The quantitative analysis of several metal elements in a solution by the confocal X-ray fluorescence thin-sample approach

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Abstract. By a comprehensive combination of confocal X-ray fluorescence and thin-sample approach used in conventional X-ray fluorescence devices, a new “confocal equivalent thin-sample method” based on confocal X-ray fluorescence setup is proposed. It is used to quantify the concentration of several metal elements in a solution. Compared with the conventional X-ray fluorescence, this method could quantify the sample directly via the thin-sample approach and required not complicated sample preparing process. In the study, a liquid solution containing Cr, Mn, Fe, Co, Cu, Zn, As, Br, and Sr was used to verify the proposed method.

1. Introduction

Recently, the confocal technology based on polycapillary X-ray optics (PXRO) has attracted the attention of researchers in different fields. The PXRO, also referred to as the Kumakhov lens, works on the total external reflection and can be used to collect the X-rays in wide energy band from a relatively large source angle [1]. According to its function, the polycapillary X-ray optics can be divided as: polycapillary focusing X-ray lenses (PFXRL) and polycapillary parallel X-ray lenses (PPXRL). The PFXRL could focus the divergent or quasi-parallel X-rays to a small output focal spot (OFS). The size of the OFS is tens of micro meters and the OFS has a gain in power density with the magnitude of the $10^3$. The PPXRL has an input focal spot (IFS). Due to this structural feature, the PPXRL could use to receive the X-rays from a finite region. When a PFXRL in the excitation channel and a PPXRL coupled with a detector in the detection channel are in a confocal configuration, the overlap of the OFS of the PFXRL and the IFS of the PPXRL, a probing volume can be formed and only the X-rays emitting from this specific volume can be detected. By successively moving sample located at the confocal position, three-dimensionally resolved information of the sample can be obtained. Therefore, confocal technology widely used in confocal X-ray fluorescence (CXRF), confocal X-ray absorption fine structure (CXAFS), confocal X-ray diffraction (CXRD), and confocal small-angle X-ray scattering (CSXS) and full-field transmission X-ray imaging technology [2-5].

So far, a few methods have been developed for the quantitative analysis by the CXRF via the PXRO. The metal elements’ concentration of the paint layers was determined by a synchrotron CXRF setup based on the independent parameter method [6]. Malzer and Kanngießer established a more detailed mathematical model to describe the confocal volume of the CXRF setup [7]. A quantification approach...
based on the Monte-Carlo simulation code was introduced by Czyzycki [8]. The above methods employed a simplified physical model and complex theoretical calculations, which inevitably increased the quantitative error.

The X-ray fluorescence (XRF) is a non-destructive method of determining the elemental composition for materials, biological and environmental specimens, food, medicine, and so on [9-13]. For thin, intermediate, and infinite thick samples, the approaches to quantification in XRF analysis are different. The main advantage of the thin-sample method is that the intensity of the characteristic X-rays is in direct proportion to the corresponding element concentration. In other words, the matrix effects can be neglected [14]. For both intermediate and infinite thick-sample methods, the matrix effects should not be neglected. Although there are many methods, which can be used to mitigate matrix effects, the latter cannot be fully eliminated [15, 16]. Therefore, errors of both intermediate and infinite thick-sample methods generally exceed that of the thin-sample method. The latter application, however, requires a more complicated sample preparation process, when determining the elemental composition by conventional XRF devices.

In order to simplify the above preparation, referring the thin-sample method used in conventional XRF, an innovative confocal equivalent thin-sample method (CETSM) based on laboratory confocal X-ray fluorescence setup, which could quantify several metal elements in solution, was applied in this study.

2. Experiment setup and theory

2.1. Confocal XRF Setup

The sketch of the CXRF is shown in Figure 1. The X-ray source used in this study is a high-power molybdenum (Mo) rotating anode X-ray generator. The spot size of the X-ray source is about 300×300 μm². It was placed at the IFS of the PFXRL with a distance of \( f_1 \) away from the input side of the PFXRL. An Nb filter was used to acquire quasi-monochromatic incident X-rays. The IFS of PPXRL overlapped with OFS of the PFXRL, and \( f_2 \) and \( f_3 \) were the output focal distance of the PFXRL and input focal distance of the PPXRL, respectively. The PFXRL, sample and PPXRL coupled with a detector were adjusted by motorized stage, respectively. The energy resolution of the detector used in the experiment was about 140 eV at 5.9 keV.

The OFS size and the gain of the PFXRL were 30.1 μm and 3400 at 17.4 keV, respectively. Figure 2 shows the IFS size and the gain of the PPXRL in different energy. In this study, a pinhole with a diameter of 500 μm was used to measure the gain in power density of the PPXRL. The IFS size of the PPXRL was measured by an X-ray source scan method [17]. The IFS size of the PPXRL decreases with the energy of incidence X-ray and the gain of the PPXRL increase inversely.

![Figure 1](image1.png)  
**Figure 1.** Scheme of the confocal X-ray fluorescence setup based on polycapillary focusing X-ray lenses and polycapillary parallel X-ray lenses.  

![Figure 2](image2.png)  
**Figure 2.** The gain in power density and input focal spot of PPXRL with energy change curve.
The profile size of the probe volume depended on the OFS size \(d_o\) of PFXRL and the IFS size \(d_i\) of PPXRL. At \(\phi = \psi = 45^\circ\), the size of the profile of the probe volume could be derived as follows:

\[
l_x = l_y = \frac{d_i + d_o}{\sqrt{2}} \tag{1}
\]

\[
l_z = \min \{d_i, d_o\} \tag{2}
\]

where \(l_x, l_y\) and \(l_z\) are the profile sizes of the probe volume along the x, y and z axes (figure 1), respectively [18]. Due to quasi-monochromatic incident X-rays, the OFS size \(d_o\) of PFXRL is 30.1 \(\mu\)m. The IFS size \(d_i\) of PPXRL depends on the energy of characteristic spectrum of the element detected in the sample. Therefore, the probe volume used for detecting different elements is varied.

2.2. Micro-PEDXRFS setup

Figure 3a shows the typical arrangement of XRF. The specimen can be seen as a thin sample with a mass per unit area, \(m\), as follows [19]:

\[
m < \frac{0.1}{\mu(E_o) cosec\phi + \mu(E_i)cosec\psi} \tag{3}
\]

where \(\mu(E_o)\) and \(\mu(E_i)\) are the total mass attenuation coefficients for the whole specimen at the energy of primary radiation \(E_o\) and the energy of characteristic X-rays of the \(i\)th element \(E_i\), respectively. \(\phi\) is the effective angle of incidence of the primary exciting beam, and \(\psi\) is the effective take-off angle of characteristic X-rays. The total mass attenuation coefficient \(\mu(E)\) for the whole specimen at the energy \(E\) is given by the mixture rule:

\[
\mu(E) = \sum_{j=1}^{n} W_j \mu_j(E) \tag{4}
\]

where \(W_j\) and \(\mu_j(E)\) are the weight fraction and the mass attenuation coefficient of the \(j\)th element present in the sample, respectively, and \(n\) is the total number of the elements in the sample.

In conventional XRF quantitative analysis, if a homogeneous sample to be analysis satisfies the equation 3, the intensity of characteristic X-rays, \(I_i\), of the \(i\)th element can be calculated as in [19]:

\[
I_i = S_i m_i \tag{5}
\]

\[
S_i = \frac{G}{\sin \theta} I_i(E_o) \varepsilon(E_i) \tau_i(E_o) \omega_i p_i \left( 1 \begin{pmatrix} 1 \\ j_i \end{pmatrix} \right) \tag{6}
\]

\[
m_i = \mu_i m \tag{7}
\]

where \(G\) is the geometry factor, \(\theta\) is the effective incidence angle for primary radiation, \(I_o(E_o)\) is the intensity of primary photons of energy \(E_o\) (monochromatic excitation), \(\varepsilon(E_i)\) is the detector efficiency for recording the photons of energy \(E_i\), \(\tau_i(E_o)\) is photoelectric mass absorption coefficient for the \(i\)th element at the energy 0, in \(\text{cm}^2.\text{g}^{-1}\), \(\omega_i\) is the fluorescence yield of the element \(i\), \(p_i\) is the transition probability of the \(k\)th line of the element \(i\), and \(j_i\) is the absorption jump at the K-edge of photoelectric absorption in \(i\)th element.
Compared with the conventional XRF analysis (figure 3a), when the probe volume just entered into the sample surface (figure 3b), only the sample in the probe volume was analyzed. At this condition, the confocal XRF could be seen as an analysis of a thin-layer sample with a thickness roughly equal to the profile size $l_y$ of the confocal micro-volume. The thickness of the thin-layer sample restricted in the probe volume could meet the requirement of the thin-sample method, which case is called the confocal equivalent thin-sample method (CETSM).

As mentioned above, a notable feature of the thin-sample method is that the absorption and enhancement effects can be neglected. In other words, the concentration of the element in a sample is proportional to the intensity of respective characteristic X-rays. The sensitivity factor $S_i$ in equation (5), which is constant for a specific element in the sample, is measured experimentally as the slope of the straight line obtained by determining a group standard sample with a different concentration of element $i$. Using this method, sensitivity factor curves for different elements can be obtained.

3. Results and discussions

Putting the probe volume into the appropriate place within the sample is important for reducing the errors of quantitative analysis with the CETSM. The confocal micro-volume might be placed at the right position within the sample as following. When the surface of the analyzed sample is scanned through the probe volume, the integral and differential distributions of the XRF intensity of cuprum (Cu) $-$ $K_{\alpha}$ in the sample are obtained, as shown in figure 4. The full width at half maximum (FWHM) of the differential curve was about 52.5 μm, which agreed with the value calculated by equation (1) based on $d_{l}$ =44.5 μm for cuprum (Cu)$-K_{\alpha}$ at 8.0 keV in figure 2 and $d_{0}$ = 30.1 μm at 17.4 keV. The center C of the differential curve (figure 4) corresponds to the part of scan with the sample surface located at the center of the confocal micro-volume. Since the profile size of the probe volume is known, it can be placed in the right position.

To acquire sensitivity factors for each studied element, a series of standard solutions were prepared. E.g., for Cr, the standard curve of the chromium (Cr) $-$ $K_{\alpha}$ fluorescence, which is the intensity corresponding to a series concentration of chrome chloride (CrCl3), is shown in figure 5. Then, the sensitivity factor of Cr could be acquired as the slope of the fitting straight line. With the same method, the sensitivity factors of other elements for the CETSM also could be obtained. Figure 6 shows sensitivity factors for Co, Cu, Zn, As, Br, and Sr, which were measured with the whole probe volume being immersed into the sample surface. As for Cr, Mn, and Fe, their sensitivity factors were measured with the confocal micro-volume partly immersed into the sample surface by 15 μm and equaled to 0.11, 0.15 and 0.19 counts/ ppm/s, respectively.
Figure 4. Integral and differential distribution of the X-ray fluorescence intensity of Cu at different depths perpendicular to the surface of sample.

Figure 5. The standard curve of the Cr Kα fluorescence.

Figure 6. Sensitivity factors for Co, Cu, Zn, As, Br, and Sr.

The sensitivity factors shown in figure 6 were obtained with the whole probe volume just immersed inside the surface of the sample. However, they correlate with the results of the sample analysis with the probe volume located at any position inside the sample with the CETSM. For example, the detected XRF intensity for the sample in the probe volume, which was placed at a depth of $t$ into the sample (figure 7) could be converted into the equivalent intensity with the probe volume just immersed inside the surface of the sample by the following equation:

$$I_{real} = \frac{I_{detected}}{e^{-(\mu_1t_1+\mu_2t_2)}}$$

(8)

where $\mu_1$ and $\mu_2$ are absorption coefficients for the sample with X-rays excited via PFXRF and XRF from the probe volume, respectively. Therefore, when the analyzed elements met the requirement of the CETSM and the total probe volume was immersed into samples, the three-dimensional data on such elements could be obtained using the CETSM.
Figure 7. The sketch of absorption correction of the sensitivity factor at a certain depth below the sample surface, where $t$ is the depth of the probe volume.

Table 1. Concentrations of elements detected by the CETSM.

| Elements | Cr   | Fe   | Cu   | As   | Sr   |
|----------|------|------|------|------|------|
| True value (ppm) | 2540 | 1850 | 1550 | 1350 | 2850 |
| Experimental value (ppm) | 2632 | 1747 | 1587 | 1299 | 2934 |
| Relative error (%) | 7.43% | 5.57% | 2.39% | 3.78% | 2.95% |

Table 2. Concentrations of elements detected by putting the probe volume at a depth of 50 μm below the sample surface.

| Elements | Cu   | As   | Sr   |
|----------|------|------|------|
| True value (ppm) | 1550 | 1350 | 2850 |
| Experimental value (ppm) | 1398 | 1456 | 3025 |
| Relative error (%) | 9.81% | 7.85% | 6.14% |

To demonstrate the CETSM effectiveness, a solution prepared with multiple ions was analyzed. The operation voltage and current of the X-ray source were 30 kV and 40 mA, respectively. The detection time was 60 s for each point. The element concentrations determined with the CETSM are listed in table 1: the whole probe volume was just immersed at the surface of sample for Cu, As, and Sr or dipped at the depth of 15 μm for Cr and Fe. Relative errors of this method in determining the concentration of ions in solution did not exceed 8%. Table 2 shows concentrations of Cu, As, and Sr in the same solution detected by putting the confocal micro-volume at a depth $t=50$ μm (figure 7) of the sample. Relative
errors were lower than 10%. Noteworthy is that, in the experiment, the liquid sample was put into a plastic bag, which non-planar surface might produce additional errors.

As shown in figure 8, various elements had different corresponding confocal micro-volumes. As mentioned above, a series of standard solutions with a single element were prepared and used to acquire the sensitivity factor of this element. However, for elements with atomic number exceeding that of Co, their sensitive factors were measured with the whole confocal micro-volume for Co just immersed into the surface in the standard solution, respectively. The reason for this was as follows. For such sensitive factors, when they were used to determine simultaneously the densities of multiple elements at any position inside the sample, the determination of $t_1$ and $t_2$ in figure 7 was the same for different elements. Therefore, such sensitive factors were convenient for determining multi-elements simultaneously.

According to equation 3, the confocal volume size had a significant influence on the application fields of the CETSM in this paper. As mentioned above, with PFXRL and PPXRL in our experiments, in order to analyze Cr, Mn, and Fe with the CETSM, the probe volume was partly immersed into the liquid sample at a depth of 15 μm, which was smaller than the profile size of the confocal micro-volume. Therefore, with PFXRL and PPXRL used here, the CETSM could only be used for analyzing the surface of a thick or thin sample with such elements as Cr, Mn, and Fe. Moreover, the fact that only some part of the confocal volume could be used by the CETSM resulted in the deviation of most of X-rays in the PFXRL. In our experiments, although the elements with a larger atomic number than that of Co could be analyzed by the CETSM with the whole probe volume used, the CETSM could only be used to determine a low concentration of heavy elements in light matrices via PFXRL and PPXRL. When the profile size of the probe volume was smaller, it was easier to meet the requirement of the thin-sample method with the CETSM when the confocal micro-volume was fully immersed into the sample. Therefore, there are more application fields for smaller probe volumes. Because the profile size of the confocal micro-volume depended on the X-ray optics foci, a confocal XRF setup with a smaller probe volume could be realized with X-ray optics with a smaller focal spot, such as Kirkpatrick-Baez mirrors, compound refractive lenses, monocapillary, and so on [20-22].

4. Conclusions
In order to improve the thin-sample method used in the conventional XRF, we proposed and tested the confocal equivalent thin-sample method (CETSM), which could use to determine the concentration of several metal elements in a light matrix. Compared with the thin-sample method used in conventional XRF, the CETSM has no need of multifarious specimen pre-treatment. Thus, CETSM has potential applications in rapid quantitative detection of several metal elements in solutions.
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