SAMPLING OF AIR FOR DETERMINATION OF HYDROGEN CYANIDE

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For sampling of hydrogen cyanide (HCN) gas in atmospheric air, a midget impinger containing NaOH aq. as absorbing solution was found to be the most suitable apparatus. The efficiency of sampling for HCN was affected by the absorbing conditions greatly. In this procedure, NaOH in the solution were consumed by CO₂ in atmospheric air gradually¹). To absorb HCN thoroughly, it was necessary to keep enough NaOH in the solution. The solution containing CN⁻-compounds generated HCN gas, if the alkalinity of the solutions was lost. Beside these, various other conditions also had to be considered to absorb CN⁻-compounds in atmospheric air.

When hydrogen cyanide (HCN) gas in atmospheric air is absorbed with an impinger containing NaOH aq. as absorbing solution, the absorbing efficiency naturally is affected by the absorbing conditions. The author observed the relations between the efficiency and the various absorbing conditions. The conditions were concentration of NaOH, volume of absorbing solution and velocity of atmospheric air passing through the absorbing solutions. Carbon dioxide (CO₂) in air also had serious influences on the absorbing efficiency. As the analytical sensitivity of CN⁻ was very high, 1 μg of CN⁻ was enough for its determination. A midget impinger was therefore used for absorption of CN⁻ in all the cases and it was found that this apparatus was the most suitable for this purpose.

EXPERIMENTS

Two impingers were connected in a series, and same volume and same concentration of NaOH aq. was put into individual impingers as absorbing solutions. The test air was passed into these impingers and HCN in the air was absorbed in NaOH aq. Fig. 1 shows the outline of the procedure. The absorbing efficiency of the midget impingers was studied with this apparatus in relation to several conditions; the concentration of NaOH, volume of absorbing solution, the passing velocity of the test air, etc.

Volume of absorbing solution in this experiment was 5, 10, 20 ml, passing velocity of the test air was 0.5, 1, 2 l/min and volume of passed air was 10⁻20 l. The concentration of HCN in the test air was 10⁻20 ppm. The amount of the captured CN⁻ in individual impinger was determined by colorimetric method (pyridine=pyrazolone
and absorbing efficiencies were calculated from the individual absorbed amounts of CN' in a pair of impingers.

DISCUSSION

In the absorbing procedure, the following two sorts of reactions proceed simultaneously.

\[ \text{HCN} + \text{NaOH} = \text{NaCN} + \text{H}_2\text{O} \]
\[ 2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \]
\[ \text{CO}_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = 2\text{NaHCO}_3 \]

1) This is the very absorbing reaction of HCN. As this is an acid-alkali reaction, the reaction proceeds perfectly and momentarily in normal conditions. If the amount of NaOH in impinger is enough and passing air contacts with absorbing solution fully, HCN in the air is always captured thoroughly.

2) CO\(_2\) in passing air also reacts with NaOH in absorbing solution, and NaOH is consumed gradually. When NaOH changes to NaHCO\(_3\), the alkalinity of the solution (pH 7~8) makes the capture of HCN in it impossible. On the contrary, CN'-compounds in the solution changed to HCN and were carried away by the passing air.

Thus two conflicting reactions proceeded constantly at the same time in the absorbing solution.
DETERMINATION OF HCN IN AIR

Capturing of HCN gas with impinger

Volume of absorbing solution. The absorption by NaOH takes place on contact with the foams of HCN. So, if the same concentration of NaOH aq. is used, the larger the volume of absorbing solution is used, the larger becomes the absorbing efficiency; for a long pass in the solution gives long time of contact. It was found even if concentration of NaOH was low, the absorbing efficiency became large as the volume of the solution increased.

Passing velocity. When the amount of NaOH was enough, absorption always proceeded thoroughly. But in case of a low NaOH concentration, perfect absorption did not always take place. Generally, it seems that the slower the velocity of the air which passes, the larger becomes the absorbing efficiency. Such expectation, however, did not apply to this procedure. On the contrary, as shown in Fig. 2, high velocity of passing air rather gave larger efficiency. This might be due to the following reasons:

![Fig. 2](image_url)

Fig. 2. Relation between absorbing efficiency and sampling condition.

(A) Absorbing solution in impinger 20 ml
(B) Absorbing solution in impinger 20 ml
(C) Absorbing solution in impinger 5 ml

- ○ - Passing velocity 2 l/min
- ● - Passing velocity 1 l/min
- ● - Passing velocity 0.5 l/min
one hand, if the velocity of passing air is large the air spouts out from the orifices violently and impinges against the bottom of impinger vigorously. So the foams are pulverized finely, and the contact area between foams and absorbing solution increases. On the other hand, the reaction between NaOH and CO₂ is also promoted, but this reaction proceeds much slower than acid-alkali reaction originally. So, only the absorbing reaction is promoted conspicuously as the passing velocity of air increases. But, if the velocity becomes too large, the absorbing solution overflows from the impinger. It is recommended that the velocity does not exceed about 2.5 l/min.

**Generation of HCN gas from CN⁻-compounds exposed to air**

*In solid state.* Solid CN⁻-compounds also react with CO₂ in air, and change into HCN gas and are lost into air gradually. For example, the following two values show this phenomenon well.

\[
\begin{align*}
\text{CN':} & \quad 6.7 \text{ ppm (Suction at about 600 l/min)} \\
\text{CN':} & \quad 66.0 \text{ ppm (Suction at about 20 l/min)}
\end{align*}
\]

The former CN⁻ was captured with a high volume air sampler and the latter CN⁻ was captured with a low volume air sampler. These two values of CN⁻ were captured on the filters at the same time and the same spot. CN⁻ captured on the filter papers was determined, and CN⁻ concentration in air was calculated from that amount. The two amounts should agree with each other if CN⁻-compounds are stable substances. The former, however, was much smaller than the latter in practice. Though these amounts have no practical meaning, they show that the greater volume of air passes, the larger the amount of CN⁻ is lost into air. Dust of these compounds, therefore, can not be successfully captured on the filter paper.

*In liquid state.* The following experiment showed that CN⁻-compounds dissolved in NaOH aq. also reacted with CO₂ in air and that generated HCN gas was lost into air. A definite amount of CN⁻ was dissolved in various concentrations of NaOH aq. and aliquot volume of it was put in impingers. Then air was passed into impingers and the remained amounts of CN⁻ in impingers were plotted. Fig. 3 shows that the rate of decrease of CN⁻ depends on the concentration of NaOH in solutions.

When aqueous solution which contained CN⁻-compounds was dried spontaneously, CN⁻ changed to HCN gas and vanished into air gradually, even if the solution was not bubbled by air. It was particularly remarkable when this solution was sprayed and was dried spontaneously. The following experiments showed this distinctly. Twenty micrograms of CN⁻ which dissolved in 1.2 ml of various concentration of NaOH aq. were spotted on the filter papers, and the papers were dried spontaneously. Then the retained amount of CN⁻ on the filter papers was determined. The results are shown in Fig. 4. CN⁻ in very concentrated NaOH solutions did not change into HCN readily.
As the sensitivity of analytical method for CN' was very high, it was enough to pass 10~20 l of test air for determination of CN'. CN' was determined by colorimetric method (pyridine=pyrazolone method). It was, therefore, convenient to use midget impinger containing NaOH aq. as absorbing solution for determination of CN' in atmospheric air. Absorption of CN' in this solution was extremely satisfactory. But to keep the absorbing efficiency to be 100%, the amount of NaOH in the impinger should always
be sufficient. It is very important that the passing velocity of test air should not be too small. For example, the following conditions were good for perfect sampling for HCN.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of passing air</td>
<td>20 l</td>
</tr>
<tr>
<td>Velocity of test air</td>
<td>2 l/min</td>
</tr>
<tr>
<td>Volume of absorbing solution</td>
<td>15 ml</td>
</tr>
<tr>
<td>Concentration of NaOH aq.</td>
<td>&gt; 0.1 N</td>
</tr>
</tbody>
</table>

NaOH in impinger is consumed by CO₂ in the passing air gradually; no more HCN is absorbed in the solution if NaOH is exhausted. On the contrary, HCN is lost from the solution by the passing air. Solid CN⁻-compounds react with CO₂ in air and are lost into the air gradually. CN⁻-compounds dissolved in NaOH aq. are also lost if the alkalinity of the solutions is lost. These phenomena were very conspicuous when the solutions were sprayed and were dried spontaneously. CN⁻ in the solution changed to HCN and entered into air rapidly and thoroughly, unless CN⁻ were dissolved in very concentrated alkali solution. This was very dangerous for the health.

References