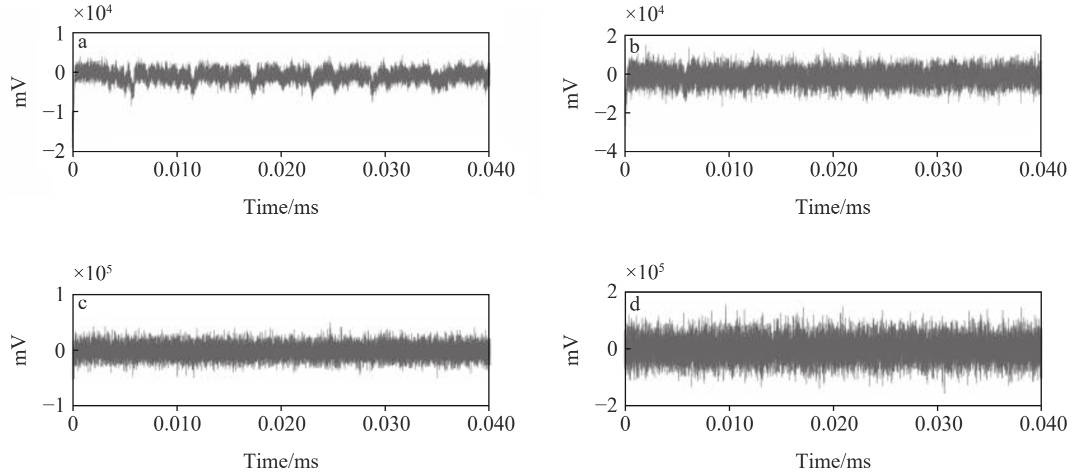
2.3 Simulation platform

For algorithm test, most of the image charge signals were acquired by simulation in the PEIT in SIMION 2020 software. A Window 10 based computer, with Intel (R) Core (TM) i7-11700 CPU@3.60 GHz, 48.0 GB RAM was used for simulation. The unit size of the potential array is 10 μm, and the image charge calculation step is 2 ns in order to achieve sufficient accuracy. The voltages on the mass analyzer were well tuned and initial energy spreads in all dimension were deliberately set small, so dephasing with the transient time is negligible.

3 Result and discussion

Some typical LC-MS spectra for organic sample were taken as example for mass species composition to generate simulation data for algorithm tests. These tests generally gave results matching the original set species very well. To challenge the SC-LSF algorithm, we preset a mass composition of 48 m/z which will cause difficulties listed in working principle section. The m/z range of the ion species is over 5 times ($m_{\max}/m_{\min}$=800/159=5.03), and there are several cases with 2 or 3 masses falling to the relations of harmonic frequency interference $\frac{f(m_1)}{f(m_2)} = \frac{i}{j}$, where i and j are integers. For example, the m/z 200, 450, 800, 300, 533.15. The artificial composition also includes some mass doublets or triplets with mass differences not able to be resolved in the fundamental or lower harmonics peaks, for example, m/z 699.99, 700, 700.01. Some harsh conditions are also combined, such as m/z 198, 792, 792.2, where both harmonic interference and closed masses are included to make data process even more challenging. Figure. S1 (download it from https://

zpxb.xml-journal.net) is a simulated transient signal of the mixed 48 challenging m/z, where each species has a preset number P_i of ions listed in Table S1. In order to get more realistic situation, different levels of noises are added in the time domain signal. Fig.3 shows image charge signals with the signal-to-noise ratios (S/N in power spectrum) at 0, −10, −20 and −30 dB, in a short time range of 0-0.04 ms. When S/N is below −10 dB, the periodical signal has been totally buried in the noise background.



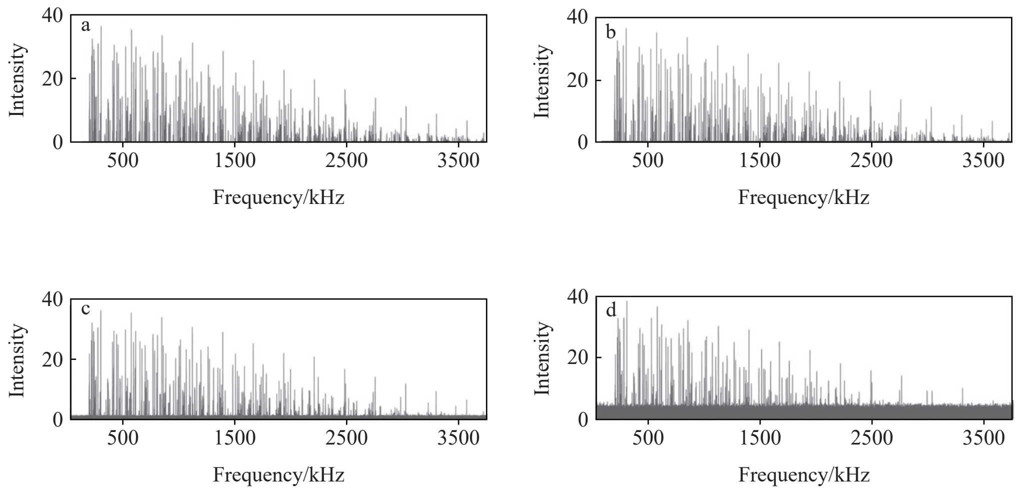
P.S. a. 0 dB; b. −10 dB; c. −20 dB; d. −30 dB; which are calculated using ratio between signal and noise spectral power

Fig. 3　Time domain image charge signals at four different noise levels

FFT was used after each signal was applied with a Hanning window and a one-fold of zero padding to obtain respective frequency spectrum. The frequency spectra for differently mixed noises are shown in the Fig.4. Apparently, the noise level in the frequency spectra is lower than that in the respective time domain signal. Here, the S/N ratios directly measured from the frequency spectrum for the lowest to highest species (a common way in FTMS) are also noted in the caption for comparison.

3.1　Identifying the fundamental frequencies

Before using the SC algorithm, we need to define a detection threshold above which a peak is detected in the spectrum. Here we define the



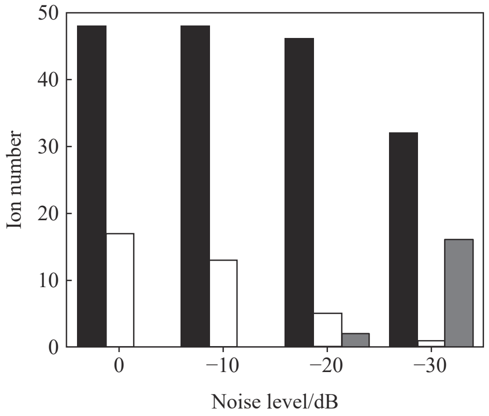
P.S. a. 0 dB: 13.1-262; b. −10 dB: 4.15-83.1; c. −20 dB: 1.31-26.2; d. −30 dB: 0.42-8.31

Fig. 4　Four frequency spectra for the same noise levels as in Fig.3, and the S/N ratios calculated in common FTMS for the lowest-highest fundamental frequency peaks

detection threshold at the level which is above 99.9% of points in the given noise spectrum, consequently, the lower the *S*/*N* of the spectrum, the higher the detection threshold will be used. The lower the *S*/*N* of the spectrum, the higher the detection threshold will be used. We firstly extracted all peaks which contain at least 5 points continually above the threshold in frequency domain. With the transient time of 400 ms and one-fold zero padding, the frequency interval is about 1 Hz. In order to get the peak position with a precision beyond the FFT limitation, 5-point parabolic fitting (2 points before and 2 points after the highest point) was adopted to estimate the peak positions.

For each spectrum of the different *S*/*N*, we harvested a set of the fundamental frequencies after the scoring classification process. With previous calibration, the constant *A* in eq (1) was known as $A = 4.827\times10^6$（Hz $\sqrt{\text{Th}}$）, for the fundamental frequencies, so every found fundamental frequency was assigned to a *m*/*z*. For one group of harmonics belongs to one species, the fundamental frequency and its associated *m*/*z* value determined by the one identified harmonic peak (say 10th order) could be different from that determined by another harmonic peak (say 5th order). The algorithm will treat those found fundamental frequencies with difference between their respective masses $<$ *m*/*z* 0.01 as from the same species, degenerating them to the value which is determined by the harmonic peak of highest order.

Fig.5 lists the fundamental frequency numbers or *m*/*z* which has been found under different *S*/*N*. It is seen that the number of successfully identified species highly depends on noise level. When the *S*/*N* is low, the detection threshold is relatively high, so the number of peaks which can be detected is reduced and the score becomes$<$2. When *S*/*N* reduced to −30 dB, the identified number of masses reduced to 32 with 16 species were not identified. It is seen some non-exist *m*/*z* have also been identified as the possible candidates, especially in case the *S*/*N* is high. These false positive species, after we have a closed check, are mostly elected because there exist species having fundamental frequency in relation with the false one as $\frac{f(m_1)}{f(m_2)} = \frac{i}{j}$, so both true and false frequencies have been validated *via* the score tests. This means that current scoring test may generate many false positive masses when mass range is set wide. However, we haven’t attempted to improve the scoring algorithm since these false positive species can be excluded through following LSF process successfully.

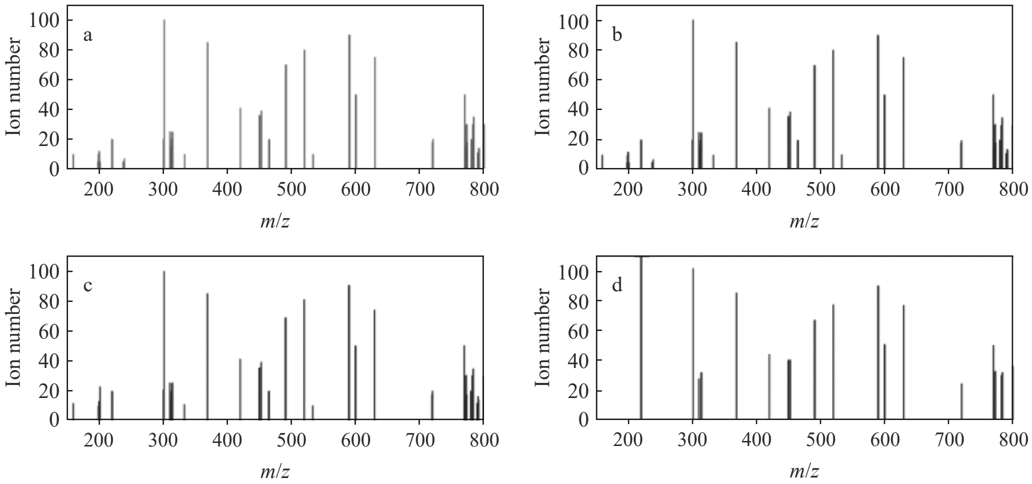


P.S. The black bars denote detected correctly, the white bars denote detected non-exist (false positive), the grey bars denote undetected

Fig. 5 Fundamental frequency numbers or *m*/*z* were found through the scoring process under different noise levels

3.2 LSF and accuracy

For the following LSF process, all basis signals were constructed in frequency domain with their frequency interval to be the same as the mixture signal. The frequency range of the mixture signal between $f_{\min}$-$10f_{\max}$ is normally very large, and there are more than 10^6 frequency points. It will be impractical if all the frequency points are used in LSF. In the algorithm, only those points with value above the threshold are selected to form the *m* dimensional subset for vector $\boldsymbol{Y}$ and $\boldsymbol{X}_i$, thus largely reduce the computation time. This may also reduce fitting error as large number of points which contain only noise or irrelevant information were removed from the process. Fig.6 gives the results of LSF in 4 noise conditions. Only the real part of fitting coefficients is used for the ion numbers and all negative results are ignored (treated as zero) in the figure. For signals with added noise up to S/N of −10 dB, the returned ion numbers for all 48 m/z almost represent the initially set numbers exactly (rounded to integers). With higher noise level, errors appear and increase with the decrease of S/N. The result for the case of S/N −20 dB is shown in Table 1, where the false positive and undetected species are also shown, and here all numbers are rounded to integers. Interestingly, all numbers for the false positive masses are very small, either being positive or negative, so are rounded to zero.



P.S. a. True; b. −10 dB; c. −20 dB; d. −30 dB

Fig. 6　SC-LSF returned number of ions in cases of different S/N

Table 1　Result of the SC-LSF algorithm as compared with the set ion species

True	Detected	True	Detected	True	Detected	True	Detected
159 (10)	159 (12)	301 (100)	301 (100)	590 (90)	590 (91)	773.6 (16)	773.6 (17)
None	192.5 (0)	310 (25)	310 (25)	599.9 (30)	599.9 (30)	774 (18)	774 (17)
None	193.25 (0)	312 (15)	312 (14)	600 (50)	600 (50)	780 (20)	780 (20)
None	196 (0)	313 (20)	313 (20)	600.05 (40)	600.05 (39)	783 (30)	783 (30)
198 (5)	None	314 (25)	314 (26)	600.07 (20)	600.07 (20)	784 (35)	784 (35)
198.5 (7)	198.5 (0)	333 (10)	333 (11)	630 (75)	630 (74)	790 (11)	790 (12)
199 (10)	199 (10)	369 (85)	369 (85)	None	636 (0)	791 (10)	791 (10)
199.7 (12)	199.7 (13)	420 (41)	420 (41)	720 (18)	720 (18)	792 (13)	792 (17)
200 (8)	200 (8)	450 (36)	450 (36)	720.4 (20)	720.4 (20)	792.2 (14)	792.2 (15)
201 (5)	201 (23)	453 (39)	453 (39)	769.99 (30)	769.99 (30)	None	798.8 (0)
220 (20)	220 (20)	465 (20)	465 (20)	770 (50)	770 (50)	800 (30)	800 (30)
237 (5)	None	491 (70)	491 (69)	770.01 (40)	770.01 (40)		
239 (7)	239 (0)	520 (80)	520 (81)	772 (15)	772 (15)		
300 (20)	300 (21)	533.15 (10)	533.15 (10)	773 (30)	773 (30)		

P.S. All items in the table denote “m/z (ion numbers)”; S/N was −20 dB

The averaged relative error in returned ion numbers after the process can be defined:

$$\varepsilon = \frac{1}{K}\sum_{i=1}^{K}\frac{|p_i - P_i|}{P_i} \tag{9}$$

Where P_i is the initially set ion numbers and p_i is the returned ion numbers through the process for the ith m/z, and K is the number of true m/z set initially (K=48 in the test). For the test data set, we calculated the average errors for each noise level and the results are shown in Fig.7. It can be seen that the algorithm is able to return accurate masses and their quantities even in high noise conditions. The average relative error of 0.183 4 in the case of −20 dB is still suitable for quantitative mass analysis, while the averaged error of 0.858 8 in the case of −30 dB may not be useful to determine the quantity of those less intense species in the mass spectrum.

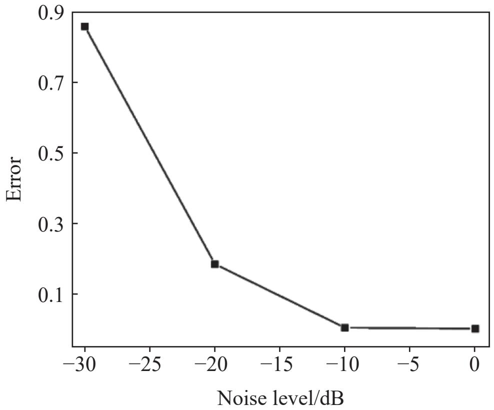


Fig. 7　Averaged relative errors for processing ion intensities under the 4 noise levels

It is important that the frequency domain data brought to LSF should be the complex coefficients rather than its magnitude. This is to satisfy the linear additive property needed for LSF, because the FFT magnitude spectra are not addable. To prove this, we tested to fit the spectra in magnitude mode, also with the different *S*/*N*. In the case of *S*/*N* −20 dB, 43 out of 48 *m*/*z* species returned with almost correct numbers of ions, which are similar to the numbers returned by fitting to the complex data. However, 5 species in two groups with very closed *m*/*z*, returned the numbers with very large error, as shown in Table 2. When species of very closed masses are involved, some of their low order harmonic peaks are not resolved or partially overlapping, even though their high harmonics are baseline resolved. The well resolved high-order harmonics provide the good frequency accuracy in the scoring process and give the fundamental frequencies accurately. However, because of the overlapping at some low harmonic peaks, the interference between the closed frequency reduces the magnitude of the overlapping peak in magnitude mode. To such a spectrum, LST inevitably gives big error.

Table 2　Returned numbers of ions in two groups which have very closed *m*/*z*, after LSF process in complex data and magnitude data

m/*z*	True	Complex		Magnitude	
		−10 dB	−20 dB	−10 dB	−20 dB
600.05	40	40	39	39	37
600.07	20	20	20	18	17
769.99	30	30	30	19	18
770	50	50	50	32	32
770.01	40	40	40	28	28

4　Conclusion

For processing non-sinusoidal image charge/ current signal from planar electrostatic ion trap, a SC-LSF algorithm was adopted. The first step includes the scoring tests to identify the harmonic order of each peak and determine the fundamental frequencies of all mass species. In the second step, LSF with frequency domain data in complex number is used to return the quantity of every identified species. The image charge signal of a specially selected mixture of 48 masses has been used to challenge the algorithm. Different levels of random noise are added to the signal to mimic the real condition with *S*/*N* down to −30 dB. It was found that the number of found *m*/*z* is determined by the noise level and set detection threshold, but most of the set mass species were identified at the *S*/*N* above −20 dB. In the step of LSF, we found it is much efficient to choose only the points where spectrum data are above the noise level to form a subset for the LSF. Fitting with both complex data and magnitude data are compared. With complex data, the fitting returned accurate numbers of ions for all testing species, but fitting with magnitude data returned correct numbers only for the well separated masses at all harmonic orders. Most of the false positive species will return negligible quantities and can be rounded out. The whole algorithm output good quantitative mass spectrum without complication or interference from the multiple harmonic orders, even at the noise level as high as *S*/*N*=−20 dB.

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