Research Article

A Simple and Selective Nanocatalytic Resonance Rayleigh Scattering Spectral Method for the Determination of Trace Re

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In the HCl medium, rhenium (VII) or Re nanoparticles exhibited strong catalytic effect on the slow Te particle reaction between Te(VI) and Sn(II) at 70°C. The product of formed Te particles shows two strong resonance Rayleigh scattering peaks at 778 nm and 540 nm. The RS intensity at 778 nm enhanced linearly with Re concentration. The enhanced RS intensity was linear Re concentration in the range of 0.01–2.0 nmol L⁻¹, with a detection limit of 0.005 nmol L⁻¹ Re. This method was applied to the analysis of Re in ore sample, and the results were in agreement with that of the spectrophotometry.

1. Introduction

Rhenium (Re) is a precious and rare metal element that exists in the lithosphere at a low content. Re is of big rigidity, anticautery, wearable ability, and good ductility that has been utilized in national defense, aviation and spaceflight, and special heating ion materials [1]. Recently, the Re-Os isotope system has been used in geochemistry, formed ore source tracer, and globe evolvement [2]. At the same time, the Re complexes were interesting to people, because they have photoisomerization and anticancer functions [3, 4]. At present, the determination of Re includes spectrophotometry, polarography, neutron activation analysis (NAA), and inductively coupled plasma mass spectrometry (ICP-MS). The spectrophotometry is simple and low cost, but its sensitivity is not high [5–7]. The Cu(II)-Te(IV) catalytic polarographic system was used to determine 0.001–0.015 μg/mL Re with high sensitivity [8], but the harmful mercury electrode was used. The NNA has high sensitivity and accuracy, but the equipment was expensive and the nuclear radiation is harmful to the human body [9]. The ICP-MS was reported to detect Re as low as 0.001–0.1 ng·mL⁻¹; its main shortage is expensive equipment [10–12]. Thus, it is necessary to a simple and low-cost, highly sensitive, and selective method for Re. Resonance Rayleigh scattering (or resonance scattering, RS) spectral method is simple, convenient, and sensitive. It has been applied in the analysis of trace inorganic ions such as Hg(II), Cd(II), Pb(II), Mo(VI), and Cr(VI) metal ions, and organic compounds [13–18]. Based on the catalytic effect of inorganic metal ions, a catalytic RSS method has been proposed for Se [19]. Nanogold has good catalysis and has been combined with immunoreaction to detect antigens [20, 21]. To date, there is no report on an RS method for the determination of trace Re. In this work, a rapid and highly sensitive and selective nanocatalytic RS method is proposed to detect Re, coupling the nanocatalytic reaction with the RS effect of Te particles.

2. Experimental

2.1. Apparatus. A model of Cary Eclipse fluorescence spectrophotometry (Varian Co., USA) was used, with a PMT voltage of 400 V, both excited slit and emission slit of 5 nm, emission filter of 1% T attenuator, and the excited wavelength λex being equal to the emission wavelength λem(Δλ = 0). A model of Nano-ZS90 nanometer and zeta potential analytical meter (Malvern Co., England), a model of TU-1901 spectrophotometry (Beijing Tongyong Instrumental Co., China), and a model of DK-8B thermostatic meter (Shanghai Jinhong Co., China) were used.
2.2. Reagents. A $1.0 \times 10^{-3}$ mol·L$^{-1}$ Re(VII) stock standard solution was prepared using NH$_4$ReO$_4$. To obtain a 0.90 mol·L$^{-1}$ SnCl$_2$, containing 3.6 mol·L$^{-1}$ HCl, a 20.3 g SnCl$_2$·2H$_2$O was dissolved in 30 mL 12 mol·L$^{-1}$ HCl solution and diluted to 100 mL. A 0.012 mol·L$^{-1}$ Na$_2$TeO$_4$ solution, containing 0.6 mol·L$^{-1}$ HCl was prepared by dissolving 0.33 g Na$_2$TeO$_4$·2H$_2$O into 5 mL HCl and then diluted to 100 mL. The $1.0 \times 10^{-4}$ mol·L$^{-1}$ Re and Te nanoparticle colloidal solutions were prepared by NaBH$_4$ reduction procedure. All reagents were of analytical grade, and the water used in experiments was doubly distilled water.

2.3. Procedure. Into a 5 mL test tube, 0.3 mL 0.012 mol·L$^{-1}$ Te(VI), 0.20 mL 0.3 mol·L$^{-1}$ tartric acid, 0.7 mL 0.90 mol·L$^{-1}$ Sn(II), and 0.36 mL 1.0 × $10^{-8}$ mol·L$^{-1}$ Re(VII) were added. Then the mixture was diluted to 3 mL with water, mixed well and heated at 70°C for 10 min. Finally, the reaction was stopped by cooling with tap water. The RS spectra and the RS intensity at 778 nm were recorded by the fluorescence spectrophotometer. The blank without factor B ($I_{778nm}$)$_b$ was also measured. The value of $\Delta I = I_{778nm} - (I_{778nm})_b$ was calculated.

3. Results and Discussion

3.1. Principle. The speed of Te particles reaction between Te(VI) and Sn(II) was very slow. When Re(VII) or Re nanoparticle existed, the Te particle reaction enhanced greatly. Results showed that the prepared Te nanoparticles also exhibited a catalytic effect on the particle reaction; this indicated that the small Te nanoparticles formed also exhibited catalytic activity on the reaction. Thus, auto-nanocatalysis exists in the nanocatalytic reaction system [22]. When catalyst Re(VII) concentration increased, the Re nanocatalyst increased, the formed Te particles increased, and the RS intensity at 778 nm enhanced linearly because the Te particles exhibited a strong RS effect at 778 nm. On these grounds, a nanocatalytic RS method can be developed for the determination of trace Re, as Figures 1 and 2 showed that there are small Te nanoparticles and big Te particles in the nanocatalytic system, with a mean size of 120 nm.

3.2. Resonance Rayleigh Scattering Spectra (RSS). Under the condition, the speed of Te particle reaction between Te(VI)-Sn(II) is very slow and its synchronous scattering signal was weak. Upon addition of a catalyst such as Re(VII) or Re nanoparticles, the particle reaction enhanced to form more Te particles that exhibited two synchronous scattering peaks at 778 nm and 540 nm. The RS spectral studies of liquid phase inorganic nanoparticles have showed that three factors such as the light source of the apparatus, absorption of a free molecule in the system, and the RS effect of particles caused synchronous scattering peaks. The light source of the apparatus has the strongest emission at 460 nm, and a scattering peak could appear at 460 nm. The Sn(II), Te(VI), and tartaric acid exhibited a very weak absorption peak at visual wavelength, so the effect of molecular absorption could be ignored. Therefore, the two peaks at 778 nm and 540 nm were caused by the RS effect of Te particles and were RS peaks. Figure 3 indicated that the peak at 778 nm was stronger than the peak at 540 nm; thus a wavelength of 778 nm was chosen for use.

3.3. Effect of Reagent Concentration. Effect of Na$_2$TeO$_4$, SnCl$_2$, HCl, and tartaric acid concentrations were considered respectively. Three acids such as HCl, HNO$_3$, and H$_2$SO$_4$ were examined as the reaction medium. Results showed that HNO$_3$ has an oxidative that reacts with SnCl$_2$, and H$_2$SO$_4$ medium gives low sensitivity. A 0.90 mol·L$^{-1}$ HCl, giving high sensitivity, was selected for the reaction that was added in the SnCl$_2$ solution to prevent its hydrolysis. Tartaric acid, containing carboxyl and hydroxy, is a good complex reagent, and it is not only a good activator for the precursor Re(VII) of the nanocatalyst but also a mask agent for eliminating
some metal ions. A 0.02 mol·L⁻¹ tartaric acid, giving good results, was chosen for use. According to the rate equation, the velocity $V = dC_{\text{Te}}/dt$, and the $I_{778\text{nm}} = kC_{\text{Te}}$. Thus, the $I_{778\text{nm}}$ is proportional to the $V$, that is, the bigger $I_{778\text{nm}}$, the bigger $V$. Figure 4 showed that the reaction rate increased with the Na₂TeO₄ concentration increasing that indicated the reaction order of Te(VI) is first. When the Na₂TeO₄ concentration was 1.2 mmol·L⁻¹, the formed Te particles are the biggest, and the Δ$I$ value attained the maximum. Thus, a concentration of 1.2 mmol·L⁻¹ Na₂TeO₄ was chosen for use. Sn(II) is a reducer in the particle reaction, the effect of Sn(II) concentration on Δ$I$ was investigated. Figure 5 showed that when the Sn(II) concentration was less than 0.24 mol·L⁻¹, the Δ$I$ value decreased and the blank value increased. To obtain high sensitivity and low blank, a 0.21 mol·L⁻¹ SnCl₂ was chosen for use.

3.4. Effect of Reaction Temperature and Reaction Time. The influence of reaction temperature (30–80°C) and reaction time on Δ$I$ were investigated, respectively. Figure 6 showed that when the temperature was less than 70°C, the Δ$I$ value increased with the increase of temperature, and the blank value was low. When the temperature was higher than 75°C, the Δ$I$ value decreased and the blank value was high. To obtain high sensitivity, a reaction temperature of 70°C was
Table 1: Analytical results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Found (µg·g⁻¹)</th>
<th>Average (µg·g⁻¹)</th>
<th>RSD (%)</th>
<th>Spectrophotometry (µg·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>215.3, 211.4, 217.4, 213.5, 214.8</td>
<td>214.5 ± 2.2</td>
<td>1.0</td>
<td>210.6</td>
</tr>
<tr>
<td>2</td>
<td>315.0, 320.8, 314.0, 316.9, 322.0</td>
<td>317.7 ± 3.4</td>
<td>1.1</td>
<td>326.0</td>
</tr>
<tr>
<td>3</td>
<td>346.2, 341.0, 357.0, 356.2, 342.6</td>
<td>348.6 ± 14.3</td>
<td>4.1</td>
<td>346.6</td>
</tr>
</tbody>
</table>

3.7. Analysis of Samples. Three molybdenum ore samples were pretreated, respectively, according to [23] to prepare the sample solution that was determined by this nanocatalytic RS method. The results were listed in Table 1 and are in agreement with those of the spectrophotometry [23]. This indicated that both method results have been good relatively.

4. Conclusion

The nanocatalytic reaction of Te(VI)-Sn(II)-Re nanoparticle was studied by resonance Rayleigh scattering spectral technique, and the analytical conditions were optimized. Thus, a simple, rapid, sensitive, and selective nanocatalytic RS method was proposed for the determination of Re in real samples with good results. These RS method results were agreement with those of the spectrophotometry.

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