Determination of Geographical Origin of Rice by ICP-MS with Helium Collision-Reaction Cell

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Introduction

Chemical analysis of food would be one of most common interests, for the chemicals in food could have significant impact on human health. For example, inorganic components such as Pb, As, Cd and Hg are well known toxic elements and so their contamination level in foods are regulated in many countries.
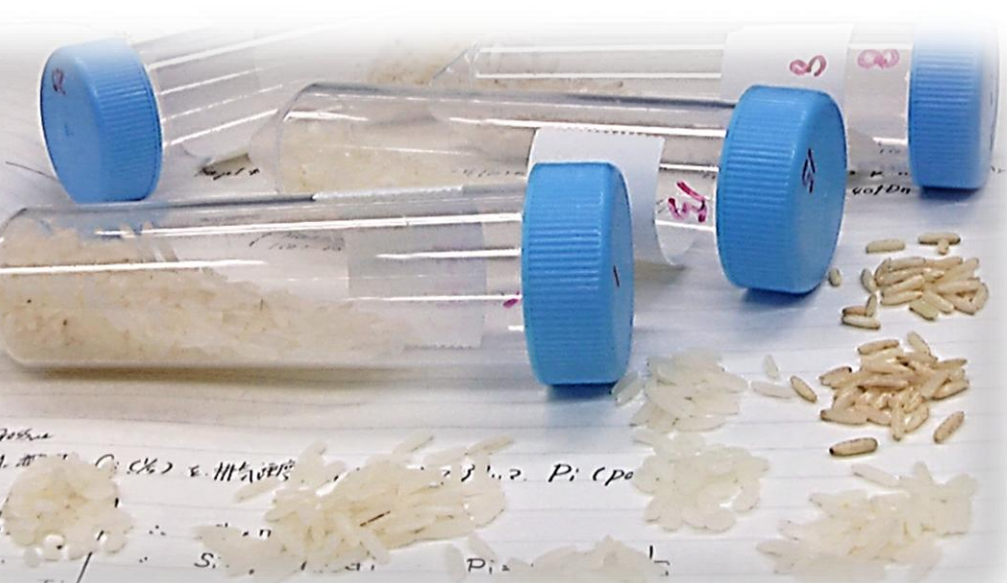
Today, with the increase of international trade of foods, importance of the analysis has been getting larger than ever, and the list of chemical species to be controlled has been and is still increasing as researchers reveal the potential risk of more chemicals to health.

Another , relatively new interest in chemical analysis of food pertains to labeling. Have you ever suspected the accuracy of the label on any foods? We have seen in the past and continue to see today numerous examples of fraud in the labeling of foods around the world. Several chemical analytical techniques were developed and actually used to ensure authenticity of foods. This poster presents the results of a feasibility study to distinguish the geographic origin of rice using elemental composition information obtained by ICP-MS.

Sample preparation and Analytical method

14 kinds of Rice samples were gathered from local markets in four different countries, including Japan. Seven of them were samples from Japan and remaining seven were from three other countries. They were all digested with MILESTONE Inc. ETHOS-1 closed vessel microwave digester which can process ten vessels at one time. Sample preparation was as follows:
1. Each raw sample was weighted to about 0.5g. Triplicated (N=3) samples were prepared from each rice sample.
2. Add 1ml H_2O_2 and 7 ml HNO_3 to samples.
3. All samples were digested in Microwave Digester using the time program given in table1.
4. Finally, the samples we brought to a final volume of 50ml.
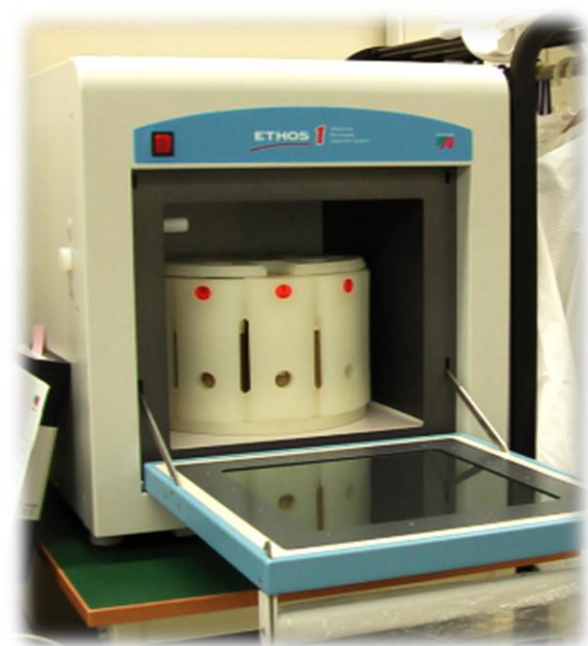
step	time –min.	Power -W	Temp. -°C
1	2	1000	50
2	3	0	30
3	25	1000	185
4	1	0	155
5	4	1000	185
6	15	1000	185
7	20	0	-

Figure 1 (left) : MILESTONE Inc. ETHOS-1 microwave digester
Table 1 (right) : Temperature program for the digestion

In total, 42 prepared samples and preparation blanks were analyzed with an Agilent 7700x ICP-MS. The method is summarized in Figure2. Analyzing foods is often challenging for ICP-MS because of the high matrix contained in the samples. Matrix in the food samples causes two problems:
One is non-spectroscopic interference leading to signal instability by deposition of matrix on interface cones or lenses. The other is spectroscopic interference which can deteriorate the accuracy of quantification. The recently developed Agilent 7700x has ability to overcome these challenges in food analysis. The ion lens called the x-lens was developed to be used under high temperature plasma conditions. These high temperature plasma conditions, called robust plasma are required for completely decomposing food samples for signal stability and for reduced signal suppression known as matrix suppression.   The x-lens can maintain high sensitivity and signal stability under robust plasma conditions, overcoming space charge repulsion. The unique He collision cell is another feature of Agilent7700x. Cell technology is now a common technique used to remove spectroscopic interferences in ICP-MS. The He collision cell removes spectroscopic interferences based on the size difference between the analyte and interfering polyatomic ion. It is the most suitable cell technique when the sample matrix is unpredictable or variable. The measured concentration of 75 elements in the 14 samples was then statistically analyzed to extract information used to distinguish the country origin by use of Agilent Mass Profiler Professional (MPP) SW.

- **Plasma condition : General purpose (RF=1550w, SD=8mm, CRGS=1.05L/min.)**
- **He mode : Energy Discrimination = 3 V He flow rate = 4.3 ml/min.**
- **Acquisition : 75 elements Integration time = 0.3 sec. Replicate number = 3**

Figure 2 : Agilent7700x ICP-MS and the analytical method

Mass Profiler Professional (MPP)

Mass Profiler Professional (MPP) is a commercially available chemometrics software tool for multivariate analysis and visualization of the result. Chemometrics is commonly used to extract meaningful information from complex analytical MS data in life sciences field. It provides multiple means of statistical analysis which are also useful for geographic origin analysis using elemental composition information in food samples.

Results and Discussion 1 – Determined Element Composition in Rice Samples

Figure 3 summarizes determined concentration of 75 elements in 14 rice samples having different countries of origin. It can be seen that some elements fluctuate widely in concentration between samples. However it is not simple to extract any rule to distinguish the geographical origin.
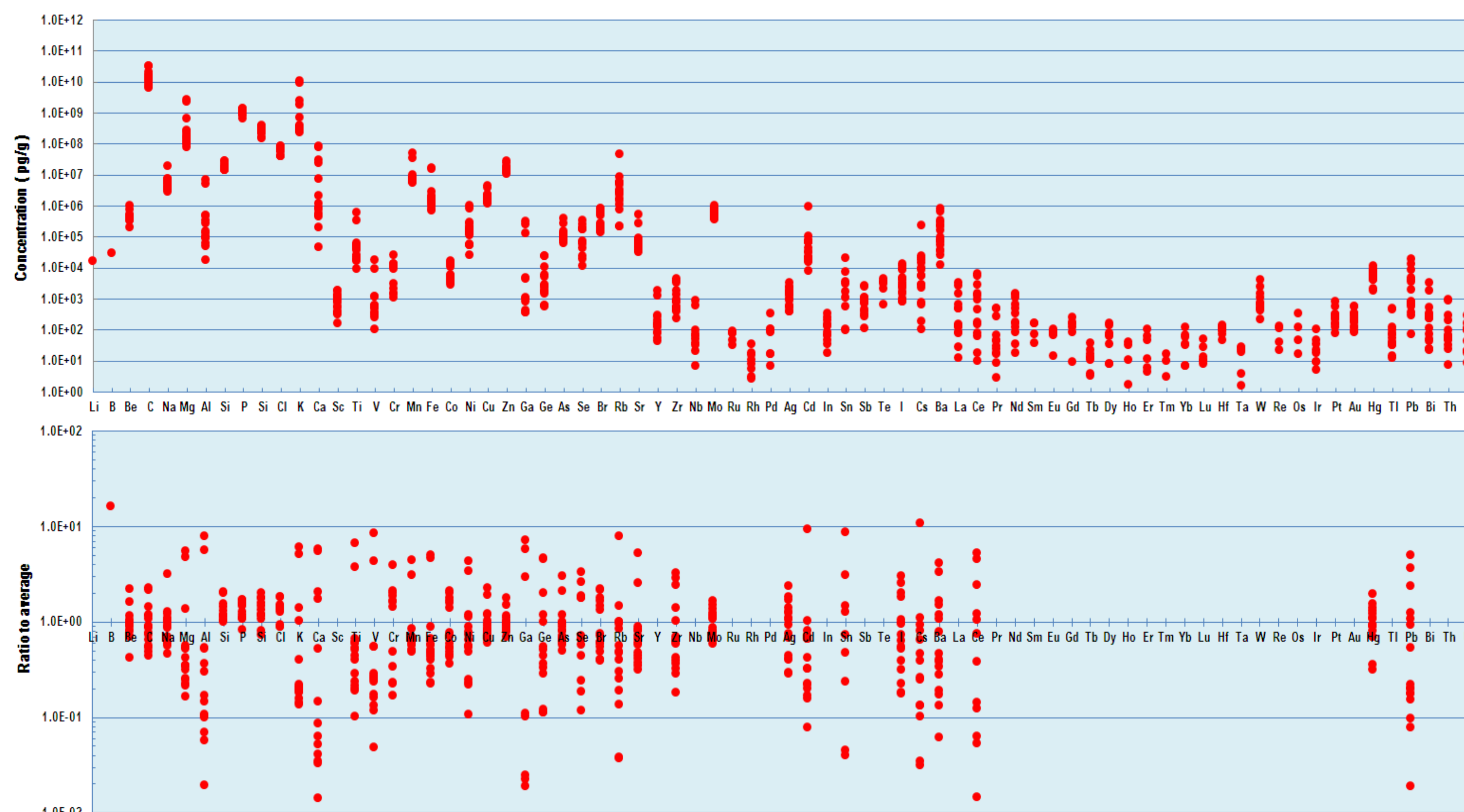

Figure 3 : The upper plot shows the measured concentration of 75 elements in 14 rice samples in pg/g . The lower plot depicts the same data ratioed to the average concentration over the 14 samples. (data lower than 1ng/g on average are removed from the lower graph for accuracy)

Result and Discussion 2 - Data mining by using MPP

The determined concentration of 75 elements in 14 samples by ICP-MS was submitted to MPP. First , Principle Component Analysis (PCA) was applied . Before PCA analysis, the data was filtered using a function of MPP to remove noise and extract as reliable information as possible using PCA. Two data filtering functions were used: The first is removing concentration data lower than 1000 pg/g , and the second extracts elements which show significant difference in concentration between Japan rice samples and others using student's t- test. As a result of the filtering steps, the number of elements which were used in PCA was reduced to nine. Those are Al, Ba, Ce, Co, Cs, Cr, La, Pb and Rb. Significant variation between samples is shown in Figure 3 for those elements. Figure 4 is the result of PCA analysis using those nine elements. In the plot we could say that country A, B, C and Japan were clearly separated by two principle components. Figure 5 shows the load of elements to two components. Cs, Al and La are elements which demonstrate a large load to the first principle component.
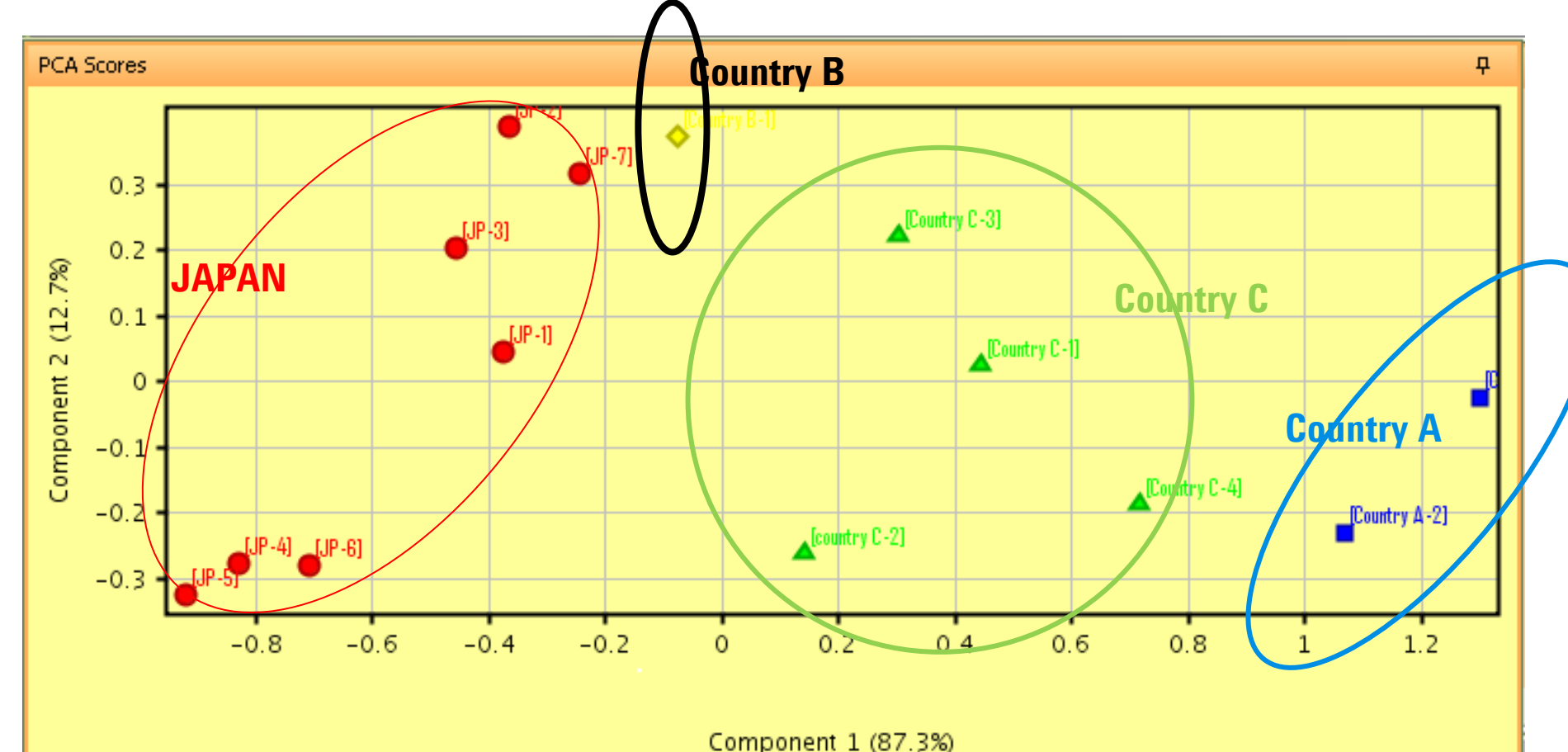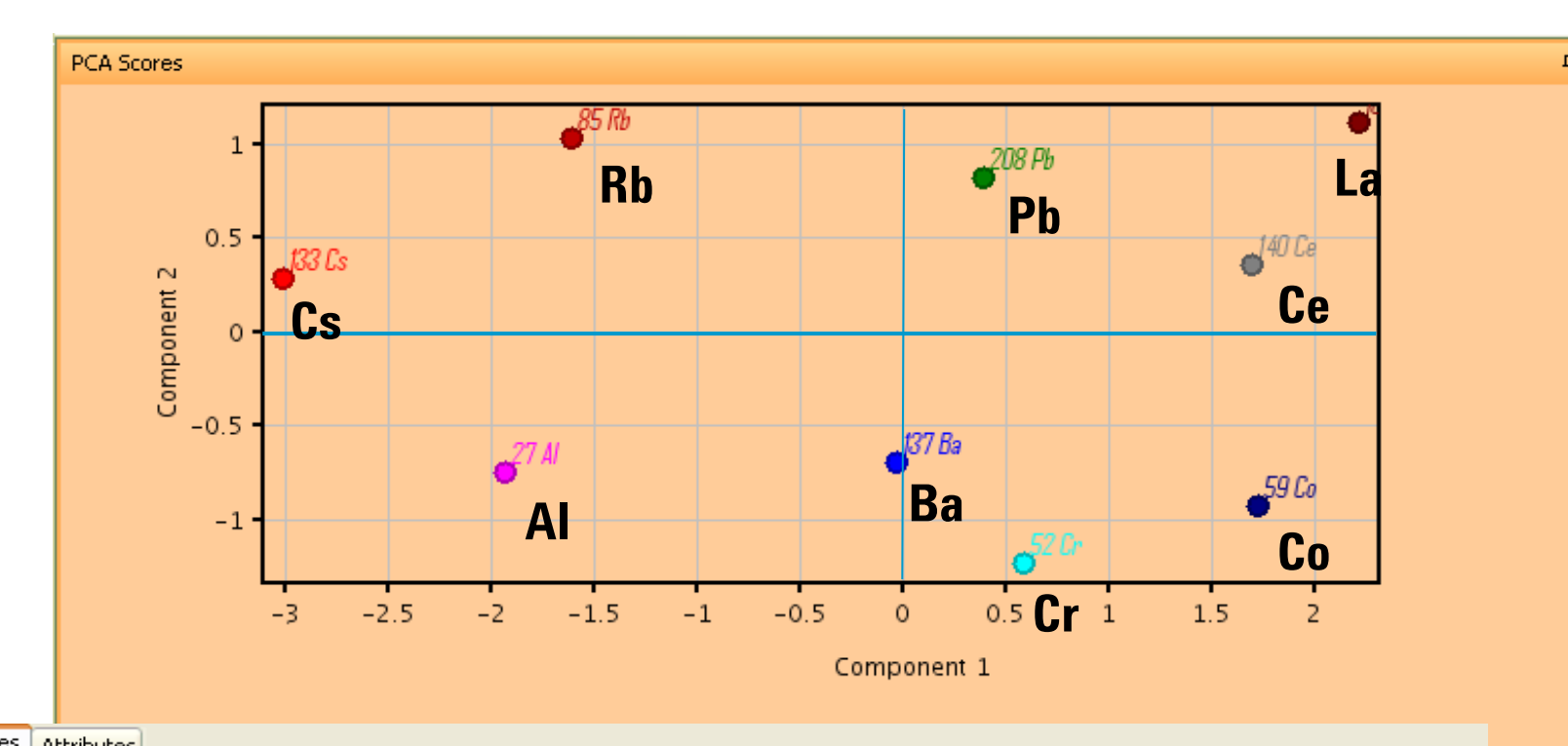

Figure 4: Result of PCA analysis – PCA plot. The four countries of origin are clearly separated.

Figure 5: Result of PCA analysis – load of each component

Another function of MPP is cluster analysis. We applied a "hierarchical" method to the same data set. This is the simplest clustering approach since it doesn't need information for the grouping. Figure 6 shows the results. The Country C-4 sample was grouped closer to the Country A-1 & A-2 samples than to the other Country-C sample though, overall the cluster analysis gave good grouping results.
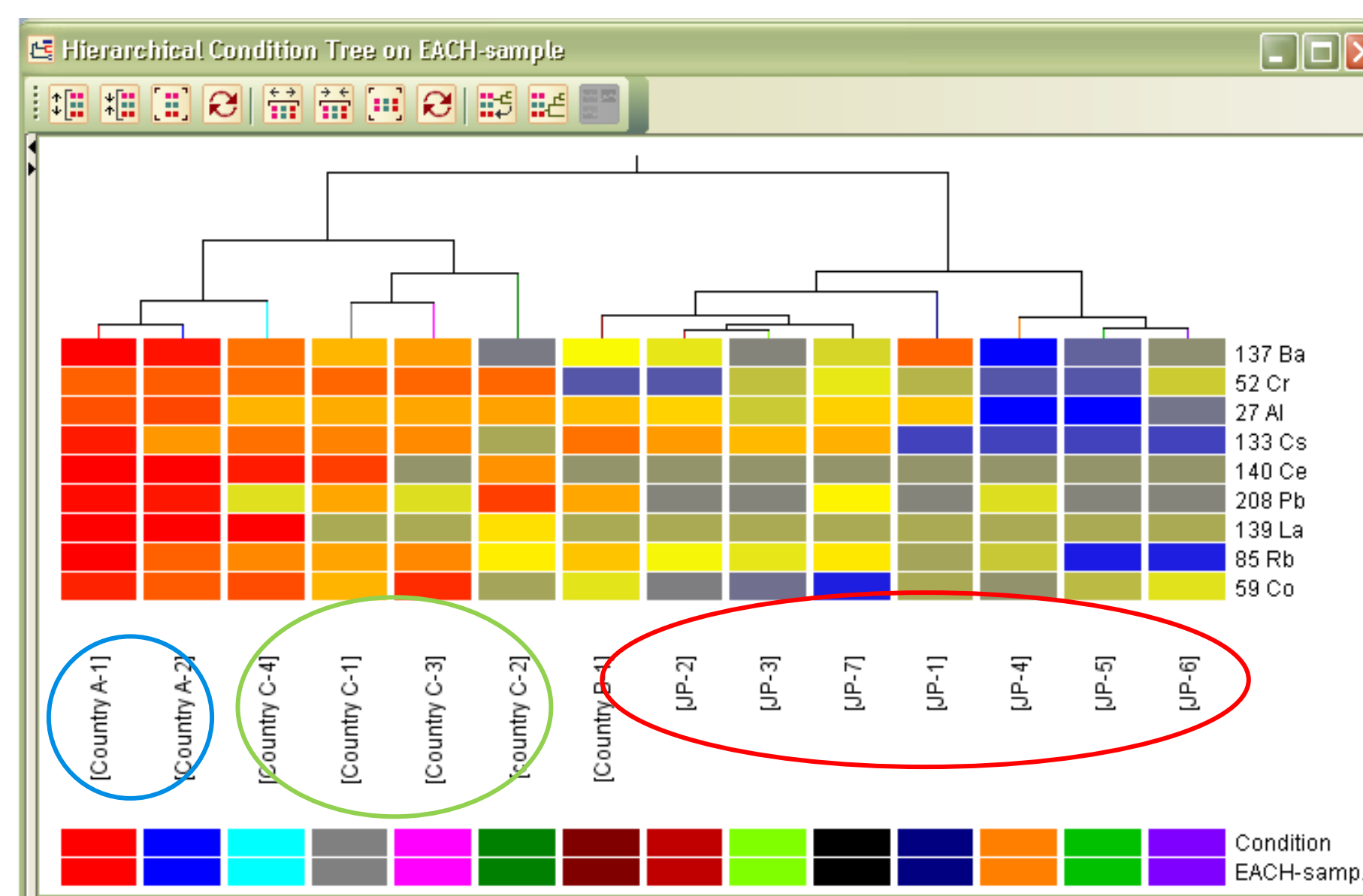

Figure 6: Results of cluster analysis

Conclusions & Future Plans

This preliminary study demonstrated the feasibility of using elemental composition data for geographic origin analysis of rice. 14 rice samples were clearly separated according to the country origin using the determined concentration of nine elements by use of a commercially available data mining SW tool.

Our future plans include:
1: Increase number of samples. More than 10 samples for each country of origin is desired to validate the method.
2: Rice samples of same species cultured in different country should be tested . It is really interesting to confirm if they are separated according to the country they are cultured.
3: To establish a chemometric model to distinguish country origin of rice. .