Solid phase extraction and spectrophotometric determination of silver using 2-(2-quinolinyloazo)-5-dimethylaminoaniline

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A new method for the determination of silver based on the rapid reaction of silver(I) with 2-(2-quinolinyloazo)-5-dimethylaminoaniline (QADMAA) and the solid phase extraction of the coloured chelate was developed. The QADMAA reacts with silver to form a violet chelate with molar ratio 1:2 (silver to QADMAA) in the buffer solution of pH=6.5 and SDS medium. This chelate is enriched by solid phase extraction with C18 cartridge and a high enrichment factor is achieved. The molar absorptivity of the complex is 1.25×10^4 L mol^-1 cm^-1 at 585 nm, and Beer's law is obeyed in the range of 0.01-0.6 μg ml^-1. This method is applied for the determination of silver in natural water with good results.

Silver is an important element, not only for industry but also for biological systems as well. A wide variety of spectrophotometric methods for the determination of silver have been reported. Each chromatographic system has its advantages and disadvantages with respect to sensitivity, selectivity and rapidity. Some 2-quinolylazo reagents have been reported for the determination of metal ions earlier also. This kind of reagent has a higher sensitivity than pyridylazo reagents because of their larger conjugated system. However, the utilization of 2-quinolylazo reagents for the determination of silver has received little attention. To select a more sensitive and selective reagent for silver, in this note, a new chromogenic reagent, 2-(2-quinolinyloazo)-5-dimethylaminoaniline (QADMAA) was synthesized, and the colour reaction of QADMAA with silver was thoroughly studied. Based on the colour reaction of QADMAA with silver and the solid phase extraction of the coloured chelate, a highly sensitive, selective and rapid method for the determination of silver in natural water was developed.

Experimental

Synthesis of QADMAA

2-aminoquinoline (6.9 g) was dissolved in 500 ml anhydrous ethanol, to which, sodamide (2.0 g) was added. The solution was refluxed for 5 h in boiling water bath. Then isomyl nitrite (7.4 ml) was added. The mixture was refluxed for 30 min in boiling water bath. The solution was cooled and placed overnight under 0°C. Diazol salt was obtained by filtering this solution. This solution with a yield of 95%. The diazo salt was dissolved in 200 ml anhydrous ethanol, and m-dimethylaminoaniline (5.7 g) was added. The carbon dioxide was vented into the solution with stirring until the pH reached about 8.0. The ethanol was evaporated and the residue was re-crystallized with 30% ethanol. QADMAA was obtained with a yield of 38%. The structure of QADMAA (I) was verified by elemental analysis, IR, 1H NMR, and MS. Elemental analysis: C_{17}H_{17}N_5 found (calculated) C 79.82 (79.08), N 23.83 (24.04), H 6.04 (5.88). IR (KBr) (cm^-1): 3300 (νN=); 1600, 1560, 1505, 1465 (νC=N); 291 (νC-H); 1380, 1323 (νC-N); 2850 (νC-H); 1465 (δC-H); 3050, 3015 (δAr-H): 1175, 1120, 865, 780, 720 (δAr-H). 1H NMR (solvent: d_6-acetone) (δ ppm): 2.28 (s 6H, N-CH3), 3.69 (s 2H, -N-H2); 6.86-7.85 (m 9H, Ar-H). MS: 291 (M^+).

A spectrophotometer (Model 722, Shanghai, China) equipped with 1 cm cells was used for all absorbance measurements. Waters Solid Phase Extraction (SPE) Device, can prepare twenty sample simultaneously. Waters Porapak® Sep-Park C18 cartridge (1cc/30 mg, 30 μm) (Waters Corporation, USA). All the solutions were prepared with ultra-pure

![Structure of QADMAA](image)
water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). A $2.5 \times 10^{-4}$ mol L$^{-1}$ of QADMAA solution was prepared by dissolving QADMAA with ethanol. A stock standard solution of silver ($1.0$ mg ml$^{-1}$) was obtained from Chinese Standard Center, and a work solution of $0.2$ µg ml$^{-1}$ was prepared by diluting this standard solution. $0.5$ mol L$^{-1}$ of pH=6.5 sodium citrate-sodium hydroxide buffer solution (containing 0.2 mol L$^{-1}$ Na-EDTA). Sodium dodecyl sulphonate (SDS) solution, 2.0% (w/v). All chemicals used were of analytical grade unless otherwise stated.

**General procedure**

To a standard or sample solution containing not more than $2.4$ µg of Ag(I) in a 250 ml of calibrated flask, $10$ ml of sodium citrate-sodium hydroxide buffer solution (containing 0.2 mol L$^{-1}$ Na-EDTA) with pH 6.5, 5.0 ml of QADMAA solution and 5.0 ml of SDS solution were added. The mixture was diluted to the volume of 250 ml and mixed well. After 10 min, the solution was passed through the C$_{18}$ cartridge at a flow rate of 20 ml min$^{-1}$. After the completion of enrichment, the chelate was eluted from the cartridge with 4.0 ml of ethanol at a flow rate 5 ml min$^{-1}$ in an opposite direction. The absorbance of this solution was measured at 585 nm in a 1cm cell against a reagent blank prepared in a similar way without silver.

**Results and discussion**

The absorption peaks of the QADMAA-SDS reagent blank and the QADMAA-Ag(I)-SDS complex are located at 462 nm and 585 nm.

The optimal pH for the reaction of Ag(I) with QADMAA is found to be 5.5–8.5. A sodium citrate-sodium hydroxide buffer solution of pH 6.5 was recommended, the use of 7–15 ml of the buffer solution (pH 6.5) per 250 ml of final solution was found to have a maximum and constant absorbance. Thus, the use of 10 ml of buffer solution was recommended. The buffer solution containing a 0.15–0.25 mol L$^{-1}$ of Na-EDTA can greatly improve the selectivity. Therefore, a buffer solution containing a 0.2 mol L$^{-1}$ of Na-EDTA was recommended to improve the selectivity.

In the presence of anionic surfactants, such as SDS (Sodium dodecyl sulfonate), SDBS (sodium dodecyl benzenesulfonate), SLS (sodium lauryl sulphonate), the absorption of the chromogenic system increased markedly. SDS was found to be the best additive and the use of 3–7 ml of SDS solution gave a constant and maximum absorbance. Hence, 5.0 ml SDS solution was recommended.

For up to $2.4$ µg of Ag(I), the use of 5.0 ml QADMAA solution has been found to be sufficient for a complete reaction. Accordingly, 5 ml of QADMAA solution was added in all further measurement.

After mixing the components, the absorbance reaches its maximum within 8 min at room temperature and remains stable for at least 8 h. After extraction into the ethanol medium, the chelate was stable for at least 20 h.

Both the enrichment and elution were carried out on a Waters SPE device, which can prepare twenty samples simultaneously. The flow rate was set to 20 ml min$^{-1}$ for enrichment and 5 ml min$^{-1}$ for elution. It was found that the QADMAA and its Ag(I) chelate could be retained on cartridge quantitatively when they pass the cartridge as aqueous solution. The capacity of the cartridge for QADMAA was 20 mg and for its Ag(I) chelate was 18 mg in a 250 ml solution. In this experiment, the cartridge has adequate capacity to enrich the Ag-QADMAA chelate and the excessive QADMAA. It was found that tetrahydrofuran, acetone, acetonitrile, ethanol and methanol could elute the QADMAA and its Ag(I) chelate from cartridge quantitatively. Ethanol was selected as eluant because of its low volatility, toxicity and price. It is easier to elute the retained QADMAA and its Ag(I) chelate from the cartridge in the reverse direction than that in the forward direction, so it is necessary to upturn the cartridge during the elution. 4.0 ml of ethanol is sufficient to elute the QADMAB and its Ag(I) chelate from cartridge at a flow rate of 5 ml min$^{-1}$. The volume of 4 ml was selected.

The calibration curve shows that Beer's law is obeyed in the concentration range of 0.01–0.6 µg Ag(I) per ml in the measured solution. The linear regression equation obtained was: $A=1.158 C$ (µg ml$^{-1}$) $+ 0.0176$, ($r=0.9998$). The molar absorptivity was calculated to be $1.25 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ at 585 nm, and the Sandell's sensitivity was $8.63 \times 10^4$ µg/cm$^2$. The relative standard deviation at a concentration level of 0.01 µg Ag(I) per ml (11 repeat determination) was 2.28%.

The composition of the complex was determined by continuous variation and molar ratio method. Both
Table 1—Tolerance limits for the determination of 1.0μg of Ag(I) with QADMAA (relative error ±5%)

<table>
<thead>
<tr>
<th>Ion added</th>
<th>Tolerable (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻, K⁺, borate, tartaric acid</td>
<td>100</td>
</tr>
<tr>
<td>Li⁺, Al³⁺, PO₄³⁻, NO₂⁻, SO₄²⁻, ClO₄⁻, oxalic acid, CO₃²⁻, ClO₃⁻</td>
<td>40</td>
</tr>
<tr>
<td>Ca²⁺, Mg²⁺, SO₄²⁻, Sr²⁺, Ba²⁺, IO₃⁻, BrO₃⁻, Br⁻, I⁻, ClO₄⁻, Cl⁻, Cr(VI)</td>
<td>20</td>
</tr>
<tr>
<td>Mn²⁺, Ce(IV), W(VI), Mo(VI), U(VI), Fe³⁺, Mo(VI)</td>
<td>5</td>
</tr>
<tr>
<td>Ti(IV), Bi(III), Y(VI), Cr(VI), F⁻, Fe²⁺, Cr(III)</td>
<td>2</td>
</tr>
<tr>
<td>Ti (III), Cd²⁺, Pb²⁺, Cr³⁺, La³⁺, Sn(IV), CT, Zn²⁺, Cu²⁺, Zr(IV)</td>
<td>0.3</td>
</tr>
<tr>
<td>Ru(III), Bi(III), Pb²⁺, Hg²⁺, Sb³⁺, Th(IV), Br⁻, Co²⁺, Ni²⁺, O₄(VIII)</td>
<td>0.1</td>
</tr>
<tr>
<td>Sc(IV), Tc(IV), Au³⁺, S₂O₃²⁻, Ir(IV), Rh(III), Ru(III)</td>
<td>0.05</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>0.01</td>
</tr>
<tr>
<td>F⁻, CN⁻, SCN⁻</td>
<td>0.005</td>
</tr>
</tbody>
</table>

show that the molar ratio of Ag(I) to QADMAA is 1:2.

The selectivity of this method was investigated by the determination of 1.0 μg/250 ml of Ag(I) in the presence of various ions within a relative error of ±5% (Table 1). Thiocyanate, cyanide and iodide gave a serious interference of negative errors. However, these interferences can be eliminated by sample digestion as in literature.¹

The proposed method has been successfully applied to the determination of silver in natural water. The results are shown in Table 2, together with results of a recovery test. A standard method using ICP-MS has also been used as reference method (Table 2).

Acknowledgement

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Reference