Supporting information for

Trace arsenic analysis in edible seaweeds by a miniature in-situ dielectric barrier discharge microplasma optical emission spectrometry based on gas phase enrichment

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1. Electrode fabrication process

The electrode fabrication process using silver paste is described as follows: High temperature sintered conductive silver paste, which has good adhesion to quartz material and is suitable for the electrode printing of various electronic components, is used for DBD electrodes. First, the silver paste is evenly coated on the outer surface of DBD's outer quartz tube and the inner surface of DBD's inner quartz tube. After that, the DBD coated with silver paste is placed in a hot bellows set to 100℃ for an hour to remove bubbles from silver paste. The DBD coated silver paste is then placed in a muffle oven at 650℃ for an hour to sintered the silver paste onto the quartz surface. The photos of silver-coated DBD, DBD's inner quartz tube and outer quartz tube were as shown in Fig.S1.

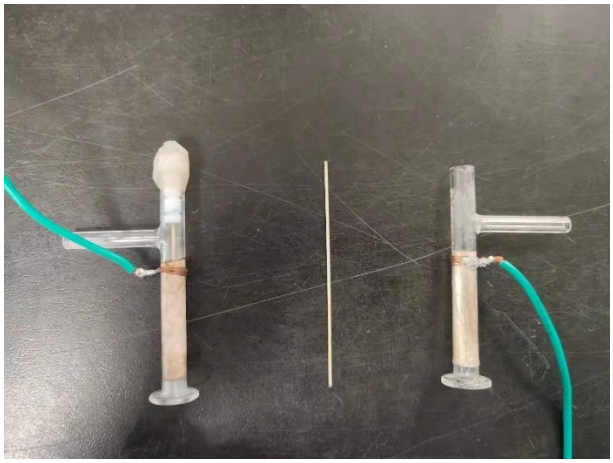

Fig.S1 The photos of silver-coated DBD, DBD's inner quartz tube and outer quartz tube.

2. Background correction method

In this paper, a background correction method is proposed to eliminate the influence of background fluctuation. In this method, a baseline is fitted according to Equation (1), in which fBase(i) indicates the intensity of point i on baseline curve, f(i) indicates the intensity of point i on initial spectrum and dAver(i) indicates the average intensity of point i and its surrounding points on initial spectrum ,which is calculated as Equation (2). In Equation (2), d indicates the number of point on one side on point i (in this experiment, d is

set as 13). After the baseline curve (fBase) is obtained, another baseline (fbase2) is calculated by replacing f(i) in Equation (1) and Equation (2) with fbase(i). The final baseline curve is obtained by replacing f(i) in Equation (1) and Equation (2) with fbase2(i). The spectrum after background correction is obtained by subtracting the final baseline curve from the initial spectrum. In addition, in order to reduce the influence of noise, Savitzky-Golay filter is performed on the spectrum after background correction. In this experiment, the window width of Savitzky-Golay filter is set as 5 points (0.4 nm) and Polynomial number is set as 2.

$$fBase(i) = \begin{cases} f(i) & f(i) < dAver(i) \\ dAver(i) & f(i) > dAver(i) \end{cases} \quad (1)$$

$$dAver(i) = \left(\sum_{j=-d}^{j=d} f(i+j)\right)/(2*d+1) \quad (2)$$

3. Detail procedure of the improved peak volume algorithm

In this article, an improved peak volume algorithm is proposed to solve this problem, where start time point and end time point of the spectrum at each concentration are determined according to a unified judgment criteria. First, the peak area at each time point is calculated, as shown in Equation 1. Then, find the maximum peak area and name its corresponding time point index N_{max}. Subsequently, find the start time point N_{start} and end time point N_{end} as shown in the flow chart 1 and 2. The unified judgment criteria was as shown in inequation (1) and (2). Starting from the time point index N_{max}, the peak area is accumulated along the time axis to both sides point by point until the addition of the peak area at a certain time point makes the increment rate of the accumulated peak area value less than the set volume coefficient. The volume coefficient in inequation (1) and (2) has been optimized. It was found that R^2 of the standard curve was poor in the range of 1-10 μg L^{-1} when volume coefficient is lower than 0.015, possibly because more noise signal was introduced at small intensity, and when volume coefficient is higher than 0.015, the linear range becomes narrower, possibly because the larger intensity loss at higher concentration. As a result, volume coefficient of 0.015 was selected, which can automatically adopt appropriate time width at different concentration. After determining the start time point and end time point, peak volume can be calculated according to Equation 2.

$$I_{area}(n \times \Delta t) = \sum_{\lambda=\lambda_{start}}^{\lambda=\lambda_{end}} I_n(\lambda) \quad (1)$$

$$I_{volume} = \sum_{n=N_{start}}^{n=N_{end}} I_{area}(n \times \Delta t) \quad (2)$$

$$\frac{I_{area}(N_{start} \times \Delta t)}{\sum_{n=N_{start}+1}^{n=N_{max}} I_{area}(n \times \Delta t)} < volume\ coefficient \quad (1)$$

$$\frac{I_{area}(N_{end} \times \Delta t)}{\sum_{n=N_{end}-1}^{n=N_{max}} I_{area}(n \times \Delta t)} < volume\ coefficient \quad (2)$$

In Eq. (1), $I_{area}(n \times \Delta t)$ is the intensity calculated by peak area of the intensity-wavelength spectrum collected at $n \times \Delta t$ time. $I_n(\lambda)$ refers to the intensity-wavelength spectrum collected at $n \times \Delta t$ time. λ_{start} and λ_{end} refer to the wavelength of starting point and ending point of the peak. In Eq. (2), I_{volume} is the intensity calculated by peak volume. N_{start} and N_{end} refer to the time index of starting intensity-wavelength spectrum and ending intensity-wavelength spectrum.

It is worth mentioning that the background correction was performed for each intensity-wavelength spectrum to reduce errors caused by baseline fluctuation before the comparison.

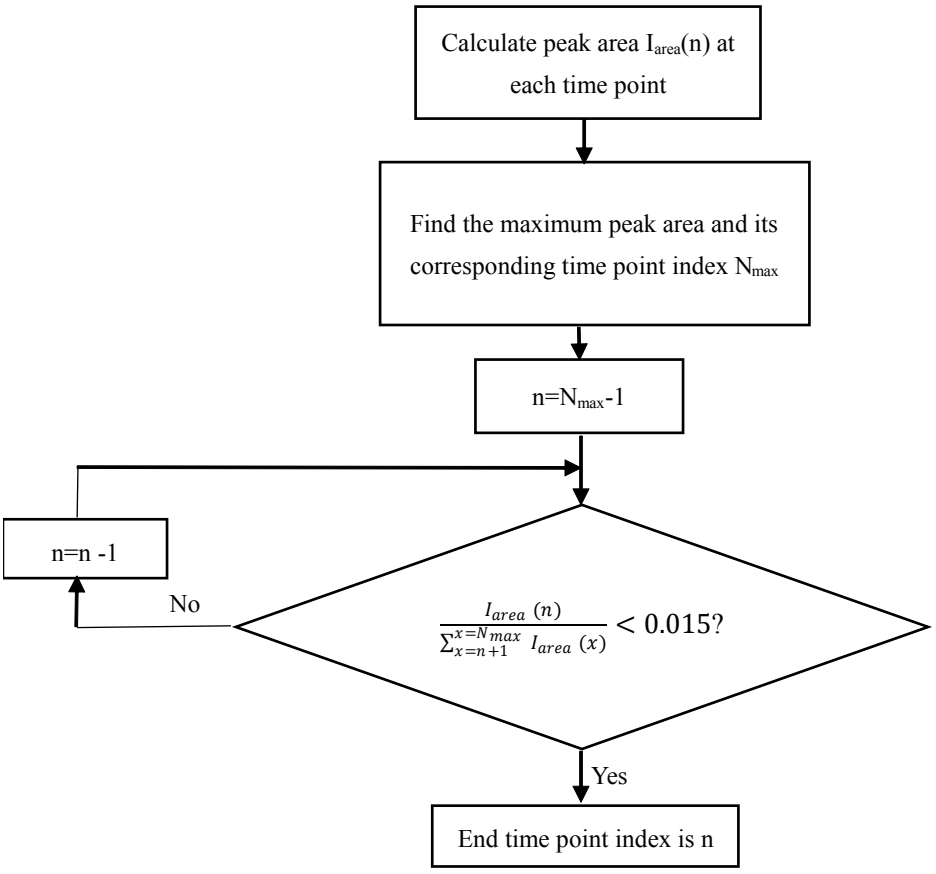

Fig.S2 Flow chart of determining start time point.

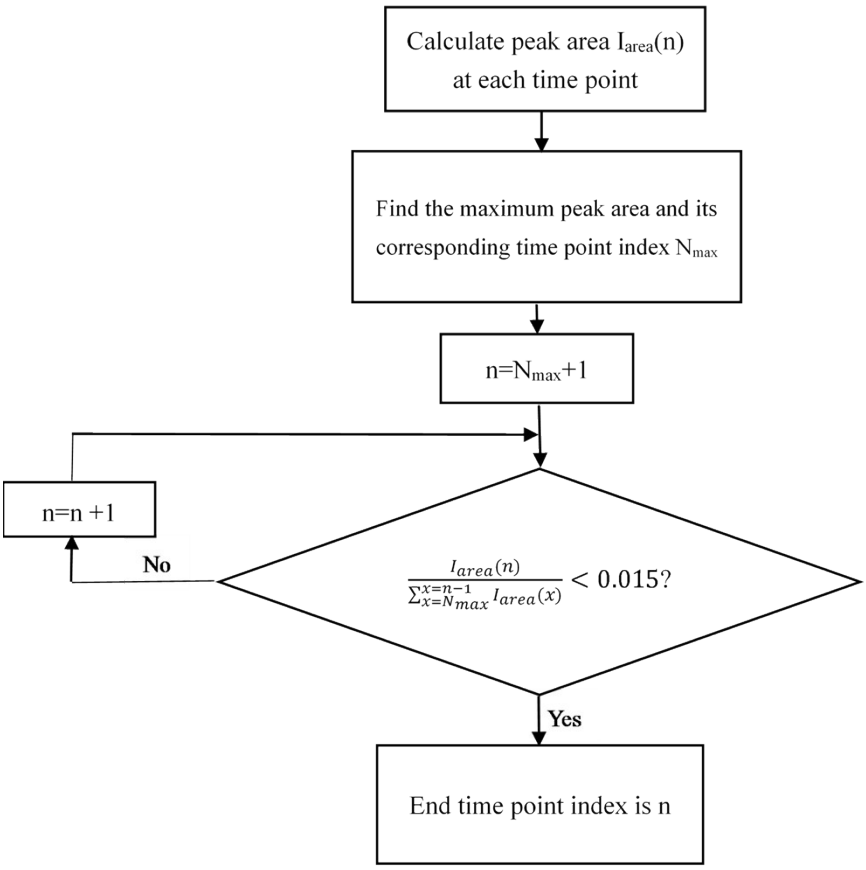

Fig.S3 Flow chart of determining end time point.

4. **The operational parameters of ICP-MS**

Table S1 Operational parameters of ICP-MS

Parameters	Values
Incident RF power	1150W
Sampling depth	120mm
Nebulizer Ar gas flow rate	0.8 L min^{-1}
Cooling Ar gas flow rate	14 L min^{-1}
Auxiliary Ar gas flow rate	1.2 L min^{-1}
Peristaltic pump rate	30 rpm
Dwell time	10 ms
Isotopes	^{75}As
Internal standard isotopes	^{72}Ge

5. Optimization of H_2 in Ar/H_2 mixture

H_2 has been validated as a crucial gas for the releasing of As from DBD's inner surface, which might supply hydrogen radical to promote the atomization of As. Ar is usually employed as the working gas of microplasmas as it could form stable and stronger plasma. Accordingly, a mixture gas of Ar and H_2 is employed as the working gas of release step in this work. The effect of the proportion of H_2 in the mixture of Ar/H_2 on the analytical signals of As was investigated. As shown in Fig.S4, As intensity decreases with the increasing H_2 proportion because higher amount of H_2 would consume the energy of DBD plasma and cause a decrease of its excitation capability. However, sever tailing of As releasing intensity could be observed when the proportion of H_2 in Ar/H_2 is below 5%. Therefore, the proportion of 5% was selected for all subsequent experiments.

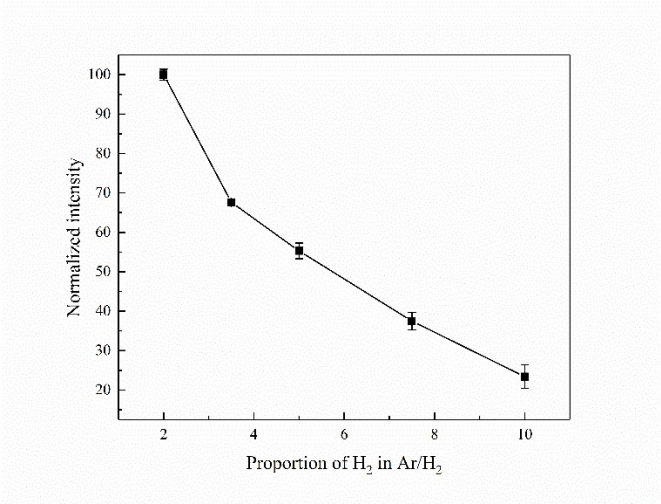

Fig. S4 Dependence of As and Sb intensities on percentage of H_2 in Ar/H_2. The intensities are normalized with that in 2% H_2 set at 100, respectively.