

Short Communication

## The Qualitative Electrochemical Determination of Multiple Components in Seaweed Fertilizer

Xinyi Zhang<sup>1</sup>, Jiakun Zhou<sup>1</sup>, Zemin Li<sup>1</sup>, Yimin Qin<sup>2\*</sup>, Ruitao Yu<sup>3,4</sup>, Huaiwei Zhang<sup>1</sup>, Yuhong Zheng<sup>5</sup>, Jiangwei Zhu<sup>6</sup>, Demeng Zhang<sup>2\*</sup> and Li Fu<sup>1,2\*</sup>

<sup>1</sup> College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou, PR China

<sup>2</sup> Ministry of Agriculture Key Laboratory of Seaweed Fertilizers, Qingdao Brightmoon Seaweed Group Co Ltd, Qingdao, PR China

<sup>3</sup> Qinghai Key Laboratory of Tibetan Medicine, Northwest Institute of Plateau Biolog, Chinese Academy of Sciences, Xining, China

<sup>4</sup> Key Laboratory of Tibetan Medicine Research, Northwest Institute of Plateau Biology, Chinese Academy of Sciences, Xining, PR China

<sup>5</sup> Institute of Botany, Jiangsu Province and Chinese Academy of Sciences (Nanjing Botanical Garden Mem. Sun Yat-Sen), Nanjing 210014, P.R. China

<sup>6</sup> Collaborative Innovation Center of Sustainable Forestry in Southern China of Jiangsu Province, (Nanjing Forestry University), Nanjing 210037, China

\*E-mail: [yiminqin1965@126.com](mailto:yiminqin1965@126.com), [zdm@bmsg.com](mailto:zdm@bmsg.com), [fuli@hdu.edu.cn](mailto:fuli@hdu.edu.cn)

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Seaweed fertilizer refers to fertilizer created by extracting the active ingredients from raw seaweed that is then applied to plants as a nutrient source to promote growth and increase yield. A quick method of analysing seaweed fertilizer quality has practical value. In this work, we established a simple electrochemical method for analysing commercial seaweed fertilizer by comparing the contributions of each electro-active ingredient. The electrochemical profiles of 3-hydroxyphenylacetic acid, gibberellin, lycine, abscisic acid, indole-3-acetic acid and zeatin were first recorded in a database. Then, the electrochemical profiles of four commercial seaweed fertilizers were recorded and examined to analyse the contribution of each ingredient.

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**Keywords:** Seaweed fertilizer; Electrochemical analysis; Differential pulse voltammetry; Electrochemical sensor; Fingerprint

### 1. INTRODUCTION

Seaweed fertilizer refers to fertilizer created by extracting the active ingredients from raw algal material grown in the ocean [1,2]. The seaweeds used in agriculture include green algae, red algae and

brown algae, but the most common seaweed fertilizer raw materials in the market are from the brown algae *Ascophyllum nodosum*, *Ecklonia maxima*, *Laminaria digitata*, *Laminaria japonica* and *Sargassum wightii*. *Ascophyllum nodosum* is mainly distributed in the North Atlantic Ocean. *Ecklonia maxima* is mainly distributed on the western coast of South Africa and in Namibia. *Laminaria japonica*, the most widely used kelp species for kelp agricultural research, is mainly concentrated in China, Japan, Russia and France [3-5].

Seaweed fertilizer can be used as a nutrient source for plants to promote growth, increase yield, and improve the quality of agricultural products [6-8]. Because seaweed grows in environments with abundant seawater, it contains not only the nutrients of terrestrial plants but also many trace elements such as iodine, potassium, magnesium, manganese and titanium as well as polysaccharides [9,10]. Seaweed contains more than 66 active ingredients, which can provide various nutrients, amino acids, polysaccharides, vitamins and cytokinins to vegetables [11-13]. Seaweed application can help vegetables establish a robust root system; enhance their absorption and utilization of soil nutrients, water and gases; increase stem vascular cells and accelerate the transport of water, nutrients and photosynthetic organic products. In addition, alginic acid reduces soil compaction and delays salinization [14-18]. However, the seaweed fertilizer sold on the market faces many quality problems. Due to the slow release effect of fertilizers, the alginic acid content and levels of other active ingredients in some seaweed fertilizers are low. Therefore, it is necessary to establish a fast method of quality analysis for the quality control of seaweed fertilizer [19,20]. 3-hydroxyphenylacetic acid, gibberellin, lycine, abscisic acid, indole-3-acetic acid and zeatin are major active constituents in seaweed fertilizer which could be beneficial for plant growth. A quick evaluation method of these compounds in the seaweed fertilizer could be reflected the quality of the seaweed fertilizer.

It is very difficult to detect the constituent materials of a complex system, often requiring complicated experiments and expensive instruments. Purification of the sample is usually carried out by chromatography. Column chromatography and thin-layer chromatography are common and effective methods for separation and purification, which conveniently replace the adsorbent and mobile phase solvent [21-25]. Inorganic component analysis of samples is usually performed by atomic emission or absorption spectroscopy for qualitative and quantitative analysis. Infrared spectroscopy is the most widely used spectral analysis method in organic analysis [2,26-29]. This method involves the widest range of samples and provides the most abundant structural information. Mass spectrometry is the only method that provides the molecular weight, elemental composition, and molecular formula of a compound [23,30-36]. This method is suitable for the analysis of compounds with thermal instability and a large molecular weight, such as polysaccharides and peptides.

It is well known that fingerprints are unique. With this discovery, the application of fingerprints has become more extensive; for example, fingerprints are used instead of stamps, for identification, for crime detection and for taking attendance [37-41]. The definition of fingerprints has gradually been extended to scientific fields. Because of the complex physical and chemical properties of substances such as medicines and foods, these substances have traditionally been identified according to their shape, colour, and one or two markers of ingredients. However, these methods do not provide a complete picture of a complex substance and cannot distinguish between substances with similar chemical compositions. We previously established an electrochemical method for recording the electroactive component profile

of a complex sample that can be used for identification [42,43]. In this work, we attempt to extend this methodology to seaweed fertilizer quality detection. First, the electrochemical profiles of 3-hydroxyphenylacetic acid, gibberellin, lycine, abscisic acid, indole-3-acetic acid and zeatin were recorded using a screen-printed electrode. Then, the electrochemical profile of four commercial seaweed fertilizers was recorded. Finally, the contribution of each component to the seaweed fertilizer was analysed and discussed.

## 2. EXPERIMENTAL

3-hydroxyphenylacetic acid, gibberellin, lycine, abscisic acid, indole-3-acetic acid and zeatin were purchased from Aladdin Co., Ltd. and was used without further purification. Other chemicals are in analytical grade. Four different seaweed fertilizers, Seaweed fertilizer (Dewoduo, Co., Ltd.), Seaweed fertilizer (Luowoshi Co., Ltd.), Leilihong (Hongyue Co., Ltd.) and Leililv (Hongyue Co., Ltd.), were purchased from Online shop. These four commercial seaweed fertilizers were denoted as S-1, S-2, S-3 and S-4, respectively.

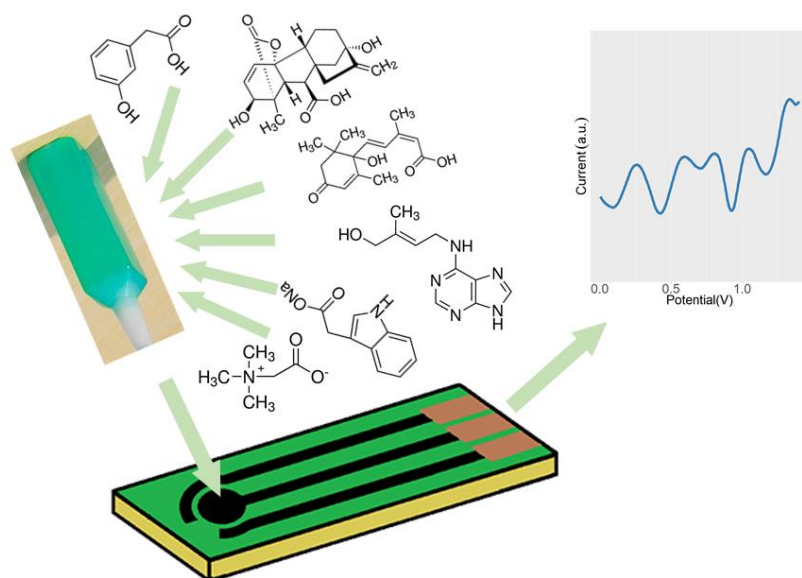
Electrochemical profiles of individual active ingredient and commercial seaweed fertilizers were recorded at a CHI1210c electrochemical workstation with a screen-printed electrode (SPE). Typically, the individual active ingredient was firstly dissolved into water to form a 0.1 M solution. 2  $\mu$ L of solution has been dropped on the working electrode of the SPE and dried naturally. For real commercial sample analysis, the real liquid seaweed fertilizer was firstly diluted 50 times before analysis. The diluted sample was then dropped on the SPE surface and dried naturally. Then, 50  $\mu$ L of PBS (0.1 M) was dropped on the SPE surface to cover three electrodes. A differential pulse voltammetry (DPV) was then carried out for electrochemical profile recording. The scan range is between 0 to 1.4 V. The amplitude is 0.05 V. The pulse width is 0.05 s. The sampling width is 0.0167 s. The pulse period is 0.5 s.

## 3. RESULTS AND DISCUSSION

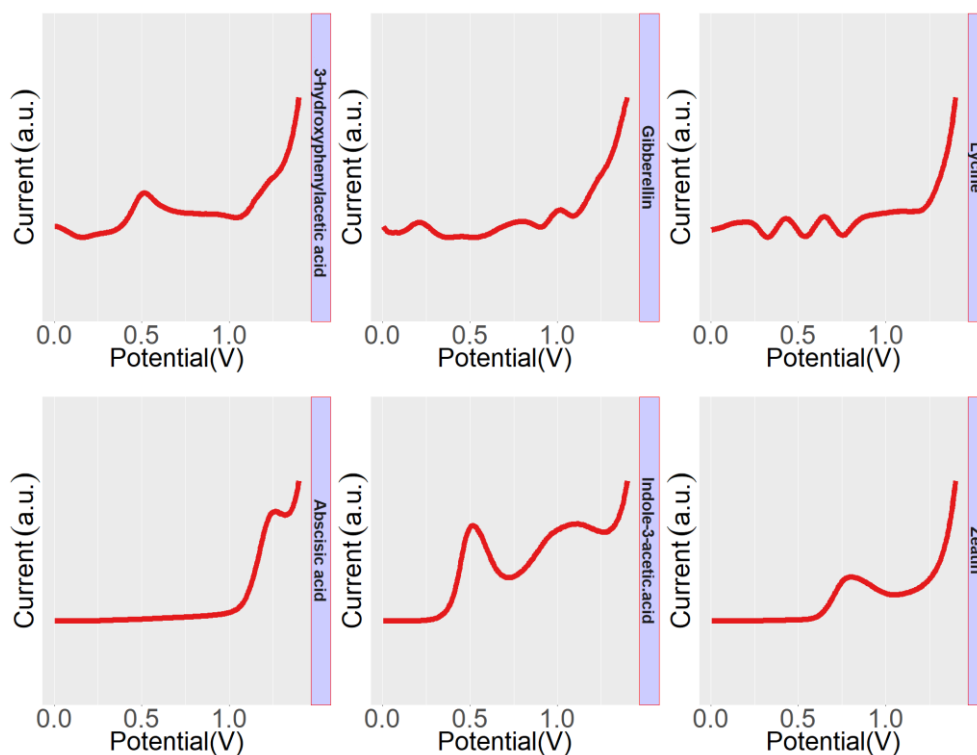
Figure 1 shows a schematic analysis of seaweed fertilizer using an electrochemical method. A typical DPV curve of a commercial seaweed fertilizer recorded using an SPE is shown in the figure. Several distinct peaks can be seen in the DPV profile that correspond to the electro-active species in the seaweed fertilizer. According to the component analysis, in addition to trace elements, the seaweed fertilizers also include many active ingredients such as 3-hydroxyphenylacetic acid, gibberellin, lycine, abscisic acid, indole-3-acetic acid and zeatin. The aim of this work was not to determine the concentration of the individual electro-active species in seaweed fertilizer but to quantify the contribution of each ingredient based on the DPV profile.

The electrochemical profiles of 3-hydroxyphenylacetic acid, gibberellin, lycine, abscisic acid, indole-3-acetic acid and zeatin are shown in Figure 2. 3-hydroxyphenylacetic acid is a isomers of hydroxyphenylacetic acid whose structural formula presents phenol with an acetic acid substituent at position [44]. 3-hydroxyphenylacetic acid shows a distinct oxidation peak at 0.512 V with a flat band at 0.864 V. In addition, another small oxidation band can be found in the centre at 1.207 V. Gibberellin is phytohormone involved in many processes of plant growth and it has been widely used in agriculture. Gibberellin can significantly promote the growth and division of cells with no acidification upon the cell

wall [45]. The electrochemical profile of gibberellin includes three peaks in the positive scan, which are located at 0.212 V, 0.796 V and 1.017 V. Similarly, the electrochemical profile of lycine also shows three oxidation peaks at 0.204 V, 0.429 V and 0.653 V. The DPV curve of abscisic acid exhibits only one distinct oxidation peak at 1.220 V. Zeatin also shows a sole oxidation peak at 0.808 V. Indole-3-acetic acid shows two distinct peaks at 0.516 V and 1.092 V. Table 1 summarizes the characteristic peaks of these six ingredients.



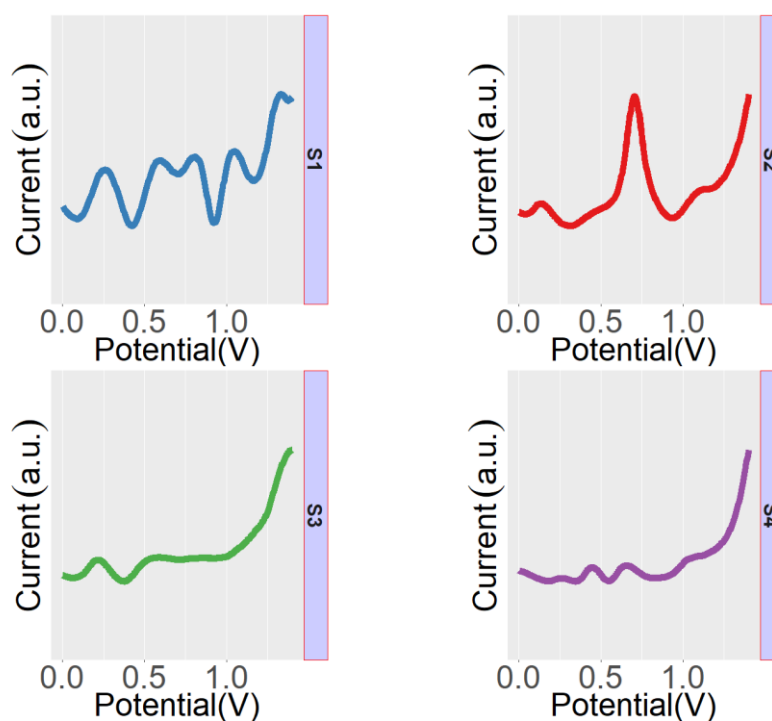
**Figure 1.** Schematic diagram of the analysis of seaweed fertilizer based on electrochemical method.



**Figure 2.** DPV profiles of 3-hydroxyphenylacetic acid, gibberellin, lycine, abscisic acid, indole-3-acetic acid and zeatin

**Table 1.** Characteristic peaks of gibberellin, lycine, abscisic acid, indole-3-acetic acid and zeatin during the DPV scan.

	3-hydroxyphenylacetic acid	Gibberellin	Lycine	Abscisic acid	Indole-3-acetic acid	Zeatin
0.204 V	×	×	★	×	×	×
0.212 V	×	★	×	×	×	×
0.429 V	×	×	★	×	×	×
0.512 V	★	×	×	×	×	×
0.516 V	×	×	×	×	★	×
0.653 V	×	×	★	×	×	×
0.796 V	×	★	×	×	×	×
0.808 V	×	×	×	×	×	★
0.864 V	★	×	×	×	×	×
1.017 V	×	★	×	×	×	×
1.092 V	×	×	×	×	★	×
1.207 V	★	×	×	×	×	×
1.220 V	×	×	×	★	×	×



**Figure 3.** DPV profiles of S-1, S-2, S-3 and S-4

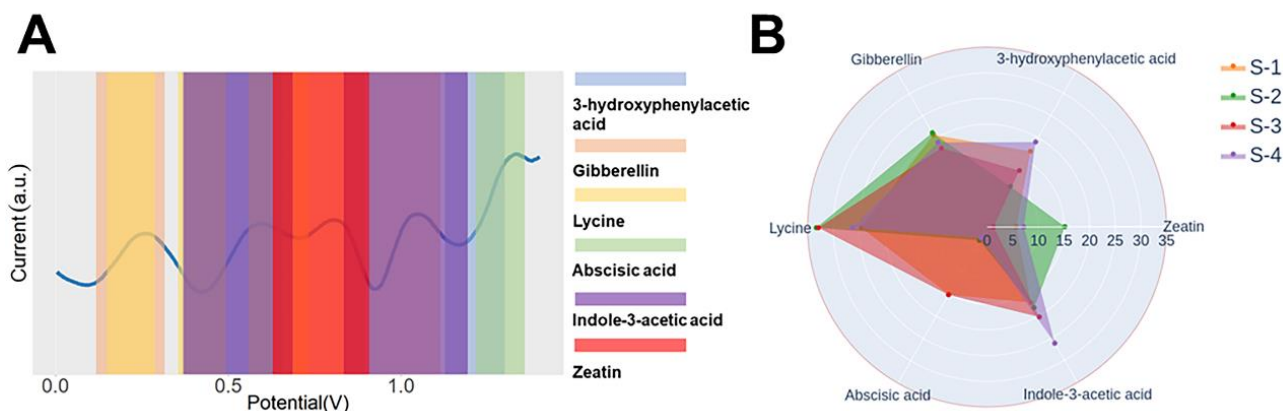
The next aspect of this study was to investigate the electrochemical profiles of commercial seaweed fertilizers. Figure 3 shows the DPV profiles of four commercial seaweed fertilizers. As shown in the figure, the DPV curve of S-1 exhibits five characteristic peaks located at 0.264 V, 0.592 V, 0.804 V, 1.041 V and 1.330 V. The DPV curve of S-2 shows three characteristic peaks located at 0.136 V,

0.704 V and 1.115 V. In addition, a small peak can be observed at 0.436 V. The DPV curve of S-3 shows two characteristic peaks located at 0.220 V and 0.553 V with a small oxidation band centred on 0.812 V. The DPV curve of S-4 shows four characteristic peaks located at 0.254 V, 0.443 V, 0.655 V and 1.061 V. These results indicate the existence of electro-active compounds in the commercial seaweed fertilizers. Although the oxidation peak can be slightly shifted in the presence of other molecules, the matching of peak locations found for the commercial seaweed fertilizers with those for the individual ingredients was carried out, and the results are summarized in Table 2. For the majority of the ingredients one distinct peak can be observed along with some other minor responses which in principle makes ingredient identification more feasible. This is similar to previous work where the electrochemical detection of curry [46].

**Table 2.** Peak match result of commercial seaweed fertilizers with the individual ingredient.

	S-1	S-2	S-3	S-4		S-1	S-2	S-3	S-4
0.204 V	×	★	×	×	0.808 V	★	×	×	×
0.212 V	★	×	★	★	0.864 V	×	×	★	×
0.429 V	×	★	×	★	1.017 V.	×	×	×	★
0.512 V	×	×	×	×	1.092 V	★	★	×	×
0.516 V	★	×	★	×	1.207 V.	×	×	×	×
0.653 V	×	★	×	★	1.220 V	★	×	×	×
0.796 V	×	×	×	×					

Some peaks could not be directly observed during the DPV scan because the electrochemical response of some ingredients overlapped with that of others. The individual responses for the main components compared to the signal observed for a seaweed fertilizer sample are also overlaid which indicates that interfering effects between the ingredients are not extensive. Therefore, the area of each ingredient was calculated to study its contributions. Due to the potential peak shifts, the area corresponding to each ingredient was adjusted slightly with respect to a range of potentials. As an example, Figure 4A shows a breakdown of the area of the DPV curve for the S-1 profile. With these areas, the contribution of each ingredient can be calculated and normalized. Figure 4B shows the contribution of 3-hydroxyphenylacetic acid, gibberellin, lycine, abscisic acid, indole-3-acetic acid and zeatin to four commercial seaweed fertilizers. The dominant components of the seaweed fertilizers were lycine and gibberellin. S-1 and S-3 showed high contributions of abscisic acid, while S-2 showed a high contribution of zeatin. Based on these results, the established electrochemical method can be used to determine the quality of commercial seaweed fertilizers with very simple on-site analysis. In addition, an unmodified SPE is required as the sensing element and therefore storage and stability of the electrode are not an issue.



**Figure 4.** (A) Area breakdown profile of DPV curve of S-1. (B) Quantitative analysis of the DPV profile of four commercial seaweed fertilizers compared with characteristic peaks of each ingredient

#### 4. CONCLUSION

In conclusion, we established an electrochemical method for quality analysis of seaweed fertilizer based on the electrochemical response of electro-active ingredients recorded on an SPE. The individual electrochemical profiles of 3-hydroxyphenylacetic acid, gibberellin, lysine, abscisic acid, indole-3-acetic acid and zeatin were first recorded and used to create a database. The voltammetric profile of each commercial seaweed fertilizer was then recorded. The result was normalized to calculate the contribution of each ingredient. This method showed excellent practicability for evaluating the quality of commercial seaweed fertilizers.

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