Determination of Individual Spectra of Sm, Eu, Gd, Tb and Dy from the UV-Vis Spectrum of Mixture Solution

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Abstract

Rare earth elements (REEs) such as Sm, Eu, Gd, Tb and Dy are potentially used as raw materials in the production of contrast agent for diagnostics using Magnetic Resonance Imaging (MRI). The combination of spectrophotometry with multivariate analysis can be an alternative method for the simultaneous determination of REE's concentration without the need of separation. The UV-Vis Spectrophotometry method was selected due to the lower cost as compared to the inductively coupled plasma (ICP).

The study aimed to determine the individual spectra of Sm, Eu, Gd, Tb and Dy from the UV-Vis spectrum of its mixture solution using the Multivariate Curve Resolution – Alternating Least Square (MCR-ALS) method. The processing of measurement data was initiated by the testing of outlier data, which followed by the testing of data normalization to determine its distribution. The result showed that the selected method was able to decompose the overlapping spectrum of mixed solution of Sm, Eu, Gd, Tb and Dy to their individual spectra using UV-Vis Spectrophotometer, with a lack-of-fit value of 0.31%.

Keywords: Rare earth elements, MCR-ALS, UV-Vis Spectrophotometer.

Introduction

Over the last few years, the necessity for rare earth elements (REEs) has increased in line with the development of advance technology industry. REEs are widely found in monazite, xenotime and apatite minerals with relatively small concentrations. Therefore, it is necessary to develop a method for determining REEs, especially the elements of Sm, Eu, Gd, Tb and Dy simultaneously without separation. The REEs, Gd and Dy, are used as the base material for preparation of positive and negative contrast agent for cancer diagnosis using MRI. Sm is used in the production of radiopharmaca ^{153}Sm-EDTMP for palliative therapy in bone cancer. Eu and Tb are raw materials on the production of paracest agent for diagnosis using MRI.

The UV-Visible spectrophotometry can be used for the determination of mixed concentration of REE in a sample simultaneously without separation, using multivariate analysis in data processing[1,2]. Multivariate Curve Resolution-Alternating Least Square (MCR-ALS) is a bi-linear method of mixed spectrum observed as a linear combination of the spectrum of pure compounds. Moreover, MCR-ALS is a method for solving mixed analysis problem, such as addressing analytical problems at the peaks overlap on HPLC-DAD chromatograms. The objective of this study was to determine the individual spectra of Sm, Eu, Gd, Tb and Dy from the UV-Vis spectrum of its mixture solution using the Multivariate Curve Resolution – Alternating Least Square (MCR-ALS) method[3-6].

Suppose collection D in the HPLC-DAD chromatograms, the row represents the elution time and the column represents the spectra. Hence, each row in the matrix D contains the spectrum recorded at a given elution time and each column corresponds to a certain wavelength (Figure 1).

The bilinear additive model is expressed in terms of equation 1[3].

$$D = CS^T + E \tag{1}$$

where C is the elution profile of all components and S^T is the pure spectrum while E is a matrix expressing an error or variance unexplained by the above equation.

The success of the MCR process is evaluated from the value of the lack of fit or the variance expressed in the equation 2[4].

$$\%\mathrm{LOF} = \sqrt{\frac{\sum_{ij} e_{ij}^2}{\sum_{ij} d_{ij}^2}} \tag{2}$$

where d_{ij} is the element of the data matrix and e_{ij} is the residual.

Material and Methods

Chemical and Equipment: In the present study, nitric acid 65%, samarium oxide and gadolinium oxide were obtained from Merck whereas europium oxide, terbium oxide and dysprosium oxide were obtained from Sigma Aldrich.

Glassware used were commonly used in chemical lab. Digital analytical balance, Thermo Scientific™ Genesys 10S UV-Vis spectrophotometer and Matlab 2010a software as well as XLSTAT 2016 were used.

Preparation and analysis of training sets: The training set was made with a number of 28 variations concentrations of samples. The concentration of training set corresponds to the concentration in table 1 and the list of training set samples in table 2.

The absorbance of each sample was measured using UV-Vis Spectrophotometer at a wavelength range of 200-800 nm with an interval of 10 nm. The resulting absorbance data processed were analyzed further using XLSTAT 2016 software to evaluate outlier data by Grubbs Test method. Decomposition of the overlapping spectrum was processed using MCR-ALS from Matlabs 2010a software and using MCR-ALS GUI 2.0 toolbox obtained from www.mcrals.info.

Results and Discussion

Absorbance data analysis of training set using multivariate analysis: Absorbance data was made by matrix m × n where m is the number of samples and n is the wavelength used in the measurement. Furthermore, preprocessing data was conducted prior to data outlier analysis. The outlier data is presented in figure 2. Our Grubbs test method showed that the absorbance from samples 24 to 28 were different compared to others (1-23). Decision-making was then constructed based on the z-score value, if the z-score is smaller than 0.05, then the data is declared outlier and must be removed from the data matrix to be analyzed further.

Analysis of the REEs spectra in the mixture into pure spectrum using the MCR-ALS method: In the present study, the preprocessing result data was then analyzed by the MCR-ALS method to determine the spectrum of the main component from a data matrix. The advantage of the MCR-ALS method is to present the pure spectrum of the absorbance response of overlapping analytical components.

Figure 3 shows spectra of each individual pure REE measured at wavelength range of 200 – 800 nm while figure 4 shows the spectrum of the absorbance measurements of the REE mixture that produces overlapping spectra resulting from each REE having almost similar properties.

Selection of main component was conducted using SVD (Singular Value Decomposition) by evaluating its Eigen value with allowed noise of 10%. Figure 5 shows pure variable detection method.

The result of calculation by MCR-ALS method showed the value of lack of fit of 0.31% indicating the mismatch of the resulting spectrum with the mixed spectrum (figure 6).

Figure 7 shows spectrum of each individual REE after the mixed spectrum being processed using MCR-ALS method. The spectrum of Sm, Eu, Gd, Tb dan Dy was similar to the spectra of each individual REE (figure 3).

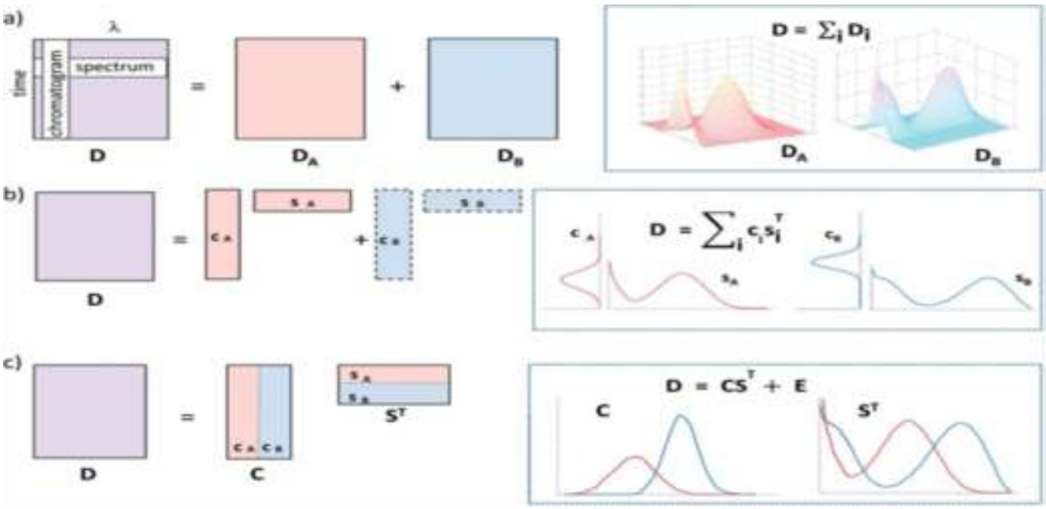


Figure 1: The result of decomposition of retention time and spectrum on HPLC-DAD using MCR-ALS

Table 1
Concentration of Training Set

Concentration (mg/L)				
Sm	**Eu**	**Gd**	**Tb**	**Dy**
259.6	70.4	155.6	53.3	351.6
389.4	102.4	233.4	65.1	450.0
475.9	134.4	311.2	76.9	562.5
605.7	160.0	389.1	100.6	675.0
692.2	192.0	466.9	122.4	759.4
822.0	198.4	544.7	124.3	871.9

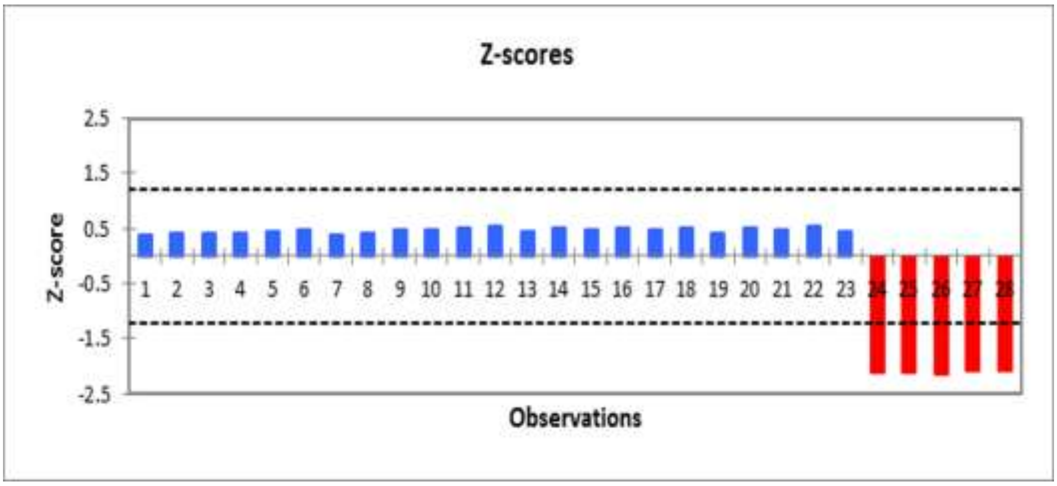


Figure 2: The outlier that presents in the samples

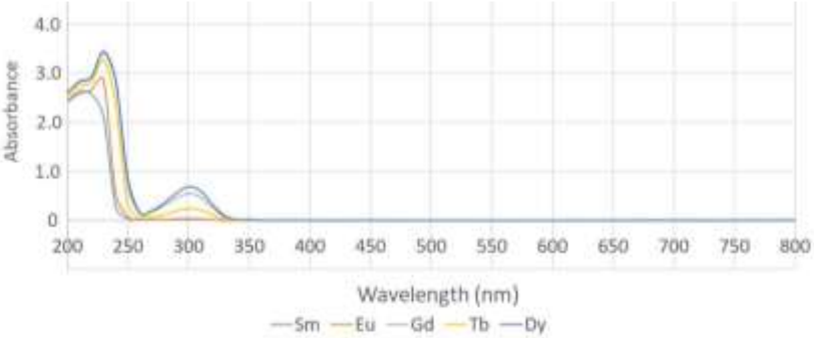


Figure 3: Spectrum of pure individual REE

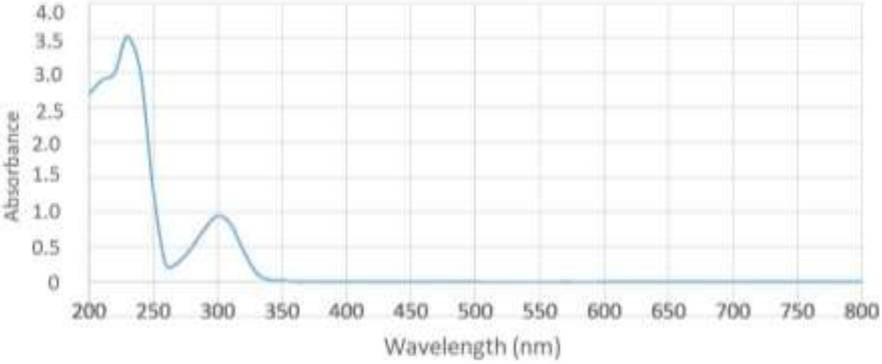
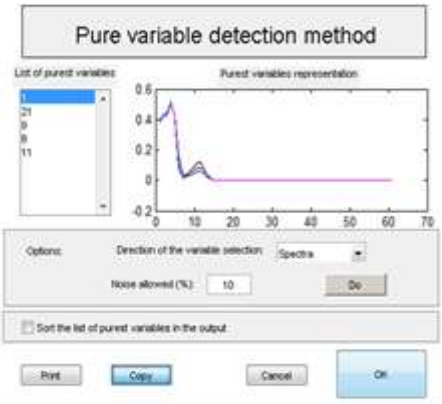
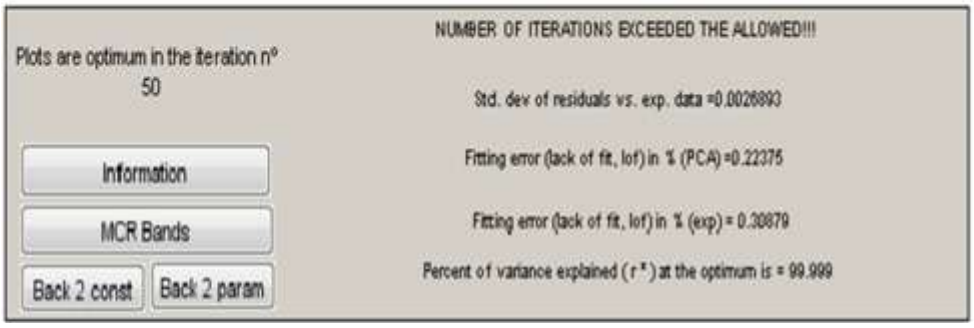


Figure 4: Absorbance of REE mixture at wavelength 200-800 nm



Options:
Direction of the variable selection: Spectra
Noise allowed (%): 10
☐ Sort the list of purest variables in the output

Figure 5: Method of detection of pure variables



NUMBER OF ITERATIONS EXCEEDED THE ALLOWED!!!

Plots are optimum in the iteration n°
50

Std. dev of residuals vs. exp. data =0.0026893

Fitting error (lack of fit, lof) in % (PCA) =0.22375

Fitting error (lack of fit, lof) in % (exp) = 0.30879

Percent of variance explained (r²) at the optimum is = 99.999

Figure 6: Result of lack of fit by MCR-ALS method

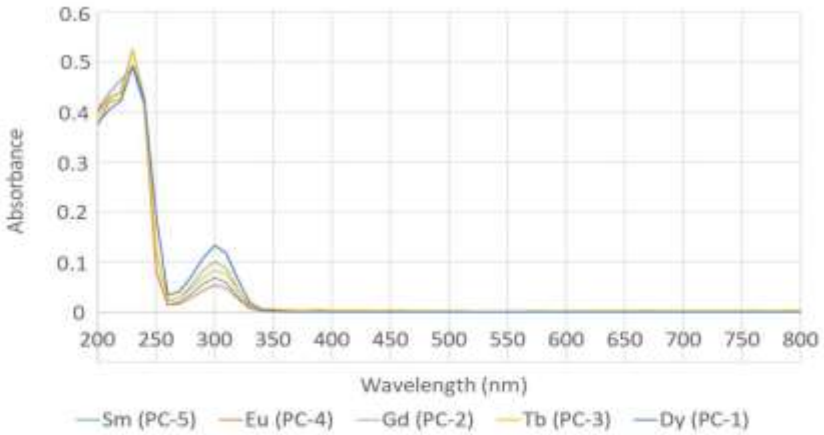


Figure 7: Spectrum of each individual REE after the mixed spectrum being processed using MCR-ALS method

Table 2
The list of samples as training set with variation of concentration

Training set											
Concentration (mg/L)											
No.	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**No.**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**
1	259.6	70.4	155.6	124.3	351.6	15	822	134.4	311.2	100.6	562.5
2	389.4	70.4	233.4	112.4	450	16	605.7	160	389.1	76.9	675
3	475.9	70.4	155.6	100.6	562.5	17	692.2	160	311.2	65.1	759.4
4	259.6	70.4	233.4	76.9	675	18	822	160	389.1	53.3	871.9
5	389.4	70.4	155.6	65.1	759.4	19	259.6	160	311.2	53.3	351.6
6	475.9	102.4	233.4	53.3	371.9	20	259.6	192	544.7	100.6	675
7	259.6	102.4	155.6	53.3	351.6	21	389.4	192	466.9	112.4	759.4
8	389.4	102.4	233.4	65.1	450	22	475.9	192	544.7	124.3	871.9
9	4759	102.4	155.6	76.9	562.5	23	605.7	192	466.9	124.3	351.6
10	605.7	102.4	233.4	100.6	675	24	692.2	198.4	544.7	112.4	450
11	692.2	134.4	311.2	112.4	759.4	25	822	191.4	466.9	100.6	562.5
12	822	134.4	389.1	124.3	871.9	26	605.7	198.4	544.7	76.9	675
13	605.7	134.4	311.2	124.3	351.6	27	692.2	198.4	466.9	65.1	759.4
14	692	134.4	389.1	112.4	450	28	822	198.4	544.7	53.3	871.9

Conclusion

In the present study, the mixed spectra of REE (Sm, Eu, Gd, Tb and Dy) can be decomposed into individual spectra by MCR-ALS method with a value of lack of fit of 0.31%.

Acknowledgement

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References

1. Belleza O.J.V. and Villaraza A.J.L., Ion charge density governs selectivity in the formation of metal–Xylenol Orange (M–XO) complexes, *Inorganic Chemistry Communications*, **47**, 87-92 **(2014)**

2. Rodionova O.Y., Tikhomirova T.I. and Pomerantsev A.L., Spectrophotometric determination of Rare Earth Elements in aqueous nitric acid solutions for process control, *Analytica Chimica Acta*, **869**, 59-67 **(2015)**

3. Jaumot J., de Juan A. and Tauler R., MCR-ALS GUI 2.0: new features and applications, *Chemometrics and Intelligent Laboratory Systems*, **140**, 1-12 **(2015)**

4. de Juan A., Jaumot J. and Tauler R., Multivariate Curve Resolution (MCR). Solving the mixture analysis problem, *Analytical Methods*, **6(14)**, 4964-4976 **(2014)**

5. Raykov T. and Marcoulides G.A., An Introduction to Applied Multivariate Analysis, Routledge, New York **(2012)**

6. Otto M., Chemometrics: Statistics and Computer Application in Analytical Chemistry, 3rd ed., John Wiley & Sons, Weinheim **(2017)**.