Improvements in Preconcentration Methods for Determining Trace Impurities in Ultra-Pure Gases by Gas Chromatography

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Key Words
Gas chromatography
Preconcentration techniques
Trace gas analysis

Summary
The blanks in preconcentration methods for determining trace amounts of impurities in ultra-pure gases, which include the preconcentration volume of sample gases, carrier gas impurities and atmospheric contamination are discussed and three concentration methods for eliminating blank errors are proposed. These are, the differential volume method by concentrating at the same flow-rate but different times (DVMSF), the differential time method by concentrating the same volumes at different flow-rates (DTMSV) and the differential volume method by concentrating for the same times but different flow-rates (DVMST). DVMST is proposed as the best method for its ability to eliminate all blank errors described. The methods are used to determine trace amounts of Ar + O₂ and N₂ in ultra-pure hydrogen. Calculations demonstrate that the methods can effectively improve analytical accuracy.

Introduction
Gas chromatography is one of the most effective methods for trace gas analysis. To improve the analytical sensitivity, high performance columns and high sensitivity detectors are used [1, 2]. In addition, preconcentration methods for increasing the amount of sample is also important, which can reduce the detection limit 3 to 4 orders [3]. However, due to long concentration time and large temperature change of the concentration column, many problems such as flow fluctuation, partial concentration of background gases, carrier gas impurities and gas contamination from the atmosphere will occur [4, 5]. Those problems will affect the analytical accuracy. Controlling release time and desorption temperature can reduce gas flow fluctu-
packed with porous polymer beads GDX-105 (80–100 mesh, Shanghai Regent Factory, China). The sample gas flow-rate and concentration volume are measured by Model D08-1 mass flow meter and controller (accuracy: ± 1 %, Beijing Jianzhong Machinery Factory, China) and Model BSD-0.5 wet test meter (accuracy: ± 1 %, Shanghai Gas Corp., China).

The chromatographic conditions are as follows: column, stainless steel tube (72 × 1/8" o.d.), packed with 5A molecular sieve (60–80 mesh); oven temperature 40 °C; carrier gas, hydrogen, 29 ml min⁻¹; modulator switching gas, hydrogen, 45 ml min⁻¹; detector, TCD, 60 °C.

**Calibration Curve**

For the measurement of O₂ + Ar and N₂ in ultra pure hydrogen, dry air is used as reference gas. The volumes of O₂ + Ar and N₂ in the air injected are plotted against corresponding peak areas. The calibration curves are all straight lines passing through the origin. The relations between peak areas and volumes are as follows:

\[
A_{N_2} = 4291.8 V_{N_2} \quad \text{and} \quad A_{O_2 + Ar} = 4237.3 V_{O_2 + Ar},
\]

where \( V_{N_2}, V_{O_2 + Ar} \) are volumes of N₂, O₂ + Ar (µl).

**Recovery Efficiency of Concentration**

As shown in Figure 1, a 6 µl sample of dry air is injected in two ways. One sample is injected directly from injection port 6, the other from injection port 2 and transported to the concentration column (−196 °C) by ultra pure hydrogen. In Table I it can be seen that the peak areas of O₂ + Ar and N₂ are only 483.1 and 1623.0 when two liters of the ultra-pure hydrogen are concentrated. Since it needs only 30 to 40 sec to transport the injected air using pure hydrogen as carrier gas the amounts of O₂ + Ar and N₂ trapped from the hydrogen are very small in comparison with the amounts of air injected. The peak areas of those impurities can be accordingly neglected in calculating the recovery efficiency. Table I shows that the concentration of O₂ + Ar and N₂ is complete at flow-rates of sample gas ranging from 200 to 600 ml min⁻¹.

**Analysis Process**

As shown in Figure 1, when a given amount of sample is concentrated at constant flow-rate the sampling valve \( V_1 \) is turned to the “ON” position and the Dewar vessel containing liquid nitrogen is removed. For a stable baseline and good quality separation, it is necessary to wait 15–20 sec to desorb the hydrogen naturally before releasing adsorbed impurities. When a hot water bath at 80 °C is placed round the concentration column the “START RUN” key on the chromatograph is pressed simultaneously.

**Minimum Detectable Level**

According to the minimum peak area detected by the integrator, the minimum detectable level for O₂ + Ar and N₂ with a 10 litre sample is around 0.2 and 0.4 ppb (v/v) respectively.

**Results and Discussion**

**Source of Blank**

The blank is a most important factor affecting analytical accuracy in trace gas analysis and will become more serious due to its accumulation during concentration. It arises mainly from the following three aspects.

1. **Preconcentration volume of sample gas.** The concentration volume is usually calculated from the initial placement of liquid nitrogen around the concentration column, but the calculated volume is not equal to the practical concentration volume. As we know, a backflow of concentrated gas will occur owing to the sharp fall in temperature at the start of concentration. This phenomenon will cause a portion of air to be adsorbed on the concentration column at a small flow-rate of sample gas. To avoid serious back-flow, a large flow-

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**Table I Recovery efficiency of preconcentration**

<table>
<thead>
<tr>
<th>Method of injection</th>
<th>Flow-rate of ultra pure hydrogen, ml min⁻¹</th>
<th>Peak areas</th>
<th>Recovery efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O₂ + Ar</td>
<td>N₂</td>
</tr>
<tr>
<td>Direct injection*</td>
<td></td>
<td>5340.1</td>
<td>20349.4</td>
</tr>
<tr>
<td>Preconcentration</td>
<td></td>
<td>5340.8</td>
<td>20349.0</td>
</tr>
<tr>
<td>injection*</td>
<td></td>
<td>5331.1</td>
<td>20320.7</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td>5335.7</td>
<td>20319.0</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>5327.3</td>
<td>20323.5</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td>483.1</td>
<td>1623.0</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 6 µl dry air injected by micro syringe.