

定量测定混合粘土矿物的新方法 — 差示光谱— 概率分布法^①

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提要 本文在系统研究差示光谱的基本理论和傅里叶变换光谱具有最高信噪比 ($1.5 \times 10^4: 1$) 的特性的基础上, 证明: 差示光谱的吸收强度偏差小于 0.01%。为此奠定了粘土矿物定量的基础。为了简化其繁杂的计算过程, 笔者把差示光谱和概率分布计算方法巧妙地融洽在一起, 推导出可以实现全频率范围的差示光谱— 概率分布定量的最终方程: $\sum_{k=1}^M B_k^m(\bar{\nu}_i) - \sum_{k=1}^M x_k B_k^r(\bar{\nu}_i) = 0$; 和 $\mu_k = \frac{1}{M} \sum_{i=1}^M X_k(\bar{\nu}_i)$ 。根据此方程, 编写成一种新的适用于混合粘土矿物定量的应用软件。为了检验新方法效果, 笔者将它应用于人工配制的五种混合粘土矿物的定量测定。结果其相对标准偏差 $\sigma < 0.5\%$, 绝对误差为 0.01—0.05%。实验结果表明, 差示光谱— 概率分布定量法是一种适用于粘土矿物快速、准确定量的可行性的方法。

主题词 差示光谱 概率分布 粘土矿物 傅里叶变换

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QUANTITATIVE ANALYSIS METHOD OF PROBABILITY DISTRIBUTION OF FT-IR DIFFERENCE SPECTRUM FOR MIXTURE MINERALS^②

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Abstract

A simple reproducible, rapid, and high precise probability density method of difference spectrum for quantitative analysis testing of mineral mixtures is discussed. It is particularly simple to use in that requires no selection of peaks and more complicated calculation like least-squares curve-fitting¹⁻⁴, and requires only to solve mean values known and unknown spectra ratio in full frequencies range. In all samples tested, this method produces results as good as.

Theory

The difference spectrum of the monomineral is given by

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^② This paper reported in international conference of IBCFTA 1987.

$$B^U(\bar{\nu}_i) - X_i B^S(\bar{\nu}_i) = 0$$

or $B^U(\bar{\nu}_i) / B^S(\bar{\nu}_i) = X_i$ (1)

where

$\bar{\nu}_1, \bar{\nu}_2, \dots, \bar{\nu}_i, \dots, \bar{\nu}_M = \text{frequencies}$

$B^S(\bar{\nu}_i) = \text{intensity of any frequency } \bar{\nu}_i \text{ for standard spectrum}$

$B^U(\bar{\nu}_i) = \text{intensity of any frequency } \bar{\nu}_i \text{ for measured spectrum}$

Ratio values X_i must be a constant, but measuring instruments are never perfect, X_i will always differ from the true value μ_K of these variables by the errors ζ_i

$$\begin{aligned} \zeta_1 &= X_1 - \mu_K \\ \zeta_2 &= X_2 - \mu_K \\ &\dots\dots\dots \\ \zeta_M &= X_M - \mu_K \end{aligned} \quad (2)$$

if $\zeta_i < \zeta < \zeta_{i+de}$

then probability of error $P(\zeta)$ is given by

$$P(\zeta) = F(\zeta) d\zeta \quad (3)$$

The all errors will conform to Gauss's (normal) error distribution equation

$$P(\zeta) = 1 / (\sqrt{2\pi}\sigma) \exp[-\zeta^2 / 2\sigma^2] \quad (4)$$

$$F(x) = 1 / (\sqrt{2\pi}\sigma) \exp[-(x - \mu_K)^2 / 2\sigma^2] \quad (5)$$

when

$$\zeta = 0, X = \mu_K$$

then

$$F(x) = F(\mu_K) = 1 / (\sqrt{2\pi}\sigma) = \max \quad (6)$$

$$\text{or } P(\zeta) = 1 / (\sqrt{2\pi}\sigma) = \max \quad (7)$$

therefore

$$Q = \sum_{i=1}^m \zeta_i^2 = \min \quad (8)$$

If the residuals R_i defined by

$$\begin{aligned}
 R_1 &= X_1 - \mu \\
 R_2 &= X_2 - \mu \\
 &\dots\dots\dots \\
 R_M &= X_M - \mu
 \end{aligned} \tag{9}$$

where

$\mu = \text{optimum value}$

Because equation (8) is minimum,
then

$$Q' = \sum_{i=1}^m R_i^2 = \sum_{i=1}^m (X_i - \mu)^2 = \min \tag{10}$$

The differential in Eq.10

$$\frac{dQ'}{d\mu} = 2 \sum_{i=1}^m (X_i - \mu) = 0 \tag{11}$$

$$\mu = \frac{1}{M} \sum_{i=1}^m X_i = \bar{X} \tag{12}$$

when

$$X \sim N(\mu, \sigma^2)$$

the distribution of \bar{X} is given by

$$\bar{X} \sim M(\mu, \sigma^2 / m) \tag{13}$$

$$\bar{X} \sim M(\mu, \sigma_{\bar{X}}^2) \tag{14}$$

where

$$\sigma_{\bar{X}} = \sigma / \sqrt{m}$$

$\bar{X} \neq \mu$ have two factors:

- (i) The increase of data points m
- (ii) The decrease of deviation σ

How is σ for Fourier transform infrared (FT-IR) spectrometer?

We can see signal and noise ratio (SNR) of FT-IR.

The rms SNR in the interferogram thus becomes

$$SNR_f = \sqrt{3} C^{1/2} 2^{b - \log_f^2} \tag{15}$$

where

C = the number of coadded scans

b = the dynamic range in bits of the A / D converter

f = the safety margin

The rms SNR in the spectrum thus becomes

$$SNR_0 = \sqrt{3/2} [C \Delta \bar{v} / (\bar{v}_{max} - \bar{v}_{min})]^{1/2} 2^{b - \log_f^2} M^{-1} \tag{16}$$

where

$\Delta\bar{\nu}$ = the resolution

M = the ratio of the spectral power

We measured rms SNR_0 corresponding

$$\Delta T = 0.00654\%$$

to be

$$SNR_0 = 15, 000$$

It indicates σ of FT_IR is minimum

therefore

$$\bar{X} \ll \mu$$

Consequently, the difference spectra of the mixture minerals $B^m(\nu_i)$ is given by

$$\begin{aligned} \sum_{k=1}^N B_k^m(\bar{\nu}_i) - X_1 B_1^s(\bar{\nu}_i) &= \sum_{k=2}^N B_k^m(\bar{\nu}_i) \\ \sum_{k=2}^N B_k^m(\bar{\nu}_i) - X_2 B_2^s(\bar{\nu}_i) &= \sum_{k=3}^N B_k^m(\bar{\nu}_i) \\ &\dots\dots\dots \\ \sum_{k=N}^N B_k^m(\bar{\nu}_i) - X_N B_N^s(\bar{\nu}_i) &= 0 \end{aligned} \tag{17}$$

therefore

$$\sum_{k=1}^N B_k^m(\bar{\nu}_i) - \sum_{k=1}^N X_k B_k^s(\bar{\nu}_i) = 0 \tag{18}$$

because

$$\mu = \frac{1}{M} \sum_{i=1}^M X_i(\bar{\nu}_i)$$

therefore

$$\mu_k = \frac{1}{M} \sum_{i=1}^M X_k(\bar{\nu}_i) \tag{19}$$

where

$k = 1, 2, \dots, K, \dots, N$ (component number in mixtures)

According to Beer's Law, component concentration in mixtures C_k^a is given by

$$C_k^u = \mu_k C_k^s \tag{20}$$

where C_k^s = concentration of standard mineral

Practical application

Table 1 list analytical results for five mineral mixtures subjected to this calculating method and to edit program.

In indicate these relative deviation $\sigma < 0.5\%$ and these absolute errors between 0.01 and 0.05%

Table 1. the results of quantitative analysis for the mineral mixtures

mineral	measure %	known %	absolute error $r \quad \zeta\%$	relative deviation $\sigma \quad \%$
musovite	12.02	12.00	0.02	0.16
quartz	19.05	19.00	0.05	0.26
orthoclase	12.98	13.00	-0.02	0.15
chromspinel	2.01	2.00	0.01	0.50
magnetite	5.97	6.00	-0.03	0.50

It indicate these relative deviation $\sigma < 0.5\%$ and these absolute errors between 0.01 and 0.05%

Conclusions

In this paper, we clearly proved are as follows:

- (1) Measured deviation σ of FT-IR can satisfied the final equations, in particular $\bar{X} \approx \mu$
- (2) We can calculate component concentrations in mixtures which used only the arithmetic mean of ratio value of intensity of every frequencies for standard and measured minerals. Don't needs any complicated calculation.
- (3) The probability density method of difference spectrum is feasible for the quantitative analysis of mixture minerals.

References

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