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Title(English)	Development of an analytical method for the determination of the position specific 13C isotopic composition of organic acids
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Isotope analysis technique is a useful tool to obtain information of organic materials, which related to their origins, metabolic pathways and also the biosphere/atmosphere interaction. This technique commonly use for compound specific isotope analysis (CSIA). CSIA is typically used to determine isotopic composition of interested target compound in single run. However, to clarify the information about its origin by using data from CSIA alone is not enough. On the other hand, position-specific isotope analysis (PSIA) can be used in an effort to go further and reach a higher level of information on the processes related to organic molecules. Indeed, PSIA has shown heterogeneous isotope distribution of organic compounds including amino acids, acetic acid, fatty acids, sugars, ethanol or hydrocarbons. Commonly, isotope composition is determined by measuring of isotope ratio of the sample against an international standard (VPDB) and expressed as delta (δ) value in per mil unit (‰).Such information is useful for the investigations of synthetic processes and metabolic pathways of target compounds. These isotope analysis techniques were also adopted to use for the food industry to assess information about botanical and geological origins of organic materials for purpose of quality control. Pyruvate, which is a cornerstone metabolite in the plant system and its isotope signature, has influence to the isotopic content of respired CO_2 and its related metabolites. Because it is a key metabolite for carbohydrate metabolism that needed for begin plant's citric acid cycle, fat and protein metabolism, pyruvate can be also used for dietary supplement. To obtain pyruvate's carbon isotope signature would be useful information for the study topic about authenticity and also its metabolic pathways in plants. In this study, the main purpose is the development of PSIA for pyruvate. Since pyruvate can be degraded into acetic acid and carbon dioxide by using H_2O_2, the analytical method for $\delta^{13}C$ of acetic acid is also involved. The improvement of acetic acid analytical method is the first part of this study. Then, this method will be later adopted to use in pyruvate $\delta^{13}C$ determination.

This study has achieved in development of the position specific ^{13}C analytical method for organic acids, which consists of two parts. The first part is about the improvement of position specific ^{13}C analytical method of acetic acid. In previous study, solid phase micro extraction (SPME), gas chromatography/combustion-isotope ratio mass spectrometry (GC/C-IRMS) and gas chromatography/pyrolysis-gas chromatography/combustion-isotope ratio mass spectrometry (GC/Py-GC/C-IRMS) systems were used for the determination of intramolecular $\delta^{13}C$ of acetic acid. Samples was extracted with SPME from headspace (HS) in vials and measured bulk and intramolecular $\delta^{13}C$ analysis respectively. This analytical method of acetic acid needed to switch between two

configuration systems. Our improvement focuses on prevent this switching to avoid errors, which can be occurs from this change and duplication of sample preparation. Acetic acid lab standards were used for making the calibration curve for intramolecular $\delta^{13}C$ calculation, which is derived from of methyl (CH_3-) and carboxyl (-COOH) part. With this principle, the intramolecular and molecular $\delta^{13}C$ of acetic acid are able to obtain within single injection analysis. The HS-SPME-GC-Py-GC-C-IRMS method, which has successfully developed can be used for obtaining the $\delta^{13}C$ values of acetic acid for both intramolecular and molecular level in a single injection analysis. Having commercial vinegar as an application, intramolecular $\delta^{13}C$ distribution of samples was determined within 0.6‰ repeatability. By using this method, we can avoid the switching between two configuration systems and the duplication of sample preparation, which are factors for unexpected errors. Also, the development of this method shows the importance of using intramolecular isotope standards for calibration.

The second part is about the improvement of position specific ^{13}C analytical method of pyruvate. Sodium pyruvate is the initial substance for experiment. First, bulk $\delta^{13}C$ of sodium pyruvate was measured by laser spectroscopy.In this study, sodium pyruvate has used H_2O_2 to decarboxylated into acetic acid and carbon dioxide. The completeness of the reaction is confirmed with the number of approximately 99.7% by the determination of manometric CO_2 with standard calibration curve. The bulk $\delta^{13}C$ of sodium pyruvate was obtained by laser spectroscopy within 0.3‰ repeatability. The intramolecular $\delta^{13}C$ of pyruvate consists of two parts, which are acetic acid and carbon dioxide respectively. The acetic acid part was determined by our developed HS-SPME-GC-Py-GC-C-IRMS method. The intramolecular $\delta^{13}C$ distribution of sodium pyruvate samples were obtained within 0.6‰ repeatability for both methyl and carboxyl part. Applying for pyruvate diet pills as an application, the intramolecular $\delta^{13}C$ distributions of samples were able to determine within 0.3‰ repeatability for both part of methyl and carboxyl. Later, $\delta^{13}C$ of CO_2 of sodium pyruvate and diet pill samples can be calculated by using pyruvate mass balance equation or direct measurement of $\delta^{13}C$ using dual inlet system of IRMS system.
The successful improved method in this study can be a useful tool for the detection of production process and raw materials.