CHAPTER 2

EXPERIMENTS

2.1 Apparatus and components

1 Personal computer:

1.0 GHz Pentium®; Intel Corporation, Santa Clara, CA

512 MB RAM; Samsung Semiconductor, San Joes, CA

40 GB hard disk; Seagate Technology, Scotts Valley, CA

2.2 Software

1 MATLAB 6.5; Math Works, Natick, MA

2 Origin 6.0; Microcal Software, Northampton, MA

3 Microsoft Excel 2002; Microsoft Corporation, Redmond, WA

2.3 Data Manipulation

In this study, all chemometric procedures were created on MATLAB environment. The data manipulation before the analysis used is schematically represented in Figure 2.1.

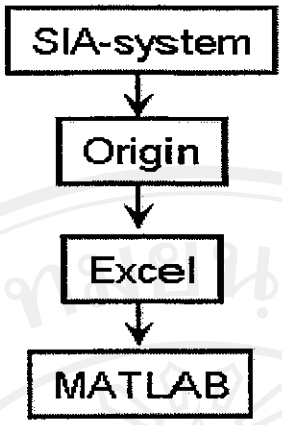

Figure 2.1 The data manipulation diagram used for the chemometric procedures.

The result data from the SI-system in .dat format were converted into .xls format by origin and excel programs, respectively. Then the data are organized into a matrix by the MATLAB function before analyzing by the chemometric procedures.

2.4 The chemometric procedures employed in these studies

2.4.1 Procedure for Principal Component Analysis, PCA

A procedure for PCA was studied. The schematic diagram of PCA procedure is summarized in Figure 2.2. The procedure is involved the use of some matrix operations and statistical techniques such as standard deviation, covariance, eigenvector and eigenvalue that are discussed in Appendix A and B. First, the data in row-wise matrix system are centered to prevent data points that are far away from

the origin of the data. Then, the covariance of each variable is calculated and set into a matrix in order to calculate the eigenvalues and the eigenvectors. Next, the significant eigenvectors are selected in order to generate a new set of new variations in the final step.

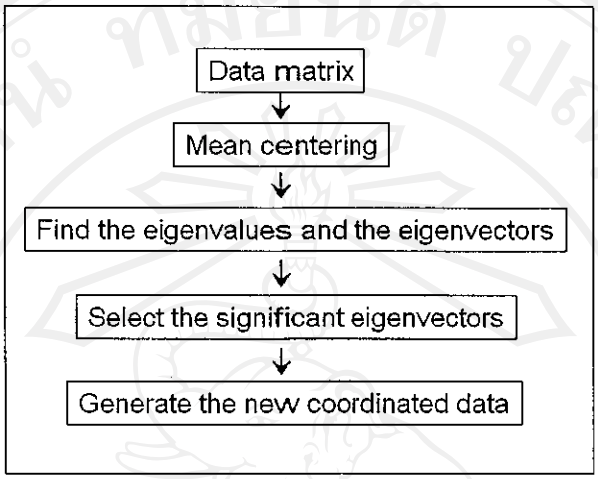

Figure 2.2 The steps of a PCA procedure.

Throughout the studied procedure, the data have been transformed into the new set of data that depend on the variation that are the contribution of all of the collected data, and by this process, it can enable the data to express them in the term of the patterns between them. The usefulness is that the data can be classified out of the combination of the variation that is the contribution from all of the data themselves by using each of those of the data that are generated.

2.4.2 Procedure for Principal Component Regression, PCR

PCR is the chemometric technique that performs a least-square regression of the principal components. The procedure is involved the use of PCA procedure for projecting the data onto the basis vector or components before the processes of calibrating and predicting. First, the independent data of the training set are transformed into the independent components. Then, the relationship between the independent components and the dependent data are calculated in order to calibrate the models. In the predicting step, the sample spectra are also transformed into the sample components then, applied to the PCR models in order to obtain the predicted concentration.

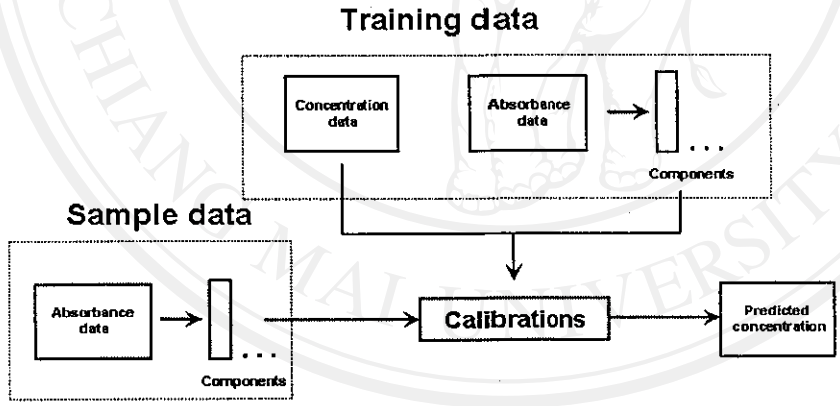

Figure 2.3 The steps of the PCR procedure.

The schematic diagram of PCR procedure is shown in Figure 2.3. The independent and dependent variables studied are the absorbance measured from samples and the concentration data of the same samples, respectively. Those of the variables are organized into separated matrices. The spectrum data are assembled into

a data matrix called absorbance matrix, and the concentration data of each analyte are also assembled into a matrix called concentration matrix. In the PCR procedure, the absorbance data of the training set are transformed into the training components. Then, the transformed absorbance components of the training data and the concentration matrix of the training set are used for performing the models. In the prediction step, the transformed absorbance matrix of the sample set is applied with the models for predicting the predicted concentration.

2.4.3 Procedure for Partial Least-Square Regression, PLS

PLS is the technique that increases the performance of analysis by establishing the relationship between the dependent data and the independent data. Like PCR, PLS involved the spectral decomposition by using iterative techniques. The difference between PCR and PLS is that the PCR decomposition is based on only the variation of the independent data, spectral data in these studies, but, in PLS, the independent and the dependent data are decomposed and weighted to each other. PLS can enhance the performance of analysis because in the decomposition steps, the data are given the information about each other.

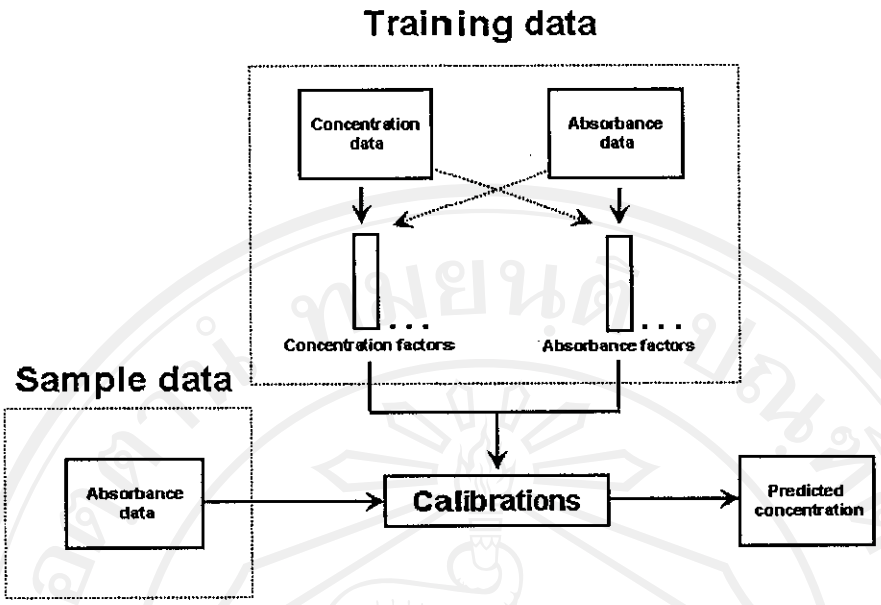

Figure 2.4 The steps of the PLS procedure.

The schematic diagram of PLS are shown in Figure 2.4. In the calibration steps, both of the absorbance data and the concentration data are decomposition into factors. The components are rotated in order to increase the inner relation between the data blocks. Then, the relationship between the factors is used for calibrating the PLS model. In the prediction steps, the unknown spectral data are applied to the model in order to obtain the concentration results.