Simple Detection of Mercury Ion Using Dithizone Nanoloaded Membrane

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Abstract

The simple Hg(II)-detection system was studied and developed using dithizone nanofiber loaded membrane. Dithizone is one of the most frequently used chemical substances for Hg(II) ions extraction in water. Hg(II)-dithizone complex substance \([\text{Hg(HDith)}_2]\) is stable in acidic condition and, presenting with the orange-brown color. To prepare dithizone nanoloaded membrane, dithizone solution (in acetone) was mixed in aqueous solution with vigorous stirring. After dithizone nanofiber dispersion was formed, the aqueous dithizone was filtered through the cellulose ester membrane. Adding ascorbic acid as a reducing agent during nanofiber preparation step and keeping dithizone membrane in aluminum bag with oxygen absorber under vacuum would improve the stability of dithizone against oxidation from air and/or light. The Hg(II)-detection was performed by simply filtering solution through the dithizone membrane and, then, quantitatively analyzing by the colorimetric equipment. It was found that the concentration range of Hg(II)-detection can be altered with sample volume. By this technique, the detection limit can be achieved as low as 0.057 ppb with sufficient precision and repeatability. Practically, it could be applied to Hg(II)-determination in real samples from environment such as artificial waste water, river water and sea water.

Key words : Mercury determination, Test strip, Metal ions

Introduction

The determination and monitoring of mercury ion, Hg(II), in samples from environment is very important.¹ The acceptable level of Hg(II) content in drinking water, recommended by WHO was 6 ppb.² The general analytical techniques such as AAS, ICP-AES, ICP-MS, utilized to determine the content of Hg(II) ions in ppb level, are expensive and required practicing of analytical skills. Simple and commonly available detection method for heavy metal ions is preferable. Nanoparticles are the intermediate state between molecules and bulk crystals. They provide high surface area and rapid response. Fiber membranes have sensitivity in 2 or 3 orders of magnitude higher than those obtained from thin film sensors due to their high surface area. Suzuki, et al. have developed a simple method for water analysis using membranes from dye nanoparticles. These nanoparticle membranes are useful as a dip test strip for preliminary screening of metal ions. Due to their water permeability, the metal ions can be enriched on their surface area by filtration of the sample solution. With this procedure, testing sensitivity was enhanced.

In this work, the dithizone membrane was prepared using a cellulose ester membrane coated by dithizone nanofibers. This dithizone membrane was simply applied to the selective enrichment of Hg(II) ions by the filtration of sample solution method. Then, the development of orange-brown color will take place due to the reaction between Hg(II) ions and dithizone membrane. The color intensity depends on the amount of Hg(II) ions extracted on the membrane. The effects of a sample volume and the flow rate of filtration on Hg(II)-extraction were then studied. The detection limit and repeatability were also evaluated. Moreover, the stability of dithizone membranes was improved against oxidation from air and/or light by adding ascorbic acid as a reducing agent and keeping dithizone membrane in an aluminum bag with oxygen absorber under vacuum. Finally, the presented technique was applied to determine the concentration of Hg(II) ions in the samples collected from various sites such as waste, river and sea.
Materials and Experimental Procedures

The dithizone nanofiber loaded membranes were fabricated by filtering nanofiber dispersion through a cellulose ester membrane under vacuum. The optimum condition of dithizone nanofiber formation was investigated by various growth periods. Nanofibers dispersion prepared by each condition was filtered through 0.1 μm sized polycarbonate membranes. Then, the morphology of nanofibers was investigated using SEM. Uniformity of the dithizone membranes along their length was examined using TLC scanning densitometer. The stability of dithizone membranes was examined by monitoring color brightness (L value) at appropriate intervals up to three months. To improve the stability of dithizone membranes, three kinds of acids (hydrochloric, citric and ascorbic acid) were separately added into the membranes and the results were compared during the nanofiber formation stage. The dithizone membranes were kept in aluminum bags with silica gel or oxygen absorber under vacuum. For detection process, Hg(II) ions in the sample solution was detected using filtration and colorimetric techniques Water, et al. (1995) Calibration curve was constructed by plotting the color intensities (from TLC scanning densitometer) versus the Hg(II) concentrations. The amount of 100 mL Hg(II) standard solutions at pH 2-3 were prepared at the concentration of 0, 2, 5, 10, 20, 50 and 100 ppb. They all were detected by a simple filtration and color development technique using dithizone nanofiber membranes. The filtration rate in this particular technique was 5-6 mL/min. Detection limit was determined using 3-sigma method from 10 replicates of a blank sample. The tolerance limit of typical 8 cations (Na+, K+, Ca2+, Cu(II), Fe(II), Zn(II), Pb(II) and Cd(II)) and 6 anions (chloride, bromide, sulfate, phosphate, carbonate and nitrate) on the determination of 10 ppb Hg(II) was studied. With the addition of 2.5 x 10^-4 M EDTA, detection of 10 ppb Hg(II) was not interfered by the presence of 10,000 ppm Na, 5,000 ppm K, 5,000 ppm Ca, 6.4 ppm Cu(II), 100 ppm Fe(III), 100 ppm Zn(II), 100 ppm Pb(II) and 10 ppm Cd(II) cations. Meanwhile, the detection of 10 ppb Hg(II) was also not interfered by 0.6 M Cl, 0.01 M Br, 0.1 M SO4, 0.01 M PO4, 0.001 M CO3 and 0.01 M NO3 anions. Moreover, this technique was applied to quantify the Hg (II) content in the synthetic waste water, certified reference material of river water (JSAC 0302) and the real-life samples, including sea water from Pacific Ocean. All water sources were spiked with 10 ppb of Hg(II) prior to analysis.

Results and Dissusions

The cellulose ester membrane was rarely obtained the uniform coating with dithizone nanofibers by filtering technique. Figure 1 shows the plot of color intensity obtained from dithizone membrane using TLC scanning densitometer. Microstructure of a dithizone nanofiber membrane was investigated using SEM technique. Figure 2 shows SEM images of top and cross-sectional surfaces of the dithizone nanofiber loaded membrane. The size of nanofiber was approximately 250 nm (Figure 2a) and the layer thickness of dithizone layer was less than 500 μm (Figure 2b). Long term stability of dithizone membranes was examined by monitoring the change in color and brightness (L value) of the membrane at appropriate intervals up to 90 days by keeping dithizone membranes in an aluminum bag with silica gel or oxygen absorber during aging period. The brightness of dithizone membranes with three different acids used was plot against the aging time as shown in Figure 3. It was clearly seen that, the brightness of dithizone membranes using ascorbic acid was stable up to 90 days and more stable than those obtained using hydrochloric acid and citric acid. Sample solutions of known Hg(II) concentration series exhibit a distinct color variation from light grey to light or dark orange-brown as shown in Figure 4. A sample contained high Hg(II) concentration presents darker orange-brown color developed by Hg(II)-dithizone complex. The Hg(II) calibration curve was obtained by plotting the color intensities as a function of Hg(II) concentrations (Figure 5). Various sample volumes, i.e., 20, 50 and 100 mL, were prepared to study the effect of detection performance. It was found that the concentration range of detection was affected by sample volume. At the sample volume of 100 mL, the detection limit of this technique was 0.057 ppb; meanwhile, the precision and repeatability were sufficient enough to monitoring Hg(II) in water from environment. The tolerance limit of typical 8 cations (Na+, K+, Ca2+, Cu(II), Fe(II), Zn(II), Pb(II) and Cd(II)) was studied. With the addition of 2.5 x 10^-4 M EDTA, detection of 10 ppb Hg(II) was not interfered by the presence of 10,000 ppm Na, 5,000 ppm K, 5,000 ppm Ca, 6.4 ppm Cu(II), 100 ppm Fe(III), 100 ppm Zn(II), 100 ppm Pb(II) and 10 ppm Cd(II) cations. Meanwhile, the detection of 10 ppb Hg(II) was also not interfered by 0.6 M Cl, 0.01 M Br, 0.1 M SO4, 0.01 M PO4, 0.001 M CO3 and 0.01 M NO3 anions. Moreover, this technique was applied to quantify the Hg (II) content in the synthetic waste water, certified reference material of river water (JSAC 0302) and the real-life samples, including sea water from Pacific Ocean. All water sources were spiked with 10 ppb of Hg(II) prior to analysis.
Table 1 shows the Hg(II) concentrations determined by this technique in comparison with those obtained by ICP-MS technique. It is conformed that the analysis results by dithizone membrane technique are comparable to those obtained by ICP-MS technique.

![Intensity at 500 nm](image)

**Figure 1.** Photograph of dithizone nanofiber loaded membrane with color intensity profile by linear TLC scanning across a dithizone membrane.

![SEM images](image)

**Figure 2.** SEM images of dithizone nanofibers loaded membrane; (a) Top-view, (b) Cross section.

![Brightness vs. time](image)

**Figure 3.** The plot of brightness as a function of time

![Detection of Hg(II)](image)

**Figure 4.** Detection of Hg(II) by dithizone nanofiber loaded membrane with filtration technique. (100 mL of Hg(II) solution at pH 2-3 with the filtration rate of 5-6 mL/min)

![Color intensities vs. Hg(II) concentration](image)

**Figure 4.** The plot of color intensities as a function of Hg(II) concentrations.

**Table 1.** Analytical results of real water sample for Hg(II)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hg(II) (ppb)</th>
<th>Dithizone membrane</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial River water</td>
<td>10.48 ± 0.20</td>
<td>10.23 ± 0.69</td>
<td></td>
</tr>
<tr>
<td>Artificial Waste Water</td>
<td>11.24 ± 0.08</td>
<td>10.77 ± 0.64</td>
<td></td>
</tr>
<tr>
<td>River Water (CRM: JSAC0302)</td>
<td>10.45 ± 0.17</td>
<td>10.26 ± 0.45</td>
<td></td>
</tr>
<tr>
<td>Sea water</td>
<td>11.17 ± 0.26</td>
<td></td>
<td>N.A.</td>
</tr>
</tbody>
</table>

Average value of four replicates, pH of samples was adjusted to 2-3 by glycine buffer and filtration rate was controlled at 4-5.5 mL/min. The 2.5 x 10^-4 M of EDTA was added to samples.
Conclusions

The filtration enrichment technique with dithizone nanofiber loaded membrane has been successfully developed for Hg(II) determination in water. Most of cations can be masked in the presence of EDTA and most anions did not interfere with the Hg(II) detection. The precision and repeatability of this technique are sufficient enough for monitoring Hg(II) in water and applicable to the determination of Hg(II) content in water.

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References


