

## A NEW SPECTRAL UNMIXING METHOD BASED ON DERIVATIVE OF RATIO SPECTROSCOPY

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**Abstract:** The precise analysis of mineral abundance is a key content of hyperspectral technology research. In the present paper, a new spectral unmixing method based on derivative of ratio spectroscopy (DRS) was employed for visible to short-wave infrared (VIS–SWIR; 0.4–2.5  $\mu\text{m}$ ) reflectance data. The mixtures of plaster and allochite with different proportions were analyzed by DRS, Fully Constrained Least Squares (FCLS) and Non-Negative Least Squares (NNLS). A high precision was observed for DRS: for plaster, RMSE at the four bands are all less than 1.5%, and PCC are all higher than 0.999; for allochite, the precision is a bit lower, but the highest RMSE is still no more than 4.5%. Comparatively, the results for NNLS and FCLS are much worse than DRS. The result shows that this new spectral unmixing method is simple, of rigorous mathematical proof, and highly precise. It has a great potential in high-precision quantitative analysis of spectral mixture with fixed endmembers.

### 1. INTRODUCTION

Hyperspectral technology can extract geology information based on the spectral characteristics of rocks and minerals (van der Meero, 1997). Although the mineral species can be identified successfully (Clark, 2003), but the precise analysis of the abundance of mineral content is still a tough problem.

Due to resolution constraints, most pixel in the hyperspectral data contain more than one kind of land covers, and the spectral is actually a mixture of variety of ingredients (Tong, 2006). Generally, spectral mixture model can be divided into linear mixing model and nonlinear mixing model (Keshava, 2002). Johnson et.al suggested that the mixing of different mineral compositions in rocks belong to intimate mixing, and the mixing spectral was a nonlinear mixture of the reflectance spectra of endmembers (Johnson, 1983; Mustard, 1998). Mineral spectral features are mainly affected by the composition of endmembers, but the particle shape, the geometric orientation of the incident light source, observation geometry, rock structures and some other factors also matter (Hapke, 1981). The founded solution framework of mineral radiation transferring model is to convert reflectance to single scattering albedo based on multi-particle scattering model and precise description of scattering characteristics of mineral particles, and then linear spectral unmixing can be performed (Hapke, 2005; Johnson, 1992). But this procedure need to obtain the absorption coefficient, the particle size distribution, the amplitude of backward effect, phase angle and some other complex parameters, which are hard to precisely obtain. Besides, the radiation transferring model is quite complex. So the application of nonlinear unmixing of minerals is still not very practical.

So far, the linear spectral mixing model is still the mostly studied and used spectral unmixing model, which is simple, efficient, with clear physical meaning, and relatively accurate in most conditions (Ichoku, 1996). Wang et.al studied characteristics of mineral spectral mixtures through spectral simulation in laboratory, and the results showed that in shortwave bands the mixed spectrum can be approximated as a linear mixture according to the relative content of endmembers (Wang, 2007). Shortwave infrared bands collect more mineral spectral characteristics than the visible light bands, and it is of high application value to do linear spectral unmixing using shortwave infrared bands.

Derivative of ratio spectroscopy is a special spectral processing method, which is widely used in the field of chemical analysis. F. Salinas et.al put forward the concept of derivative of ratio spectroscopy, and carried on quantitative analysis of UV absorption spectra of mixed solution consisting two components using this new method (Salinas, 1990). J. J. Berzas et.al improved the derivative of ratio spectroscopy to achieve a quantitative analysis for solution of three components (Nevado, 1992). Until now, the Derivative of Ratio Spectroscopy is still a popular method of chemical drug analysis (Bahram, 2012; Vipul, 2007; Zaazaa, 2009). The ratio of spectral processing can enhance the contrast of endmembers; derivative spectra processing can reduce the correlation coefficient between the similar spectra, extract overlapping absorption features, enhance spectral contrast, and improve the precision of

target information extraction (Debba, 2006; Zhang, 2004). Derivative of ratio spectroscopy integrates the advantages of ratio spectra processing and derivative spectra processing, has rigorous mathematical proof and clear physical meaning, and the accuracy of quantitative analysis is very high; comparing with the method of solving simultaneous equations, the derivative of ratio spectroscopy can better separate the overlapping spectra of similar components, and has higher computer running efficiency (Erk, 1998). However, no one ever apply the derivative of ratio spectroscopy in reflectance spectral unmixing analysis.

This paper presents a new way to perform linear reflectance spectral unmixing based on derivative of ratio spectroscopy, and uses it to extract the relative contents of minerals in mixtures of two components. Also we compare the unmixing results with classic Fully Constrained Least Squares (FCLS) and Non-Negative Constrained Least Squares (NNLS) methods, and investigate the practical value of derivative of ratio spectroscopy.

## 2. METHODS AND EQUATION

### 2.1 Linear Spectral Mixing Model

In the linear mixture model, the reflectance of a pixel in each spectral band is expressed as a linear combination of the characteristic reflectances of its component endmembers weighted by their respective areal proportions within the pixel. Thus, the reflectance  $r(\lambda_i)$  of a pixel in the  $i$  th band is given by

$$r(\lambda_i) = \sum_{j=1}^n F_j r_j(\lambda_i) + \xi(\lambda_i) \quad (1)$$

with  $i = 1, 2, \dots, n$  and  $j = 1, 2, \dots, m$  where,  $r_j(\lambda_i)$  denotes the reflectance of the  $j$  th component of the pixel in the  $i$  th spectral band;  $F_j$  is the proportion of the  $j$  th component in the pixel;  $\xi(\lambda_i)$  is the error term in the  $i$  th spectral band;  $m$  represents the number of spectral bands while  $n$  stands for the number of components in the pixel.

Supposing all the endmembers are included, the following normalization constraint will be satisfied

$$\sum_{j=1}^m F_j = 1 \quad (2)$$

Moreover,  $F_j$  should meet the non-negative conditions

$$F_j \geq 0 \quad (3)$$

Given the endmember spectral and the mixed spectral, we can solve the composition of endmembers.

### 2.2 Derivative of Ratio Spectroscopy (DRS)

When a pixel contains only two endmembers M and N, the Linear Spectral Mixing Model can be simplified as

$$r(\lambda) = F_M \times r_M(\lambda) + F_N \times r_N(\lambda) \quad (4)$$

If equation (1) is divided by the corresponding equation for the spectrum of N, the following equation can be written:

$$\frac{r(\lambda)}{r_N(\lambda)} = F_N + \frac{F_M \times r_M(\lambda)}{r_N(\lambda)} \quad (5)$$

To obtain the ratio spectral  $\frac{r_M(\lambda)}{r_N(\lambda)}$ , the reflectance ratio at each wavelength is calculated. For determining M in

the presence of N, use the first derivative of equation (5)

$$\frac{d}{d\lambda} \left( \frac{r(\lambda)}{r_N(\lambda)} \right) = F_M \times \frac{d}{d\lambda} \left( \frac{r_M(\lambda)}{r_N(\lambda)} \right) \quad (6)$$

Equation (6) indicates that the “derivative ratio spectrum” of the mixture is dependent only on the values of  $F_M$ .

If equation (6) is divided by  $\frac{d}{d\lambda} \left( \frac{r_M(\lambda)}{r_N(\lambda)} \right)$

$$F_M = \frac{\frac{d}{d\lambda} \left( \frac{r(\lambda)}{r_N(\lambda)} \right)}{\frac{d}{d\lambda} \left( \frac{r_M(\lambda)}{r_N(\lambda)} \right)} \quad (7)$$

At a given wavelength, the fraction of M can be calculated by

$$F_{M\lambda_i} = \frac{\frac{d}{d\lambda} \left( \frac{r(\lambda_i)}{r_N(\lambda_i)} \right)}{\frac{d}{d\lambda} \left( \frac{r_M(\lambda_i)}{r_N(\lambda_i)} \right)} \quad (8)$$

N can be determined by an analogous procedure (wavelength not necessarily the same)

$$F_{N\lambda_j} = \frac{\frac{d}{d\lambda} \left( \frac{r(\lambda_j)}{r_M(\lambda_j)} \right)}{\frac{d}{d\lambda} \left( \frac{r_N(\lambda_j)}{r_M(\lambda_j)} \right)} \quad (9)$$

## Data Analysis Techniques

### 1. Scheme of Mineral Mixture

In the experiment, plaster and allochite samples were crushed into powder, and a set of mixtures of different proportions were made under accurate measurement of electronic balance and graduated cylinder. The mineral mixture scheme is shown in Table 1.

**Table 1 Mineral mixture abundance**

Mixture No.	Plaster	Allochite
Mixture 1	5%	95%
Mixture 2	10%	90%
Mixture 3	30%	70%
Mixture 4	50%	50%
Mixture 5	70%	30%
Mixture 6	90%	10%
Mixture 7	95%	5%

A SVC HR-1024 Hand-held Spectrometer covering the UV, Visible, and NIR wavelengths from 350 nm to 2500 nm was used to measure in-situ reflectance with a 25° field of view and 1m above the species. Spectral reflectance was calculated as the ratio of measured radiance to the radiance from a white standard reference panel. The spectral

reflectance data were obtained between 9.00pm and 12.00pm, in dark conditions. In order to facilitate the subsequent derivation, the original reflectance spectra were resampled to 1nm intervals.

## 2. Abundance Calculation Procedure

For determining plaster, the stored spectra of the mixtures were divided by the spectra of allochite. The first derivatives were calculated with  $\Delta\lambda = 4\text{nm}$ . The concentration of plaster was proportional to the amplitude of the derivative of ratio spectra. For allochite, the corresponding procedure was used.

## 3. Band Choice

Mixture 1, 4 and 7 were chosen to set up the calibration set samples, as these nearly covered the whole abundance range. Based on the spectral of these mixtures and pure endmembers, the abundance will be calculated at all bands through the procedure of 3.2. Then the Pearson Correlation Coefficient (PCC) and the Root Mean Square Error (RMSE) would be calculated, and the bands with highest PCC and lowest RMSE would be chosen to build a model to calculate the abundance of the other mixtures.

## 4. Spectral Mixture Analysis

The spectral mixture analysis presented is a factor analysis method, based on a two-stage procedure: a calibration step, in which a mathematical model is built by using component concentrations and spectral data from a set of references, followed by a prediction step in which the model is used to calculate the concentrations of unknown samples from their spectrums. The first step was introduced in 3.3, in which the best bands to calculate the abundance of plaster and allochite were chosen. In the second step, the abundance of the two endmembers in Mixture 2, 3, 5 and 6 would be calculated. The evaluating metrics will be the same as in 2.3.

# 3. RESULTS & DISCUSSION

Figure 1: shows the reflectance spectras. Plaster is a typical sulfate mineral with the formula of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The reflectance spectrum of plaster has three consecutive water absorption features at 1449nm, 1490nm and 1535nm, a diagnostic sulfate absorption feature at 1750nm, and a strong water absorption feature at 1948nm. Allochite is a kind of calcium silicate with the formular of  $\text{Ca}_2\text{Fe}_3 + \text{Al}_2\text{O} \cdot \text{OH} \cdot \text{Si}_2\text{O}_7 \cdot \text{SiO}_4$ . The spectrum of allochite has an absorption feature of Fe-OH at 2256nm, and a diagnostic strong absorption feature between 2335nm and 2342nm. The spectrums of mixtures are between plaster's and allochite's, and the spectral feature are a combination of both of them.

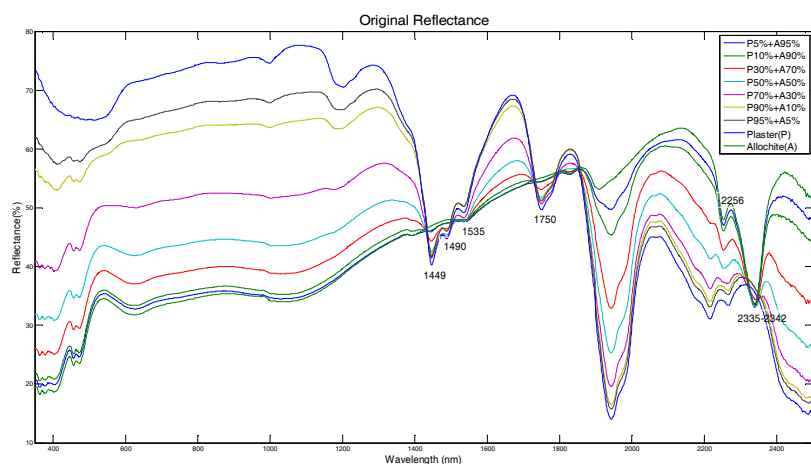
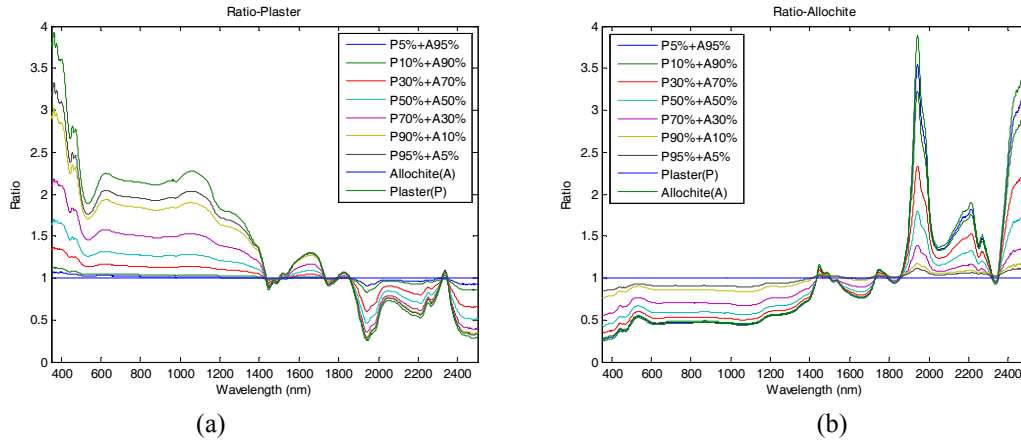


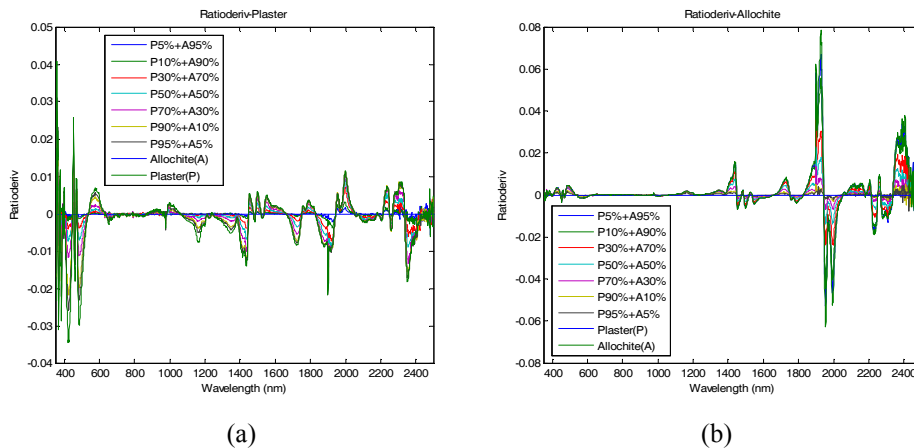
Figure 1: Original reflectance of mixtures and endmembers

Figure 2: shows the ratio spectra of mixtures and endmembers (a: spectrums divided by the spectrum of allochite; b: spectrums divided by the spectrum of plaster). As shown in the figure, plaster's strong spectral features are prominent in Fig.2a, while in Fig.2b allochite's are prominent. In summary, spectral ratio procedure can suppress the divisor's spectral feature as background and highlight the other component's features.



**Figure 2:** Ratio spectra of mixtures and endmembers  
 (a:Ratio spectra of Plaster(divided by reflectance of Allochite);  
 b:Ratio spectra of Allochite(divided by reflectance of Plaster))

Figure 3: shows the first derivatives of the ratio spectra. The first-derivative amplitudes at most wavelengths are proportional to the abundance of plaster or allochite (a: proportional to plaster; b: proportional to allochite). As can be seen from formula (6), derivative of ratio spectra is linear correlated with one component's abundance, independent of the other's. In other words, through the procedure of the first derivative of ratio spectra, we can eliminate the influence of one kind of component, while making the spectral values linear correlated with the other component. Any band in the derivative of ratio spectra can be used to solve the abundance of one of the component with equation (8) or (9). In order to achieve more accurate result, the abundance of plaster and allochite would be solved separately with different bands.



**Figure.3:** Ratio-derivative spectra of mixtures of Plaster and Allochite  
 (a:Ratio-derivative spectra for Plaster(divided by reflectance of Allochite);  
 b:Ratio-derivative spectra for Allochite(divided by reflectance of Plaster))

Table 2 and Table 3 show the result of band choice (detailed description in 3.3). The listed bands have the highest PCC and the lowest RMSE, and the rank of PCC and RMSE are consistent with each other for these four bands. For plaster, the best bands are around 1738~1740 nm and 1437nm. While for allochite, the top four bands are around 1512~1513nm and 1857~1858nm.

**Table 2: Band Choice Result of Plaster**

Samples	Calculated Abundance of Selected Bands				Actual Abundance
	Rank1:1740nm	Rank 2:1739nm	Rank 3:1738nm	Rank 4:1437nm	
Allochite	0.00000	0.00000	0.00000	0.00000	0%
Mixture1	0.05159	0.04564	0.04649	0.04742	5%
Mixture4	0.50340	0.50076	0.49772	0.49645	50%
Mixture7	0.94967	0.95223	0.95297	0.94056	95%
Plaster	1.00000	1.00000	1.00000	1.00000	100%
RMSE	0.00168	0.00222	0.00230	0.00465	
PCC	1.00000	0.99999	0.99999	0.99997	

**Table 3: Band Choice Result of Allochite**

Samples	Calculated Abundance of Selected Bands				Actual Abundance
	Rank1:1513nm	Rank 2:1512nm	Rank 3:1857nm	Rank 4:1858nm	
Allochite	1.00000	1.00000	1.00000	1.00000	100%
Mixture1	0.95569	0.95211	0.94634	0.95880	95%
Mixture4	0.49372	0.50470	0.49860	0.50082	50%
Mixture7	0.04655	0.06101	0.06359	0.06802	5%
Plaster	0.00000	0.00000	0.00000	0.00000	0%
RMSE	0.00409	0.00543	0.00632	0.00898	
PCC	0.99997	0.99996	0.99993	0.99987	

Assuming the compositions in Mixture 2, 3, 5, and 6 are unknown, we use the selected bands to solve the abundance of plaster and allochite in these four mixtures. The results are summarized in Table 4 and Table 5. A high precision was observed for DRS: for plaster, RMSE at the four bands are all less than 1.5%, and PCC are all higher than 0.999; for allochite, the precision is a bit lower, but the highest RMSE is still no more than 4.5%. Comparatively, the results for NNLS and FCLS are worse than DRS, and NNLS is much better than FCLS. It is noteworthy that for NNLS, the accuracy of allochite is higher than plaster, which is just opposite of DRS. The reason need to be more detailed research.

**Table 4: Spectral Unmixing Results for Plaster**

Samples	Calculated Abundance				NNLS	FCLS	Actual Abundance
	1740nm	1739nm	1738nm	1437nm			
Mixture2	0.10067	0.09855	0.09985	0.10340	0.07626	0.06730	10%
Mixture3	0.29504	0.28925	0.28432	0.29173	0.21719	0.19625	30%
Mixture5	0.72632	0.72237	0.72069	0.71699	0.55378	0.52969	70%
Mixture6	0.91153	0.90772	0.90606	0.89971	0.78388	0.77665	90%
RMSE	0.01458	0.01301	0.01333	0.00960	0.10282	0.11838	
PCC	0.99966	0.99960	0.99947	0.99963	0.99659	0.99409	

**Table 5: Spectral Unmixing Results for Allochite**

Samples	Calculated Abundance				NNLS	FCLS	Actual Abundance
	1513nm	1512nm	1857nm	1858nm			
Mixture2	0.92202	0.93304	0.90295	0.91022	0.89259	0.93270	90%
Mixture3	0.73887	0.74509	0.72006	0.72619	0.71002	0.80375	70%
Mixture5	0.22197	0.23516	0.28719	0.29238	0.36248	0.47031	30%
Mixture6	0.10414	0.11434	0.13282	0.13641	0.19097	0.22335	10%
RMSE	0.04500	0.04340	0.02033	0.02331	0.05553	0.11838	
PCC	0.99388	0.99444	0.99857	0.99863	0.99994	0.99409	

#### 4. CONCLUSIONS

We presented a new spectral unmixing method based on Derivative of Ratio Spectroscopy, and applied it to solve the concentrations of mineral powder mixtures. The new method could combine the advantages of ratio spectroscopy and derivative spectroscopy, and could solve the concentration of different components separately with only one band. A complete model building and predicting procedure has been accomplished.

According to the results, DRS can be successfully applied in spectral unmixing, which is simple in application and provides reliable analytical results. Through further study, this method can be developed to resolve more complex mixtures, and it has a great potential in mineral component analysis. Besides, DRS can be used to research on the spectral mixing mechanism through analyzing the results at different bands.

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