Determination of copper ions in waters by electrochemical stripping chemiluminescence analysis

in situ

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A novel stripping chemiluminescence (CL) method in situ has been developed which is a combination of selective stripping and CL detection in situ. This method consists of a concentration (pre-electrolysis) step, in which the analyte metal ion is reduced at a controlled potential whilst being deposited as the metal on a solid electrode placed in an electrogenerated chemiluminescence flow cell, a subsequent media exchange step and finally the stripping–CL step, in which the CL emission on the electrode surface is detected in situ when the CL reagent solution is delivered into the cell to react with metal ions which has just been stripped by oxidation. The concentration of analyte is quantified by CL intensity. Copper ion as a representative analyte was investigated. The solution is delivered into the cell to react with the metal ion which has just been stripped by oxidization. The concentration of analyte is quantified by CL intensity. The copper ion which has just been stripped by oxidization. The concentration of analyte is quantified by CL intensity. We define this ion which has just been stripped by oxidization. The concentration of analyte is quantified by CL intensity. The copper ion which has just been stripped by oxidization. The concentration of analyte is quantified by CL intensity.

Keywords: Stripping analysis; chemiluminescence; flow system; copper; luminol, water

Chemiluminescence (CL) analysis is becoming increasingly important in various fields owing to its simple instrumentation, high sensitivity, wide dynamic range, reproducibility, simplicity and rapidity.1–3 However, it is limited by poor selectivity of the CL reaction, which is commonly based on the use of the catalytic function of metal ions in CL reactions with CL reagents such as luminol, lucigenin, lophine, and oxalate esters.3–6 Accordingly, the development of new CL techniques of high selectivity is essential for wider applications.

Some efforts have been devoted to improving the selectivity of CL analysis. A promising approach is to separate the analyte metal ions from other metals or sample matrix. This can be achieved by chromatography, although incompatibility of separation conditions and post-column reception conditions becomes a serious problem in many applications.1–4 CL flow systems based on preconcentration of certain metal ions on resin columns has been successfully applied to the determination of metal ions in seawater.7–9 However in these methods, elution of the preconcentrated metal ions from the substrates is required, usually with strong acids, followed by delivery to the flow cell where the CL detection reactions take place, thus inevitably resulting in problems with analyte dilution and incompatibility of the acid eluents and the CL reactions which commonly proceed at basic conditions. Nakayama, et al.10 reported an automated determination of Mn in seawater by electrolytic concentration and CL detection. In this method, Mn(II) in a sample solution is oxidized to Mn(IV) oxide, which is electrodeposited onto the glassy carbon fiber electrode, followed by elution with acidic hydrogen peroxide solution. The resulting eluate is mixed with an alkaline luminol solution after removing the contaminating metal ions by column extraction based on extraction chromatography, and then the mixture is introduced into the cell. The Mn concentration is obtained from the CL intensity. However, the preconcentration cell and the detection cell are separated and the CL reaction cannot be controlled by electrochemical techniques. Electrogenerated chemiluminescence (ECL) has important advantages over conventional CL in which reagents or precursors participating in the reaction needed for the reaction are generated in situ when required at the electrode. The reaction can therefore be controlled and manipulated by alterations to the applied potential. Haapakka, et al.11 have successfully developed the ECL method for determining Cu(II) based on the catalytic function to the luminol oxidation on the electrode of the metal ions. However, this method also suffers from low sensitivity and poor selectivity.

In the present work, a novel stripping chemiluminescence analysis in situ has been proposed with the aim of improving the selectivity and sensitivity of CL and ECL for determination of metal ions. This method consists of a concentration (pre-electrolysis) step, in which the analyte metal ion is reduced at a controlled potential whilst being deposited as the metal on a solid electrode placed in an ECL flow cell, a subsequent media exchange step and finally the stripping–CL step, in which the CL emission on the electrode surface is detected in situ when the CL reagent solution is delivered into the cell to react with metal ion which has just been stripped by oxidation. The concentration of analyte is quantified by CL intensity. We define this method as ‘Stripping chemiluminescence analysis in situ’. This technique offers advantages compared with conventional CL. First, the selectivity and the detection limit can be improved owing to the selective concentration and stripping process. Second, the analysis process is easily automated because it can be controlled and manipulated by alterations to the applied potential. In this paper, the concept of the method has been proposed and the copper ion was taken as a representative analyte with luminol and cyanide as the CL detection system. The optimization of the analysis conditions and its application for determination of copper in water are presented.

Experimental

Apparatus

A schematic diagram of the instrument used for the stripping CL flow system is shown in Fig. 1.

The instrument integrates a flow system, ECL flow cell, electrochemical analyzer and a chemiluminescence meter. The ECL flow cell was made of a mini glass column (20 × 3 mm id), which was provided with a gold plate working electrode (10 × 2 mm id) exposed directly in the front of the light detector, a silver wire pseudo-reference electrode and counter electrode of a stainless-steel tube placed at the exit of the flow cell. The flow cell was enclosed in a light-tight box. For all experiments, the
potential of the working electrode was controlled by an XJP-821B Electrochemical Analyzer (Jiangsu Electrochemical Analytical Instrument Factory, Jiangsu, China).

The CL emission was transferred to an electric signal without wavelength discrimination by a Hamamatus R 456 photomultiplier tube and recorded with an XWT-204 recorder (Shanghai Dahua Instrument Factory, Shanghai, China).

Reagents
All the reagents were of analytical-reagent grade and the water used were deionized and doubly distilled. Nitric acid and hydrochloric acid was purified by sub-boiling quartz-distillation. A potassium chloride solution of 5.0 mol dm$^{-3}$ was purified by controlled cathodic current electrolysis with a mercury pool electrode. Stock standard solution of copper(II) was made by dissolving 0.1000 g of pure copper metal in 1% (v/v) nitric acid. A 0.25 mol dm$^{-3}$ stock solution of luminol (Sigma, St. Louis, MO, USA) was prepared by dissolving 4.43 g of luminol in 100 cm$^3$ of 0.10 mol dm$^{-3}$ sodium hydroxide solution, which was used after storing at room temperature for 3 d. The stock solution of potassium cyanide was prepared by dissolving 0.651 g of potassium cyanide (Beijing Chemical Reagents Factory, Beijing, China) in 100 cm$^3$ of water to give a concentration of 0.10 mol dm$^{-3}$. Working solutions were prepared freshly from the stock solutions by dilution. Except where stated reagents are from Xi’an Chemical Reagents Factory, Xi’an.

Procedure
As shown in Fig. 1, flow lines were inserted into sample/standard solutions, washing solutions (dilute hydrochloric acid) and CL reagent solutions respectively. With a six-way injection valve in the washing position, the peristaltic pump was started for a fixed time. During the next step, the valve was returned to the stripping position so that the sample/waste solution was delivered to the flow cell and the deposition reaction could be effectively eliminated (discussion in detail below).

Fig. 1 Schematic diagram of the stripping chemiluminescence flow system. a, Sample solution; b, washing solution; c, chemiluminescence reagent solution; V, six-way injection valve; ECL cell, electrogenerated chemiluminescence flow cell; PMT, photomultiplier tube; NHV, negative high voltage.

Chemiluminescence reagent solution into the flow cell and the electrochemical stripping was run by changing the potential to the stripping potential at +0.20 V, so that stripped copper ion reacted with luminol and cyanide, in situ, producing CL emission. The concentration of copper was quantified by CL intensity.

Results and discussion
Optimization of electrochemical deposition step
Important experimental parameters including sample acidity, deposition potential and deposition time in the electrochemical deposition step were optimized for the preconcentration system.

On consideration of the electrolyte deposition and the hydrolysis of metal ions, which affected the deposition of copper onto the gold electrode, several electrolytes such as potassium chloride, ammonia–ammonium chloride and hydrochloric acid were examined in the flow system. Using the above electrolytes, almost identical copper signals were obtained with hydrochloric acid. The dependence of copper accumulation and the CL response on the concentration of hydrochloric acid in the range of 0.001–1.0 mol dm$^{-3}$ was tested by using 0.10 µg dm$^{-3}$ copper(II) standard solution. The results were shown that the amount of accumulated copper and thus the CL intensity, increased upon increasing the sample acidity until 0.20 mol dm$^{-3}$ and thereafter remained almost constant. A sample acidity of 0.20 mol dm$^{-3}$ HCl with high CL intensity and better reproducibility was finally selected for the subsequent work.

The influence of deposition potential on the CL intensity was checked at the potential between +0.10 and −0.70 V. As shown in Fig. 2, the CL intensity increased from −0.05 V and the maximum CL intensity was obtained at −0.40 V. However, at potentials more positive or negative than this value CL intensity decreased, probably because of deficient reduction of copper(II) onto the gold electrode or the evolution of hydrogen at the electrode preventing the deposition of copper. In order to achieve high intensity and also to avoid interfering species from accumulating on the electrode a deposition potential at −0.40 V was employed for optimized experimental conditions. The optimized deposition potential in present work is in agreement with that reported by Wang, et al. In this case, serious interference by other metal ions associated with the CL reaction could be effectively eliminated (discussion in detail below).

The dependence of the deposition time on CL intensity was examined from 0 to 300 s. As expected the CL intensity increased linearly with the deposition time between 0 to 300 s.

Fig. 2 Effect of deposited potential on chemiluminescence intensity for 0.10 µg dm$^{-3}$ copper(II); deposition time, 2 min; stripping potential: +0.20 V; chemiluminescence reagent solution: 1.2 × 10$^{-4}$ mol dm$^{-3}$ luminol, 8 × 10$^{-5}$ mol dm$^{-3}$ potassium cyanide, 1 × 10$^{-2}$ mol dm$^{-3}$ sodium hydroxide and 0.20 mol dm$^{-3}$ potassium chloride; flow rate; 3.0 cm$^3$ min$^{-1}$.
As required for near real-time monitoring, most of the subsequent work employed a 60–300 s deposition, which is sufficient for monitoring copper in relevant water samples. Considering a compromise between analysis time and sensitivity, a deposition time of 120 s was chosen for the following work.

**Optimization of the stripping step**

The stripping process is followed by a CL reaction. The Cu$^{2+}$–CN$^-$–luminol CL reaction may be made pseudo-first-order with respect to the copper(II) concentration so that the CL intensity is directly proportional to the analytic copper(II) concentration when both luminol and cyanide are in excess. The more positive the final potential, the higher the rate of heterogeneous electron transfer. From the high concentration of copper(II) ion in the neighborhood of the gold electrode it can be naturally predicated that the CL response would be enhanced with a more positive potential. Various stripping modes including linear potential sweep stripping, pulse potential stripping, constant potential stripping, constant current stripping and chemical stripping, can be used in this work. The mode of constant potential stripping was chosen in our work because of its excellent selectivity and sensitivity.

The effect of stripping potential on the CL intensity was studied in the range from −0.10 to +0.40 V. The result is shown in Fig. 3. It can be seen that the CL intensity increased rapidly from +0.05 to +0.20 V and thereafter increased gradually. The CL emission from the electrochemical oxidation of luminol was observed at potentials more positive than +0.25 V. No background CL which results from the electrochemical oxidation of luminol on the gold working electrode was observed at the potential between −0.40 to +0.25 V. The maximum signal/noise of CL intensity was found at +0.20 V. Therefore, the stripping potential of +0.20 V was selected as optimum.

**Effect of chemiluminescence reagent concentration**

The optimization of CL reagent concentration was carried using a modified simplex algorithm (written in house). The key variables for maximizing the sensitivity of CL emission were considered to be the flow rate of CL reagent solution and the compositions of CL reagent solution, including the concentration of sodium hydroxide used as carrier solution containing 0.20 mol dm$^{-3}$ potassium chloride (it was kept equal to provide a homogeneous pH for the CL reaction and constant concentration of chloride for the reference electrode), the concentration of luminol and the concentration of potassium cyanide, as well as the negative high voltage applied to the photomultiplier tube. The starting point for the simplex was taken from a previously reported manifold.13,14 The ranges, step sizes, starting conditions and optimum conditions for copper determinations are shown in Table 1. All subsequent experiments used these optimum conditions unless otherwise stated.

**Determination of copper**

Under the recommended conditions and by use of the manifold depicted in Fig. 1, CL response to copper(II) concentration was linear in the range 0.040–40 μg dm$^{-3}$. The regression equation was $I = 3.85 + 47.3[Cu^{2+}](μg dm^{-3})$ with a correlation coefficient of 0.999 in a deposition time of 120 s. Multiple determinations ($n = 7$) gave relative standard deviations of 4.6 and 3.4% at copper concentrations of 0.10 and 1.0 μg dm$^{-3}$, respectively. The detection limit (d.L.) was 0.02 μg dm$^{-3}$ (3σ) for a deposition time of 120 s. This detection limit is much lower than that obtained using a flow injection CL method based on the same CL reaction (data not shown) and square wave anodic stripping voltammetry reported recently (d.L., 2.6 μg dm$^{-3}$; deposition time: 180 s).15 Better (lower) detection limits can be achieved if the deposition time was prolonged. A satisfactory detection limit of the proposed method is therefore feasible.

**Interference studies**

The influence of foreign species was tested by analyzing a standard solution of 1.0 μg dm$^{-3}$ copper(II). The tolerable limit of a foreign species was taken as a relative error not greater than 5%. Without the use of pre-electrolysis deposition, the interference study of the Cu$^{2+}$–CN$^-$–luminol CL system was performed. It was found that the selectivity of the CL system was rather poor and serious interference resulted from 0.5-fold Fe$^{2+}$, Fe$^{3+}$, and Mn$^{2+}$, 2-fold of Co$^{3+}$ and 5-fold of Ni$^{2+}$. However, with the method developed, none of these metals ions at 1000-fold showed any effect on the CL signal. In addition, the test also showed that more than 1000-fold excess of Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Zn$^{2+}$, Al$^{3+}$, Sn$^{4+}$, Ti$^{4+}$, Cr$^{6+}$, V$^{5+}$, W$^{6+}$, Mo$^{6+}$ and Cr$^{3+}$, less than 200-fold excess of Hg$^{2+}$, Ag$^{+}$ and Cd$^{2+}$, and less than 50-fold excess of Sn$^{2+}$, Pb$^{2+}$ and Bi$^{3+}$ did not interfere. Under the applied specific conditions, all these metal ions either could not be deposited effectively on the gold electrode or could not be stripped out of the electrode to interfere with the CL detection of copper. Besides these metal ions, some nonmetal ions were studied for their potential interference. The tolerable concentration ratios were more than 1000-fold of NH$_4^+$, NO$_2^-$, CO$_2^-$, HPO$_4^{2-}$, F$^-$, Ac$^-$, SO$_4^{2-}$, Br$^-$, SO$_3^{2-}$, NO$_3^-$, As$^{3+}$ and Te$^{VI}$, respectively. A satisfactory selectivity of the proposed method is therefore evident.

**Table 1** Results from simplex optimisation of the constant-potential stripping CL method for copper(II) showing the range, step, starting conditions and optimum conditions of each variable

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>Range</th>
<th>Step size</th>
<th>Starting conditions</th>
<th>Optimum conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Luminol]</td>
<td>mol dm$^{-3}$</td>
<td>10–10$^{-5}$</td>
<td>Variable</td>
<td>$1 \times 10^{-5}$</td>
<td>$1.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>[Cyanide]</td>
<td>mol dm$^{-3}$</td>
<td>10–10$^{-5}$</td>
<td>Variable</td>
<td>$2 \times 10^{-5}$</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>[NaOH]</td>
<td>mol dm$^{-3}$</td>
<td>10–10$^{-4}$</td>
<td>0.05</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>PMT voltage</td>
<td>kV</td>
<td>0.50–0.90</td>
<td>0.5</td>
<td>$0.5$</td>
<td>$0.80$</td>
</tr>
<tr>
<td>Flow rate</td>
<td>cm$^3$ min$^{-1}$</td>
<td>2.0–4.0</td>
<td>2.0</td>
<td>$2.0$</td>
<td>$3.0$</td>
</tr>
</tbody>
</table>
Application
Determination of trace amounts of copper in tap water and underground water collected in 50 cm³ polyethylene bottles and filtered through a standard 0.45 micrometer filter was performed. A 20 cm³ portion of the sample was treated with 5 cm³ of 0.10 mol dm⁻³ HCl, and then diluted to 50 cm³ with doubly-distilled water. The copper content of the resulting solution was determined by the recommended procedure and by atomic absorption spectrometry, respectively. The results obtained are listed in Table 2. It shows that results obtained by the present method agree well with those obtained by atomic absorption spectrometry (AAS).

Exploration of the ECL mechanism of Lu–CN⁻ with stripping copper
The CL mechanism of the luminol–Cu²⁺–CN⁻ stripping copper geneous electron transfer step may be the determining step. 16 The CL intensity was directly proportional to positive stripping scan rate from 10 to 200 mV s⁻². The enhanced CL intensity was not observed with the stop technique. However, it was found that CL intensity was directly proportional to positive stripping scan rate from 10 to 200 mV s⁻¹. This suggests that the CL reaction should be only conducted in a magnitude of a micron. So the higher signal to noise ratio in the method should be achieved in a thin ECL cell.

Conclusions
The stripping chemiluminescence analysis proposed here is promising and is easily performed. The high selectivity and sensitivity of the present method suggests that electrochemical concentration and CL detection in situ is a suitable strategy for CL analysis.

One further point should be emphasized. A novel CL flow-through sensor has been developed for the determination of copper which is based on the analytical reagents including luminol and cyanide, co-immobilized permanently on an anion exchange column, while the analyte copper is retained temporarily by the proposed method. More applications will be used in CL analysis.

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References

Table 2 Results of the determination of copper in water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Present method/µg dm⁻³</th>
<th>ASS/µg dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water 1</td>
<td>1.3(3.6)</td>
<td>1.2(4.0)</td>
</tr>
<tr>
<td>Tap water 2</td>
<td>1.0(5.0)</td>
<td>1.0(5.4)</td>
</tr>
<tr>
<td>Ground water 1</td>
<td>2.4(3.4)</td>
<td>2.3(3.2)</td>
</tr>
<tr>
<td>Ground water 2</td>
<td>3.5(4.8)</td>
<td>3.2(5.0)</td>
</tr>
</tbody>
</table>

* Average value of four determinations (%RSD).