TECHNICAL REPORT

In-Line Gas Chromatograph for Analysis of UF₆ and/or F₂

Susumu SUGIKAWA and Takeshi TSUJINO

Fuel Reprocessing Laboratory, Division of Nuclear Fuel Research, Japan Atomic Energy Research Institute*

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With the view of continuous analysis of UF₆ and/or F₂ in the fluorination of U for the development of the fluoride volatility process, an in-line gas chromatograph, made of anti-corrosive materials against the fluorides, has been constructed using two different columns and automatic sampling system.

The separation columns used, were optimized for the simulated process gas composition \((\text{N}_2, \text{O}_2, \text{F}_2)/(\text{UF}_6)=18, (\text{N}_2, \text{O}_2)/(\text{F}_2)=3.3\), in order to obtain the complete peak separation. The column selected for UF₆ analysis is 0.4 cmφ Cu tubing of 3 m long packed with 40% of poly-trifluoromonochloro-ethylene oil which is loaded on poly-tetrafluoroethylene powder. The column for F₂ analysis is the combination of the above column with a conversion column of 0.4 cmφ tubing of 2 m long packed with KCl powder.

Under these column conditions, the analytical time is 9 and 3 min for UF₆ and F₂, respectively at the flow rate of 100 ml/min. The calibration curves are linear with a zero intercept, and the analytical limits are, respectively 0.2 and 1 mmHg in partial pressures of UF₆ and F₂ with 10 ml of sampling volume.

In actual adaptation to the fluorination of uranium oxides, the in-line gas chromatograph was satisfactorily able to measure the reaction rate and to detect the end of fluorination.

KEYWORDS: in-line gas chromatograph, uranium hexafluoride, fluorine, separation column, automatic sampling system, peak separation, accuracy, differential thermal conductivity cell, reaction monitor, fluoride volatility process, fluorination

I. INTRODUCTION

An in-line analysis of UF₆ and F₂ is indispensable in the reprocessing by fluoride volatility process and also in the UF₆ production for isotopic enrichment.

The various analytical methods have been reported such as gas chromatography, mass spectrometry, infrared spectrometry and differential thermal conductivity cell (TCC). In all the analytical equipments, material limitations, however, are encountered due to the high reactivities of fluorides.

Among the various analytical procedures, the in-line gas chromatograph is widely used with the advantage of easy design providing many data.

The analysis of halogens and their compounds such as UF₆, F₂, HF, Cl₂ and Cl₂ by an in-line gas chromatograph has been reported by Hamlin, Million and Swope et al. in the region of low concentration.

The in-line gas chromatograph for the high concentration of UF₆/F₂ was constructed by the present authors to use in the fluorination of uranium oxides with F₂.

In this paper, are described of the chromatograph system, the results obtained in column optimization test and the performances in the actual analysis.

* Tokai-mura, Ibaraki-ken.
II. SYSTEM OF IN-LINE GAS CHROMATOGRAPH

1. Design Concept

(1) Gas Composition

The objective gases for analysis in the fluorination of uranium oxides, are UF₆ (0~10%), F₂ (0~20%), O₂ (0~10%) and N₂ (80~100%).

(2) Column Selection

As the simultaneous peak separations are difficult with a single column for the above gas compositions, two different columns are necessary for the separation of UF₆ from the other gases and for that of F₂ from the rest. In the latter separation, F₂ must be converted to Cl₂ by KCl to get easily peak separation. The UF₆ separation column must be operated at slightly higher temperatures than that of the ambient surroundings to avoid condensation of UF₆.

(3) Note about Reactive Fluoride Gases

Against reactivities of the fluorides, such anti-corrosive materials as Ni, Cu, brass, poly-trifluoromonochloro-ethylene (PTFE) and poly-tetrafluoro-ethylene (Teflon), have to be used for tubing, sampler as well as column. Air-tightness of the system is also necessary to prevent in-leakage of atmospheric moisture and leakage of process gases. Leak rates are limited below 10⁻³ atm.cc/sec under the pressure difference of 380 mmHg.

The sample gases after analysis, are treated chemically with soda lime traps to avoid their release to atmosphere.

(4) Easy Maintenance

The exchanges of columns and traps are easily possible keeping the air-tightness.

(5) Short Analytical Time

The short time separation of UF₆ is preferable to obtain as many data as possible in 3 to 5 hr of the fluorination of uranium oxides.

2. System of Gas Chromatograph

A schematic diagram of the system is shown in Fig. 1.

(1) Operation Principle

Before analysis in the run, the apparatus is repeatedly treated with F₂ and UF₆ to eliminate the reactive materials such as moisture and impurities. The process gases are continuously drawn into a sampling tube from the fluorinator with a diaphragm pump through the soda lime trap. The carrier gas flows into the thermal conductivity detector.

By automatic operation of the sampler valves, the sample gas in the sampling tube is swept into the column (I or II) with the carrier gas. Output of the detector is finally recorded.

(2) Principal Components

The sampler which consists of six brass pneumatic valves (Hoke Co. Ltd., USA) is shown in Fig. 2.

Their preparative and analytical actuations are automatically made by means of the programmed timer, opening or closing the corresponding valves.
The thermal conductivity detector is a flow-through type made of two Ni filaments (30 Q) and Teflon body (Okura Co. Ltd., Japan).

The pressure gage (A) used for calibration, consists of Ni bellows, differential transformer and converter. The measurable pressure range is from 0 to 50 mmHg abs.

III. OPTIMIZATION OF COLUMN CONDITIONS

Although the separation columns for trace amounts of UF6 or F2 have been studied, these column conditions are not suitable to separate completely the peaks with high concentrations of UF6 formed in the fluorination of uranium oxides and residual F2. In order to optimize the column conditions so that the complete peak-separations may be obtained, the preliminary experiments were conducted.

1. Peak Separations

(1) UF6 Separation Column (column I)

Based on the available data, PTFE oil and Teflon powder were chosen for column loading and support, respectively.

Optimization experiments were made to find an operational column conditions with the parameters of gas flow rate, column length and PTFE oil grade and its concentration. The optimized column conditions are summarized in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Optimum column conditions for objective UF6 and F2 separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
</tr>
<tr>
<td>Conversion column</td>
</tr>
<tr>
<td>Reactant</td>
</tr>
<tr>
<td>Length &amp; diameter</td>
</tr>
<tr>
<td>Separation column</td>
</tr>
<tr>
<td>Support Teflon (32~80 mesh)</td>
</tr>
<tr>
<td>Loading 40% PTFE oil</td>
</tr>
<tr>
<td>(degree of polymerization)</td>
</tr>
<tr>
<td>Japan</td>
</tr>
<tr>
<td>Length &amp; diameter</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Total flow rate</td>
</tr>
</tbody>
</table>

As seen in Table 2, the peak of UF6 is completely separable from those of N2, O2 and F2 under the simulated process conditions. The retention time (tR) and resolution (R) are about 6 min and above 1.2, respectively. Although large sampling volume (V) is preferable in order to raise sensitivity, R is lowered with increasing V. The limitation of V is thus estimated to be about 12 ml by analyzing experimental data.

<table>
<thead>
<tr>
<th>Table 2 Example of column characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Columns</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>F2</td>
</tr>
<tr>
<td>I</td>
</tr>
<tr>
<td>108</td>
</tr>
<tr>
<td>II</td>
</tr>
<tr>
<td>84</td>
</tr>
</tbody>
</table>

Sampling conditions: Sampling volume, 5 ml
Compositions: UF6 40~60 mmHg, F2 200~250 mmHg, N2 700 mmHg, air 710 mmHg

(2) F2 Separation Column (column II)

To separate the peak of F2 directly from those of N2 and O2, a sintered silicagel column was first tested at -78°C. The resolution was obtained to be only 0.7 so that this column was not suitable for the purpose.

In the present method, F2 in the sample gas is converted into Cl2 by the reaction...
with KCl powder in the reaction part of column II and the Cl₂ produced flows into the separation part in the same column. As seen in Table 2, the peak of Cl₂ is well separated from those of N₂ and O₂ with the optimized column. The unconverted fraction of F₂ to Cl₂ is constant at about 3~4% which is negligible in the analysis.

The UF₆ which coexists with F₂, can also be separated by the combination with a NaF trap as used already in the TCC system\(^{(5)}\).

2. Other Characteristics of Column I

Peculiar behavior of UF₆ in the column I was found that the asymmetry (As) of the peak is large in tail, which indicates instability and low sensitivity. Effect of the flow rate on the HETP\(^{(11)}\) (Height Equivalent to a Theoretical Plate) is shown in Fig. A1. The curve for nitrogen fits more closely than that for UF₆ to the theoretical equation (1) which is defined in Appendix. However, the UF₆ curve is abnormal indicating interaction between UF₆ and loading liquid. The concentration effect of UF₆ on the distribution coefficient \((K)\) is shown in Table 3.

<table>
<thead>
<tr>
<th>UF₆ (mmHg)</th>
<th>11</th>
<th>21</th>
<th>41</th>
<th>55</th>
<th>64</th>
<th>75</th>
<th>84</th>
</tr>
</thead>
<tbody>
<tr>
<td>(t_R (\text{min}))</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
<td>10.8</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>(K)</td>
<td>109</td>
<td>109</td>
<td>109</td>
<td>109</td>
<td>109</td>
<td>109</td>
<td>111</td>
</tr>
</tbody>
</table>

\(^{1}\) With 5 ml of sample volume

The \(K\) values are nearly constant, showing that the concentration dependency of the column I is linear type in the range tested.

IV. OPERATING TEST AND ACTUAL UTILIZATION

1. Operating Test

(1) Stability

In order to obtain the stable column conditions, especially for the column I, the system must be treated repeatedly with F₂ and/or UF₆ just before the analysis to eliminate the moisture accompanying with the carrier gas and leaking in the apparatus.

The constant UF₆ peak was obtained only after more than eight samplings of 10 ml (20 mmHg partial pressure of UF₆) in this system. After the system was left in un-used state for about 2 days, this peak height decreased by several tens percent due to intake of humidity in the column. However, the peak was recovered by the treatments described. It is recommended that the calibration curve must be checked just before and after the analysis.

(2) Response Time

Total response time for the analysis including sampling, separation in the column and detection is about 9 min for UF₆ and 3 min for F₂. Most of the response time is due to separation in the column. The transport lag of about 3 min in the sampling line is negligible compared with the 3 to 5 hr fluorination of uranium oxides.

(3) Calibration Curves

The calibration curves were obtained by the standard UF₆ and F₂ gases. As shown
in Fig. 3, their calibration curves are linear with a zero intercept. The standard deviations are about 4 and 6%, respectively. The detection limits are about 0.2 and 1 mmHg (10 ml sampling), corresponding respectively to about 0.02 and 0.1% in the concentrations of UF₆ and F₂ under the sampling pressure at about 1,000 mmHg.

2. Actual Utilization

(1) Use as Reaction Monitor
The in-line gas chromatograph was actually used for the continuous analysis of UF₆ in the fluorination of uranium oxides by the 3 in. diameter fluid-bed. The examples of gas chromatogram obtained are shown in Fig. 4.

![Fig. 4 Example of gas chromatogram obtained in U fluorination](image)

By altering the reaction conditions such as F₂ concentrations and temperature, the change of reaction rates was correspondingly measured and the end of the reaction was clearly indicated. As seen in Table 4, which shows the material balance of UF₆, the integral results of in-line analysis agree within 13% with those obtained batchwise by spectrophotometry. Reliability of the reaction monitor was thus demonstrated. By the integral uranium quantities which are precisely measured by spectrophotometry, each analytical value found by gas chromatograph could be corrected to a small bias value.

(2) Comparison with TCC
The TCC system has the advantage of simplicity in structure. However, its output is influenced by variations of the flow rate, pressure, surge noise and HF in the sample gas.
On the other hand, the gas chromatogram is not affected by the above variations, but the apparatus is more complicated than the TCC because of the gas chromatograph possesses the unstable columns and the intricate sampling system. The sensitivities and accuracies are estimated to be the same as those of the TCC.

In the application as the in-line monitors, the gas chromatograph is suitable for analysis of multi-component gases especially including impurities (e.g. HF and other halides). The TCC is preferable in simple analysis of UF₆ and F₂ as a reaction monitor.

(3) Technical Problems
To increase the accuracy of analysis, the improvement of air-tightness and the removal of moisture from the carrier gas are actually effective, especially in the solenoid valves and detector equipped with Teflon joint and also in the ordinary carrier gas system.
As makeshift means, the leakages were prevented with adhesive agent and silicon grease.
Stability and durability of the UF₆ column must further be studied, and the manifold has to set so as to facilitate the calibration before and after the analysis.

V. CONCLUSION

An in-line gas chromatograph constructed trially, has been used successfully in the continuous analysis of UF₆ as the reaction monitor in the fluorination of uranium oxides. The process data on reaction rate were obtained and end of fluorination was clearly shown.
Further studies are necessary on improving the system air-tightness to increase the UF₆ column stability and on framing easy calibration system.
[NOMENCLATURE]

As: Asymmetry, \( W / (W - (HW_T - HW_L)) \)

HW: Half peak width

R: Resolution, \( t_{R1} - t_{R2} / (HW_1 - HW_2) \)

tR: Retention time, W: Peak width

\( \sigma \): Standard deviation

Suffix

T: Tail in peak, L: Lead in peak

1. Object peak, 2: Influencing peak

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REFERENCES


[APPENDIX]

HETP and Distribution Coefficient

From the rate theory, HETP generally defined as:

\[ HETP = A + B/u + C \cdot u \]  

(A1)

where A is the eddy diffusion term and B the molecular diffusion term and C the mass transfer term. The HETP is shown as a function of the linear velocity (u).

From the mass transfer theory, the distribution coefficient (K) is defined as:

\[ K = V_O / V_L (t_R / t_{RC} - 1) \]  

(A2)

where \( V_O \) and \( V_L \) are the gas volume of gas phase and the liquid volume of liquid phase in unit column length, respectively. The \( t_{RC} \) is the retention time for the carrier gas.

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Fig. A1 Effect of flow rate on HETP in column I