Preconcentration with membrane cell and adsorptive cathodic stripping voltammetric determination of aniline in air

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Aniline in air is preconcentrated in a membrane cell and its content has been determined using adsorptive cathodic stripping voltammetry. Aniline in air samples is preconcentrated in a membrane cell using 3.0 mol/L HCl solution, to form a diazotized aniline- HCl salt, which is reduced to phenylhydrazine in the presence of NaNO₂, The hydrazine reacts with formaldehyde to form phenylhydrazine, which adsorbs at the mercury electrode and yields a sensitive adsorptive cathodic stripping voltammetric wave. The peak currents are linearly proportional to the concentration of aniline over the range 6.0×10⁻⁹ - 5.0×10⁻⁵ mol/L. The detection limit is 2.0×10⁻⁹ mol/L.

Aniline is widely used for the manufacture of polyurethanes and rubber, with lesser amounts consumed in the production of pesticides, defoliants, dyes, antioxidants and vulcanization accelerators and is very toxic. Various methods for the determination of aniline in water, waste water and air samples have been cited in the literature.

The application of membrane separations in analytical chemistry has been reported. Moskvin recommended a chromatomembrane method which is a technique for the mass-exchange between a polar liquid phase and non-polar liquid or gas phase within a membrane cell. This technique has been used to collect the air pollutant. The analyte is continuously extracted from a certain phase using membrane cell. In the present note, a membrane cell has been designed (Fig. 1), and used to collect aniline in air using HCl solution as absorbing solution. In a dilute HCl solution, the aniline reacts with NaNO₂ to form a diazonium compound which can form phenyl hydrazine in the presence of Na₂SO₃, the hydrazine reacts with formaldehyde to form phenylhydrazine, which can yield adsorptive cathodic stripping voltammetric wave on the hanging drop mercury electrode (HDME). Therefore aniline is determined by adsorptive stripping voltammetry.

Principle of operation of a membrane cell

Membrane cell is a device for mass-exchange between a polar liquid and a non-polar liquid or gas phase within a membrane cell (Fig. 1). In a membrane cell, the mass-exchange process is carried out in the capillary medium of hydrophobic material. The micropores membrane 4 is a hydrophobic one. The mass-exchange layer 3 is made up of porous polymer particles such as porous polytetrafluoroethylene (PTFE). The porosity between the particles forms macropores with a radius of 0.5-3.0 mm. In the polymer particles there are numerous open micropores with a radius of 0.03-1.0 μm. The macropores form channels for the polar liquid which do not wet the surface of the hydrophobic material, and the micropores form channels for the non-polar liquid or gas phase. When the non-polar liquid or gas moves within the micropores it can contact with the polar liquid within the macropores, thus the analyte transfer from original phase into the other.

Throughout the mass-exchange space the gas or non-polar liquid phase does not enter into the macropores because the polar phase pressure is maintained higher than the pressure of the gas phase, and polar liquid phase also can not penetrate into micropores because the capillary pressure of micropores can prevent this penetration.

The capillary pressure \( P_c \) depends on the contact angle between the liquid and the membrane material (θ) and the pore radius (γ):

\[
P_c = \frac{(2\gamma \cos \theta)}{\gamma} \tag{1}
\]

In order to prevent the capillary effects, in the design of membrane cell, the \( P_c \) should exceed the value calculated from the above equation. In case of PTFE porous matrix, the capillary effects become negligible for pores larger than 0.1 mm radius. Hence it is confirmed that the polar liquid phase moves within the macropores and the non-polar liquid or gas phase moves within the micropores.

Experimental

The experimental membrane cell(Fig. 1) was made up of PTFE. The cell had a membrane of 0.8 mm thickness with an average pore size of about 0.7 μm.
In the mass-exchange units (20×20×40 mm) the micropore size is uniform, 0.7 μm, and the average diameter of macropore size is 0.5 mm. The cell in this study allow variation of the aqueous phase flow within 0-500 ml/min range and of the air flow within 0-1.5 dm³/min range.

The stripping voltammograms were recorded on an MP-2 stripping voltammetric analyzer (Shandong Instrumental Factory) with an Epson printer and a JM-01 (manual micrometric screw delivery) hanging mercury drop electrode, controlled by microprocessor. The electrolytic cell has a three-electrode system: a HDME as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode. A PAR Model 273 potentiostat/Galvanostat with a PAR Model 303 static mercury drop electrode, controlled by PAR Model 270 software, was used for pulse polarography, linear scan voltammetry, cyclic voltammetry and other electrochemical measurements. For pulse polarography the instrumental parameters were as follows: accumulation time, 180 s; accumulation potential, -0.40 V; pulse period, 2 s; equilibrium time, 15 s.

Standard solutions of aniline was prepared. Into a 25 ml brown flask 10 ml of 0.10 mol/L HCl solution was added, and weighed. Then 3-5 drops of aniline which was newly distilled were added to the solution, and again weighed. The accurate weight of aniline was obtained. The mixture was diluted to 25 ml with 0.10 mol/L HCl solution, and the solution was kept at 5°C. The solutions of lower concentration were prepared by serial dilution with 0.10 mol/L HCl solution.

A stock solution of NaNO₂ (0.30 mol/L) was prepared by dissolving 1.04 g of NaNO₂ (AR) in 50 ml of water. A stock solution of Na₂SO₄ (0.025 mol/L) was prepared by dissolving 0.315 g of Na₂SO₄ (AR) in 100 ml of water. A stock solution of formaldehyde (0.60%) was prepared by diluting 1.5 ml of 40% formaldehyde solution to 100 ml with water. Other reagents were of suprapure or analytical-reagent grade. Water, redistilled in a fused-silica apparatus, was used throughout.

Procedures
Preconcentration of the aniline in air

The experimental device for preconcentration of aniline in air samples is shown in Fig.2, and the procedure for preconcentration of aniline in air is as
follows: the valves were closed initially, and the pump 8 was started. Then the triton valve 3 was rotated to connect line 2 with line 3 to let absorbing solution to fill the membrane cell. When the solution outflows from the cell the triton valve 3 was rotated to cut off line 2 and 3. The triton valve 3 was again rotated to connect line 1 with line 3, and valve 7 was regulated to make the flow rate of air in 0.5 dm³/min. After about 5 min the valve 7 was closed, and the triton valve 3 was immediately rotated to connect line 2 with line 3 to collect about 1.0 ml of absorbing solution. On repeating above steps, a 3-5 ml of the solution (total volume) was collected.

**Adsorptive stripping voltammetric determination of aniline**

**Stripping voltammetry of pure aniline solution.** In a 10 ml beaker, 0.50 ml of 1.0×10⁻³ mol/L aniline solution and 0.10 ml of 0.50 mol/L NaNO₂ solution were taken and mixed well. After standing for 2 min, 1.00 ml of 0.025 mol/L Na₂SO₄ solution was added, and the pH of the solution was adjusted to 3 with dilute NaOH solution. Then 1.00 ml of 0.010 mol/L HCl solution and 0.10 ml of 0.60% formaldehyde solution were added, and mixed well, and allowed to stand aside for 3 min. To this mixture, 0.10 ml of 0.60% Triton X-100 solution was added, and the mixture was diluted to 10 ml with water, and transferred to electrolytic cell. The derivative stripping voltammograms were recorded with potential scan rate of 100 mV/s, starting the potential scan at -0.40 V. The peak potential is -0.73 V.

**Analysis of air samples.** Using the collected aniline sample solutions in place of aniline standard solution, the analysis was performed as described above for pure aniline solution.

**Results and discussion**

**Conditions for preconcentration**

The amines such as aniline in air are best collected in 3.0 mol/L HCl solution. In this study, a 3.0 mol/L HCl solution was used to absorb aniline in air samples.

The analyte is easy to dissolve in an absorbing solution, with the larger the flow rate of the sample, the shorter the time of concentration can be. However, the flow rate of the samples must be less than that which the membrane cell tolerates. In order to absorb the aniline in air samples completely, in this study, the flow rate of the air samples was controlled at 0.5 dm³/min.

**Adsorptive stripping voltammetric determination of aniline**

Aniline is not reducible on the mercury electrode, but phenylhydrazine has electrochemical activity and can yield voltammetric wave. So, first aniline reacts with NaNO₂ in a dilute HCl solution to form a diazoate which can be reduced in presence of Na₂SO₄ to phenylhydrazine. Hydrazine reacts with formaldehyde to form phenylhydrazine.

\[
C₆H₅NH₂ + NaNO₂ + 2HCl \rightarrow C₆H₅N₂⁺Cl⁻ + 2H₂O + NaCl \tag{2}
\]

\[
C₆H₅N₂⁺Cl⁻ + 4H⁺ \xrightarrow{Na₂SO₄} C₆H₅NNH₂ + HCl \tag{3}
\]

\[
C₆H₅NNH₂ + HCHO \rightarrow C₆H₅NN=CH₂ + H₂O \tag{4}
\]

The phenylhydrazine solution is adsorbed on the mercury electrode and undergoes electro-chemical reaction to yield sensitive adsorptive cathodic stripping voltammetric peak (Fig. 3e) on the HDME.

\[
C₆H₅NN=CH₂ + 2e + 2H⁺ \rightarrow C₆H₅NNHCH₃ \tag{5}
\]
The detection limit is $6.0 \times 10^{-6}$, which can be used to determine the trace aniline. Over the range $6.0 \times 10^{-9} - 5.0 \times 10^{-3}$ mol/L, the peak currents are linearly proportional to the concentration of aniline. The detection limit is $2.0 \times 10^{-9}$ mol/L, which was taken as the concentration that gave a signal equal to three times the standard deviation of the blank signal, calculated from the calibration slope. The reproducibility was evaluated by 20 repetitive experiments on $5.0 \times 10^{-2}$ mol/L aniline solution. The relative standard deviation is found to be 8.1%.

The HCl concentration affected the azo-reaction and peak current. The azo-reaction of aromatic amines was carried out best in 0.10 mol/L HCl solution, so the aniline was diazotized in a 0.10 mol/L HCl solution.

In the test solution, the concentration of HCl affects on the peak currents. The suitable concentration of HCl is found to be in the range $8.0 \times 10^{-4}$ to $2.0 \times 10^{-3}$ mol/L, hence a HCl concentration of $1.0 \times 10^{-3}$ mol/L was chosen for subsequent studies.

The NaNO$_2$ concentration affected the peak current. When its concentration is less than $2.0 \times 10^{-3}$ mol/L, the $i_p$ increases rapidly with increasing NaNO$_2$ concentration. For NaNO$_2$ concentration greater than $2.0 \times 10^{-3}$ mol/L, the $i_p$ remains constant. Accordingly, a NaNO$_2$ concentration of $3.0 \times 10^{-3}$ mol/L was used throughout for maximum sensitivity.

The effects of Na$_2$SO$_3$ concentration on the peak current were examined experimentally. The suitable Na$_2$SO$_3$ concentration is found to be in the range $1.8 \times 10^{-3}$ to $4.0 \times 10^{-3}$ mol/L. So Na$_2$SO$_3$ concentration of $2.5 \times 10^{-3}$ mol/L was used throughout for maximum sensitivity.

The effect of formaldehyde concentration on the peak current was determined. It was seen that with concentration less than 0.0045%, the $i_p$ increases with increasing formaldehyde concentration, and larger than 0.0080%, decreases. Accordingly, a formaldehyde concentration of 0.0060% was chosen for subsequent studies.

Various cathodic, anodic and nonionic surfactants such as cetyltrimethylammonium bromide(CTMAB), sodium lauryl sulphate(SLS), $p$-octylpolyethylene glycol phenyl ether(OP), Tween-80 and Triton X-100 were tested, and Triton X-100 was found to be the best. The peak current increases rapidly on increasing Triton X-100 concentration. In the range 0.0050% to 0.010% for Triton X-100 the maximum peak currents were obtained. As Triton X-100 concentration increases beyond 0.010%, the peak current decreases. The suitable Triton X-100 concentration for this study was 0.0060%.

The effect of temperature on the peak current was examined experimentally. The temperature lower than 30°C did not affect the peak current. So all operations for the determination of aniline were carried out at room temperature. At room temperature, the diazo-reaction was carried out rapidly and completed in 1-3 min. So after mixing aniline and NaNO$_2$ solution, the mixture was allowed to stand for 2 min.

For $5.0 \times 10^{-7}$ mol/L aniline solution when the accumulation time is larger than 150 s, the peak current remained constant. In this study, the accumulation time of 180 s was chosen for maximum sensitivity. The effect of accumulation potential on the peak current was examined experimentally, which showed that the accumulation potential did not affect the peak current.

**Cyclic voltammetry**

Figure 4 shows the cyclic voltammograms of aniline system. The phenylhydrazone gives a cathodic peak at about -0.73 V due to its reduction, and no peak was observed on the anodic branch, indicating that the reduction of phenylhydrazone is irreversible. In Fig.4 subsequent repetitive scans yielded significantly smaller (but stable) cathodic peaks corresponding to the reaction of dissolved species. This behaviour indicates that phenylhydrazone is adsorbed on the mercury electrode, which agrees with normal pulse polarographic data.

**Analysis of samples**

The adsorptive cathodic stripping voltammetric procedure proposed in this note is used to determine the aniline in air samples.
The standard aniline solutions were used for the preparation of calibration graph. The regression equation of the calibration line is of the form:

\[ \frac{Y}{mg/ml} = 8.54X - 0.03 \]  

... (6)

where \( Y \) is the peak current in \( \mu A \) and \( X \) is the aniline concentration in \( \mu g/ml \). The correlation coefficient was 0.998. The results of determination of aniline in the air samples were summarized in Table 1. The data sampled with impinger are also shown in Table 1. These data are smaller than those sampled with the membrane cell, which shows that the membrane cell is more effective than the impinger for the preconcentration of aniline in air samples.

### References


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**Table 1—Determination of aniline in air samples**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Membrane cell</th>
<th>Impinger*</th>
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<tbody>
<tr>
<td></td>
<td>Aniline(Found),mg/m³</td>
<td>RSD,%</td>
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<td>Atmosphere</td>
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<tr>
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<tr>
<td>(workshop)</td>
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<td>7.1</td>
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</table>

*Main of three parallel determinations.