

## **Elimination of AsF<sub>3</sub> from anhydrous HF using AgFAsF<sub>6</sub> as a mediator<sup>†</sup>**

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<sup>†</sup>Dedicated to the late Professor Neil Bartlett in recognition of his many achievements in inorganic fluorine chemistry, including transition metal fluorides in high oxidation states.

## Abstract

Elimination of the arsenic (III) impurity  $\text{AsF}_3$  from anhydrous hydrogen fluoride has been demonstrated using a bench-scale apparatus (~500 mL of HF), with a Ag(II) salt  $\text{AgFAsF}_6$  as a mediator. In this process,  $\text{AsF}_3$  is oxidized by  $\text{AgFAsF}_6$  to  $\text{AsF}_5$ . In the next step,  $\text{AsF}_5$  is eliminated from HF by reaction with NaF. The oxidizer,  $\text{AgFAsF}_6$ , is reduced to  $\text{AgAsF}_6$  which is regenerated to  $\text{AgFAsF}_6$  by  $\text{F}_2$  in HF at room temperature. This method can reduce the arsenic content in HF from a few hundred ppm to the industrially-required level (<3 ppm). The results for three other methods (distillation, oxidation by  $\text{F}_2$  gas, and oxidation by  $\text{K}_2\text{NiF}_6$ ) are reported and compared with the  $\text{AgFAsF}_6$  method in a preliminary examination (using ~4 mL of HF).

## 1. Introduction

Hydrogen fluoride is the precursor for many fluorine-containing materials and is also used as a fluorinating reagent or a solvent. Hydrogen fluoride is manufactured on a scale of millions of tons per year, mainly by the reaction of fluorite (also called fluorspar) and sulfuric acid, but resources of the high-quality fluorite required for industrial preparation are limited to certain areas, such as China. However, appropriate treatment may reduce impurities in the resulting HF, allowing lower-quality fluorite to be used.

The main impurities resulting from the reaction between fluorite and sulfuric acid such as  $\text{SiF}_4$  and  $\text{SO}_2$  are usually removed by fractional distillation. Impure fluorite can contain arsenic species with an oxidation state of three, which is much more difficult to remove from HF. This is because the As(III) species is converted in anhydrous HF to  $\text{AsF}_3$  which has similar physical and chemical properties to HF (*e.g.* boiling point: 19 °C for HF and 57 °C for  $\text{AsF}_3$ ) [1,2]; in addition there is a possibility of interaction between HF and  $\text{AsF}_3$  molecules that may impede the separation by distillation. Several techniques have already patented for the removal of  $\text{AsF}_3$  from HF [3]. One plausible method would be oxidation of As(III) to As(V) using a strong oxidizer such as  $\text{F}_2$  or  $\text{H}_2\text{O}_2$ . The product  $\text{AsF}_5$ , as opposed to  $\text{AsF}_3$ , has completely different physical and chemical properties to those of HF, so it can be more easily removed. However, slow reaction rate, oxidizing reagent recovery, and generation of industrial wastes remain problematic.

In this communication, a new oxidizing pathway for As(III) to As(V), using a silver complex salt

Ag(II)FAsF<sub>6</sub>, is examined to allow effective removal of As impurity from HF. The target As content in HF was below 3 ppm, which represents a sufficient purity for industrial use. The starting As content was adjusted to a few hundred or thousand ppm to reflect HF synthesized from As-containing fluorite such as that produced in Mexico. The oxidizing salt, AgFAsF<sub>6</sub>, was first reported in 1982 [4], and was characterized by several methods [5-7]. The solid-state structure of AgFAsF<sub>6</sub> contains a cationic (Ag-F)<sub>n</sub> chain, and an octahedral AsF<sub>6</sub> group cross-linked to the chain via F bridges [5]. On the other hand, AgFAsF<sub>6</sub> dissociates into AgF<sup>+</sup> and AsF<sub>6</sub><sup>-</sup> in anhydrous HF, resulting in lower oxidizing power than the naked Ag<sup>2+</sup> cation [7-10]. Following the oxidation of As(III) to As(V), AgFAsF<sub>6</sub> can be easily regenerated using F<sub>2</sub> gas at room temperature. Although the oxidation can be performed using other AgFAF<sub>6</sub>-type compounds (for example, AgFSbF<sub>6</sub>), AgFAsF<sub>6</sub> is preferred because the risk of contamination is lower.

## **2. Results and discussion**

### *2.1 Preliminary examination*

Table 1 summarizes typical preliminary examination results for the removal of As from HF using AgFAsF<sub>6</sub>, as well as for methods using distillation, elemental fluorine, and K<sub>2</sub>NiF<sub>6</sub> which were performed for comparison.

#### *2.1.1 Distillation*

According to the analysis, the As concentration in the original, distilled, and residual HF samples

was the same, at 1600 ppm each. The original HF sample was prepared from AsF<sub>3</sub> and HF. The distilled HF sample was produced by distillation into another reactor, and the residual HF sample was that left behind after distillation. If the distillation works, then distilled sample should be poorer in As(III) than original sample, and the residual sample should be richer in As content than original sample. This result means that simple distillation is not effective for reducing the As content in HF.

### 2.1.2 Oxidation by elemental fluorine

The effectiveness of elemental fluorine in removing the As impurity was examined (at room temperature) by introducing F<sub>2</sub> in the gas phase over HF containing AsF<sub>3</sub> (eq. 1) and treating with NaF to completely remove the product AsF<sub>5</sub> (eq. 2).



According to the patent covering this process, a small amount of F<sub>2</sub> gas is quite effective, even within a short period [3]. However, the results of the current study suggest that F<sub>2</sub> gas treatment under ambient conditions does not decrease As concentration to the target level (As < 3 ppm). This is presumably due to the low solubility of F<sub>2</sub> gas in HF, although different experimental conditions, such as water impurity and the agitation method used, may have affected the results.

### 2.1.3 Oxidation by $K_2NiF_6$

Removal of As was also performed via oxidation by  $K_2NiF_6$ , which is a very strong oxidizer of Ni(IV) [11,12]. The process is based on the following equation (eq. 3).



Further treatment to fix  $AsF_5$  was not necessary, since it was trapped in the reactor as nonvolatile  $KAsF_6$ . The final sample was obtained by distilling HF from the  $K_2NiF_6$  reactor to another reactor.

This treatment is effective for reducing the As content from a few hundred ppm to a value below 3 ppm. The high solubility of  $K_2NiF_6$  in HF is thought to facilitate the fluorination of  $AsF_3$  even under ambient conditions. However, the supply of costly  $K_2NiF_6$  is a drawback since the regeneration of the products to  $K_2NiF_6$  requires fluorination by elemental fluorine at a high temperature.

### 2.1.4 Oxidation by $AgFAsF_6$

The use of  $AgFAsF_6$  as an oxidizer to remove As from HF is based on the following reaction (eq. 4).



The reaction proceeds readily since  $AgFAsF_6$  has sufficient solubility into HF. In this case treatment with NaF is necessary for fixing  $AsF_5$  (eq. 2). However, the concentration of  $AsF_5$  after

the first cycle was low even before treating with NaF. This is because of the high solubility of AsF<sub>5</sub> into the residual HF in the reactor. Repetitive AgFAsF<sub>6</sub> treatments gave increasingly more AsF<sub>5</sub> in the distilled HF. After NaF treatment, the final HF had less than 3 ppm of As, compared to a starting concentration of a few hundred ppm. Unlike oxidation by elemental fluorine, this method does not require removal of F<sub>2</sub> from the anhydrous HF product and continuous oxidation is possible as long as AgFAsF<sub>6</sub> exists in the system.

Since the validity of the AgFAsF<sub>6</sub> treatment was confirmed in the preliminary examination, this method was scaled up as shown in the next section.

## 2.2 Bench-scale demonstration

The concept of As removal using AgFAsF<sub>6</sub> at an industrial level is shown in Fig. 1. A schematic illustration of the reaction line for the bench-scale demonstration is shown in Fig. 2. A photograph of the PFA (poly(tetrafluoroethylene-*co*-perfluoro(alkyl vinyl)ether)) reactor used in the bench-scale demonstration can be seen in Fig. S1 (Supplementary material).

The oxidizing reagent AgFAsF<sub>6</sub> was prepared from AgAsF<sub>6</sub> in 70 mL of aHF, by fluorination with diluted F<sub>2</sub> gas (F<sub>2</sub> : N<sub>2</sub> = 30 : 70), under vigorous agitation in Reactor (B) (eq. 5).



Diluted F<sub>2</sub> gas was used because it is less corrosive than 100% elemental fluorine, so it is the preferred choice in industrial application. Figure 3 shows the time dependence of the pressure in

the reactor during fluorination, where the gas phase consists of the diluted  $F_2/N_2$  gas and HF vapor. The solution began to turn blue within a few minutes of introducing fluorine gas, and the pressure showed a steep decline during the first twenty minutes. The decrease in pressure ceased within 90 minutes. At this stage, the color of the HF solution was dark blue. The yield of  $AgFAsF_6$ , calculated using the uptake of  $F_2$  gas and the initial amount of  $AgAsF_6$  was 87 %. It should be noted that the amount of  $F_2$  gas consumed in the first minute of the reaction could not be measured, as the pressure in the reactor had not yet stabilized. The yield can be increased by adding this amount of  $F_2$  gas.

In the next step, approximately 430 mL of a mixture of HF and  $AsF_3$  was prepared in Reactor (A) and transferred into Reactor (B) by distillation. Arsenic trifluoride was oxidized by  $AgFAsF_6$  in Reactor (B) and the resulting HF sample was transferred to Reactor (C) by distillation, where  $AsF_5$  was trapped by NaF as  $NaAsF_6$ . The final HF was sampled from Reactor (C) by distillation. This 500 mL-scale demonstration successfully reduced the As impurity from a few hundred ppm in the original HF to a concentration below 3 ppm. The solution in Reactor (B) became less and less blue as the  $AgFAsF_6$  treatment was repeated, and finally became colorless. Regeneration of  $AgFAsF_6$  from  $AgAsF_6$  was performed in the same manner as its preparation above. In practical processes, accumulating  $NaAsF_6$  must be removed from the reactor after a certain number of treatments. If  $AgFAsF_6$  regeneration or  $NaAsF_6$  removal is time-consuming, a second reactor may need to be installed in parallel to the first.



### 3. Experimental

#### 3.1 General experimental procedure

Moisture-sensitive materials were handled in a glove box under a dry Ar atmosphere. Volatile materials were handled in a reaction line made of stainless steel pipes (SUS-316, 1/2-inch o.d.) which were connected by stainless steel unions and valves with Kel-F tips. The line was connected to a rotary vacuum pump through a soda lime chemical trap, which was connected in series to a liquid nitrogen trap. Occasionally, direct pumping was performed through the liquid nitrogen trap only, in order to obtain a high vacuum ( $1 < \text{Pa}$ ). The pressure and vacuum of the line were monitored by Bourdon and Pirani gauges.

#### 3.2 Reagents

For bench-scale demonstration, anhydrous hydrogen fluoride (Stella Chemifa, purity > 99 %) was used as supplied, but for the small-scale demonstration it was treated with  $\text{K}_2\text{NiF}_6$  prior to use. Arsenic trifluoride was prepared by reaction of  $\text{As}_2\text{O}_3$  and HF according to the literature method [13] and stored over NaF. Diluted  $\text{F}_2$  gas was prepared by mixing  $\text{F}_2$  (Daikin Industries) and  $\text{N}_2$  (extra pure grade, Japan Air Gases) in a ratio of 30 to 70 prior to use.

#### 3.3 Reactions in the preliminary examination

Unless otherwise specified, the term “distillation” is taken to mean the transfer of volatile compounds from a reactor at room temperature to another reactor at  $-196\text{ }^\circ\text{C}$ . An h-shaped PFA

reactor, equipped with a stainless steel valve at the top and with a PFA valve at the side-arm, was used for the preliminary reactions (Fig. S2 in Supplementary data). The PFA reactor, HF container, and AsF<sub>3</sub> container were connected via a three-way PFA connector. To prepare HF with the AsF<sub>3</sub> impurity, AsF<sub>3</sub> was distilled into the main arm of the h-shaped reactor, and about 4 mL of HF was distilled on it. The amount of AsF<sub>3</sub> was roughly estimated using the volume of the reaction line, The mixture was then warmed up to room temperature and stirred for a few minutes.

### *3.3.1 Removal of As impurity by distillation*

Approximately 4 mL of HF with AsF<sub>3</sub> impurity was prepared in the main arm of an h-shaped reactor, using the method described in section 3.3. Half of the sample was poured into the side arm and the PFA valve was closed. The other half in the main arm was distilled onto ~4 mL of frozen H<sub>2</sub>O to give Sample D-1. Half of the mixture in the side arm was distilled onto ~4 mL of frozen H<sub>2</sub>O in another PFA reactor and collected as Sample D-2 and the remainder was distilled onto ~4 mL of frozen H<sub>2</sub>O in one more PFA reactor (Sample D-3). These samples provide the As content in three states: the original HF (Sample D-1), the distilled HF (Sample D-2), and the residual HF (Sample D-3), as shown in Table 1.

### *3.3.2 Removal of As impurity using elemental fluorine*

Approximately 4 mL of HF with AsF<sub>3</sub> impurity was prepared in the main arm of an h-shaped reactor, using the same method described in section 3.3. Half of the HF sample was poured into

the side arm, and the PFA valve was closed. The other half was distilled onto ~4 mL of frozen H<sub>2</sub>O in another PFA reactor (Sample F-1). The contents of the side tube were then distilled into a separate PFA reactor (~80 mL in volume) equipped with a stainless steel valve. Approximately 0.4 atm of F<sub>2</sub> gas was introduced into the gas phase at room temperature, followed by vigorous agitation for 40 minutes. The fluorine gas was pumped off under vacuum at -85 °C for a few minutes, and the HF sample was distilled into a PFA reactor containing 100 mg of NaF. The solution was warmed up to room temperature and stirred for five minutes, during which time the NaF completely. Most of the resulting HF was distilled onto ~4 mL of frozen H<sub>2</sub>O in another PFA reactor to give Sample F-2. Complete transfer of HF was difficult at this stage, due to the strong HF-absorption ability of NaF (forming Na(FH)<sub>n</sub>F [14,15]). Sample F-1 provided the As content of the original HF, and Sample F-2 provided that of the HF treated with F<sub>2</sub> as shown in Table 1.

### 3.3.3 Removal of As impurity using K<sub>2</sub>NiF<sub>6</sub>

Approximately 4 mL of HF containing AsF<sub>3</sub> impurity was prepared as described in 3.3. Half of the HF sample was poured into the side arm of the h-shaped tube and the PFA valve was closed. The HF in the main tube was distilled onto ~4 mL of frozen H<sub>2</sub>O in a PFA reactor (Sample Ni-1). The contents of the side tube were then distilled onto K<sub>2</sub>NiF<sub>6</sub> (128 mg) in a PFA reactor equipped with a stainless steel valve. A red-purple HF solution of K<sub>2</sub>NiF<sub>6</sub>, obtained by warming up the mixture to room temperature, was stirred for five minutes. Most of the resulting HF sample was

distilled onto ~4 mL of frozen H<sub>2</sub>O in another PFA reactor to give Sample Ni-2. The As content of the original HF (Sample Ni-1) and the K<sub>2</sub>NiF<sub>6</sub>-treated HF (Sample Ni-2) were obtained, as shown in Table 1.

#### *3.3.4 Removal of As impurity using AgFAsF<sub>6</sub>*

Approximately 4 mL of HF with AsF<sub>3</sub> impurity was prepared as described in section 3.3. Half of the HF sample was poured into the side arm of the h-shaped tube and the PFA valve was closed. The HF in the main tube was distilled onto ~4 mL of frozen H<sub>2</sub>O in another PFA reactor (Sample Ag-1). The contents of the side arm were distilled onto AgFAsF<sub>6</sub> (100 mg) in a PFA reactor equipped with a stainless steel valve. A blue solution, obtained by warming up to room temperature, was stirred for five minutes. This sample was distilled onto 100 mg of NaF in another PFA reactor, warmed up to room temperature, and stirred for five minutes to give Sample Ag-2. These samples provide the As content of the original (Sample Ag-1) and AgFAsF<sub>6</sub>-treated HF (Sample Ag-2).

### *3.4 Reactions in the bench-scale demonstration*

#### *3.4.1 Preparation and regeneration of AgFAsF<sub>6</sub> in the bench-scale demonstration*

The starting compound AgAsF<sub>6</sub> (8.222 g, 0.02867 mol) was loaded in a PFA reactor (~ 1 L in volume, Fig. S1) under a dry Ar atmosphere, and the reactor was connected to the reaction line

(Fig. 2) as Reactor (B). Approximately 70 mL of anhydrous HF was distilled onto the AgAsF<sub>6</sub> in Reactor (B) from a storage vessel. Tanks (A) and (B), each containing 1 L of diluted F<sub>2</sub> gas (F<sub>2</sub>: N<sub>2</sub> = 30 : 70), were connected to the reaction line. The gas in Tank (A) was introduced to Reactor (B) and the valve of Tank (A) was closed once pressure equilibrated. The gas in Tank (B) was also introduced to Reactor (B), but its valve was kept open during the reaction. This led to a volume of ~2.1 L for the gas phase contained in Reactor (B), Tank (B), and the connecting portion. The HF solution was vigorously agitated during the reaction, and the end point was confirmed by a change in color and pressure.

#### 3.4.2 Oxidation of AsF<sub>3</sub> in the bench-scale demonstration

Approximately 430 mL of HF was condensed from a storage cylinder to Reactor (A) at -90 °C. Reactor (B) contained AgFAsF<sub>6</sub>, prepared as described in sub-section 3.4.1, and Reactor (C) contained NaF (2.2 g, 0.05 mol). An amount of AsF<sub>3</sub> estimated from the volume of the reaction line was condensed onto the HF in Reactor (A) at -90 °C. The mixture was warmed up to room temperature and stirred for five minutes. Approximately 4 mL of the HF in Reactor (A) was distilled onto ~4 mL of frozen H<sub>2</sub>O in a PFA tube (Sample Bench-1). The rest was distilled onto 70 mL of HF in Reactor (B) at -90 °C. The solution was warmed up to room temperature, stirred for five minutes, and distilled into Reactor (C), where AsF<sub>5</sub> was trapped by NaF as NaAsF<sub>6</sub>.

Approximately 4 mL of the final HF in Reactor (C) was distilled onto ~4 mL of frozen H<sub>2</sub>O in another PFA tube (Sample Bench-2).

### *3.5 Analysis*

The HF sample distilled onto H<sub>2</sub>O in a PFA reactor for all the treatments above was diluted with more H<sub>2</sub>O, and sent for analysis as 3~10% hydrofluoric acid. The concentration of As in the sample was measured by ICP-AES (SPS3000, Seiko Instruments Inc.), and the concentration of HF was measured by titration.

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### **Appendix A. Supplementary data**

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jfluchem.2010.04.006](https://doi.org/10.1016/j.jfluchem.2010.04.006).

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Table 1 Summary of As removal results in preliminary examination<sup>a</sup>

	As content before treatment / ppm		As content after treatment / ppm	
Distillation <sup>b</sup>	(D-1)	1600	(D-2)	1600
Elemental fluorine	(F-1)	1600	(F-2)	18
AgFAsF <sub>6</sub>	(Ag-1)	489	(Ag-2)	<3
K <sub>2</sub> NiF <sub>6</sub>	(Ni-1)	464	(Ni-2)	<3

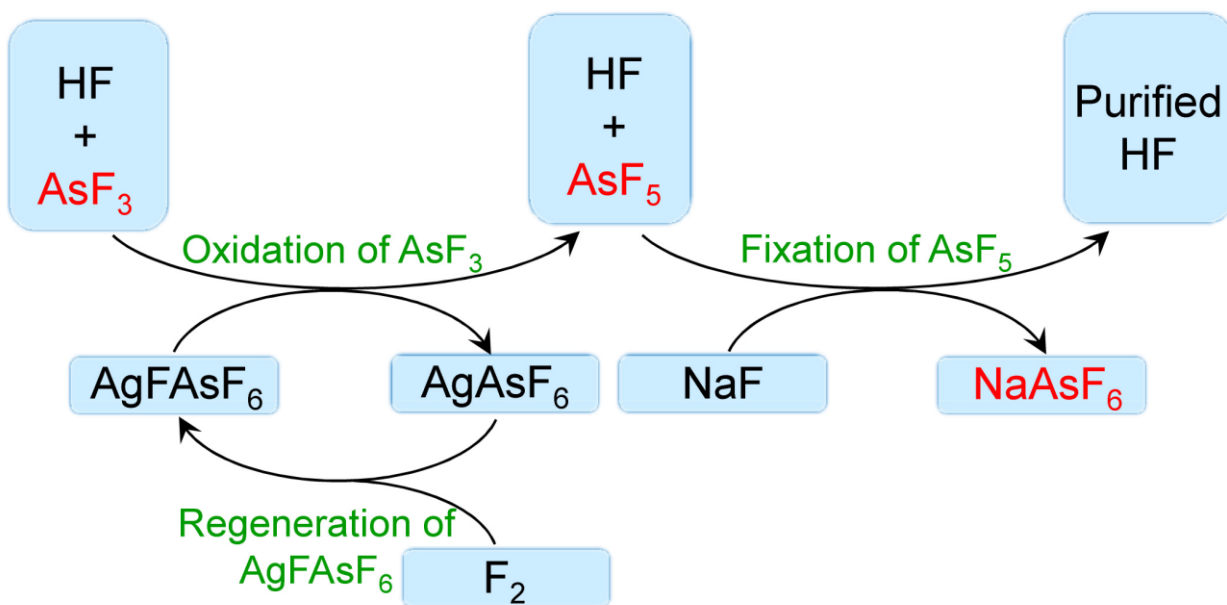
<sup>a</sup> The symbol of each result such as (D-1) refers to the sample name in Experimental section. <sup>b</sup> The As content in the residual HF sample (D-3) was also 1600 ppm.

## Figure captions

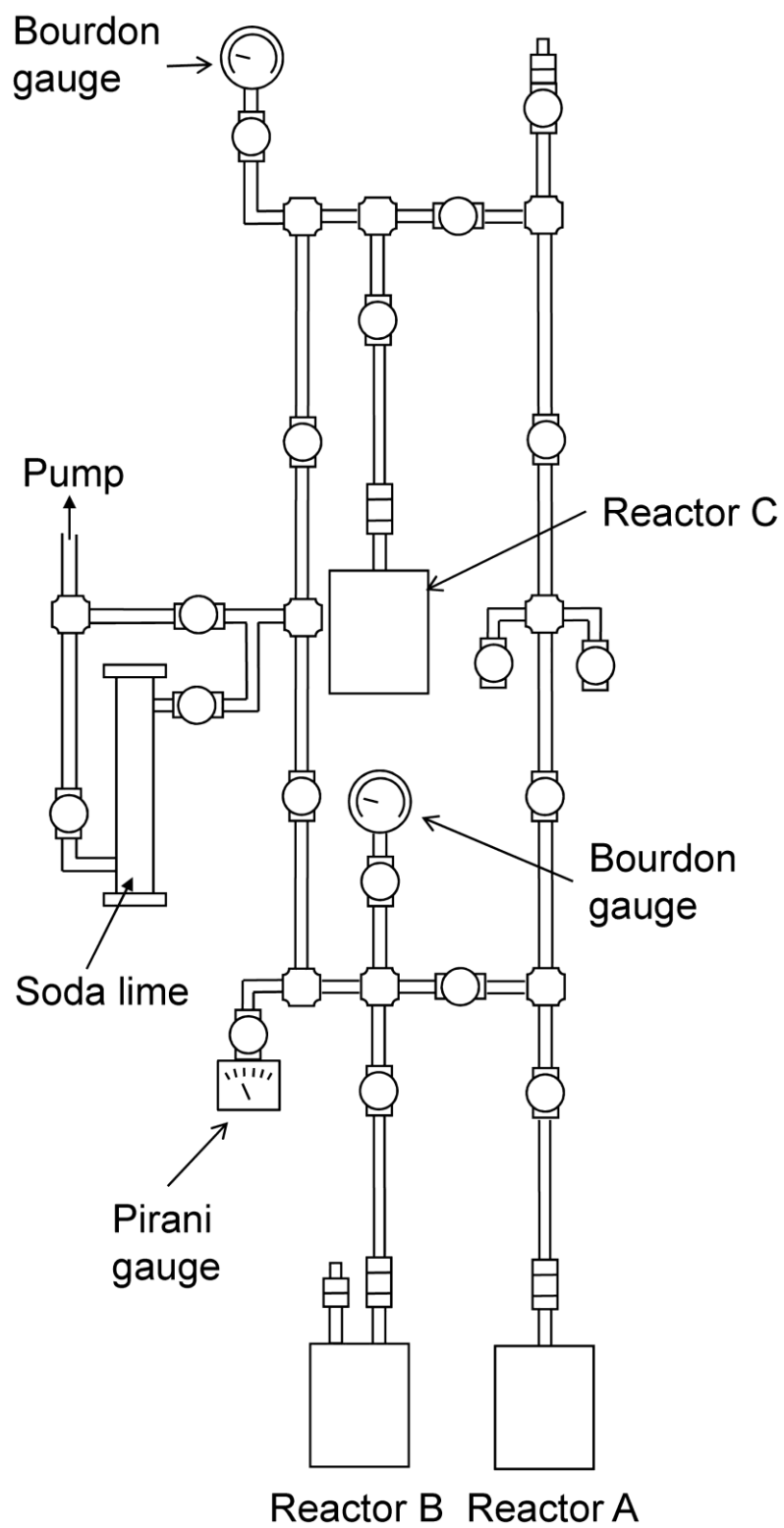
**Fig. 1** Concept of the removal of As using AgFAsF<sub>6</sub>.

**Fig. 2** Schematic illustration of the reaction line used in the bench-scale demonstration.

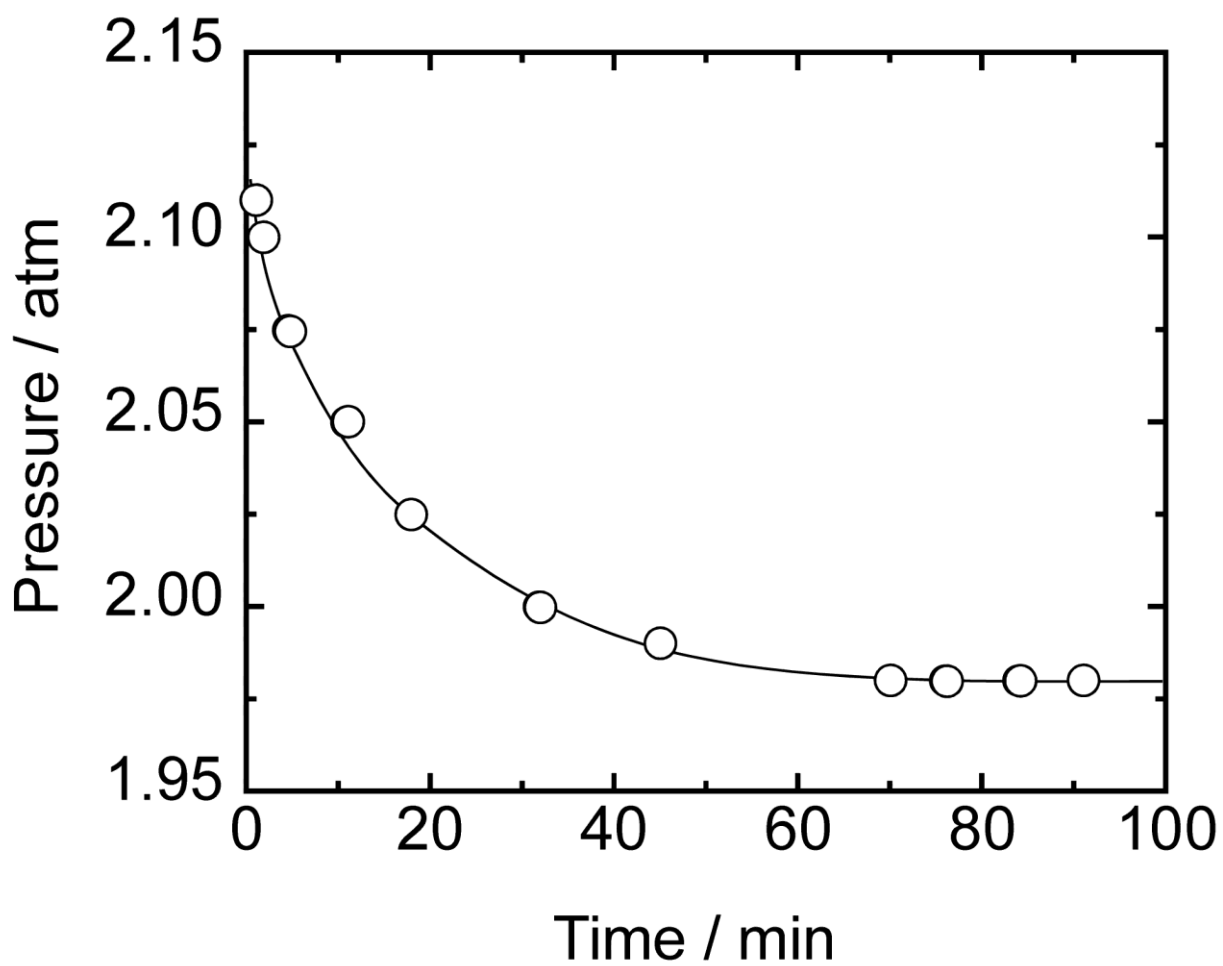
**Fig. 3** Time dependence of the pressure in the reactor during fluorination of AgAsF<sub>6</sub> by F<sub>2</sub> gas in the bench-scale demonstration.



**Fig. 1** Concept of the removal of As using  $\text{AgFAsF}_6$ .



**Fig. 2** Schematic illustration of the reaction line used in the bench-scale demonstration.



**Fig. 3** Time dependence of the pressure in the reactor during fluorination of  $\text{AgAsF}_6$  by  $\text{F}_2$  gas in the bench-scale demonstration.

## Supplementary Contents

**Elimination of AsF<sub>3</sub> from anhydrous HF by using AgFAsF<sub>6</sub> as a mediator<sup>†</sup>**

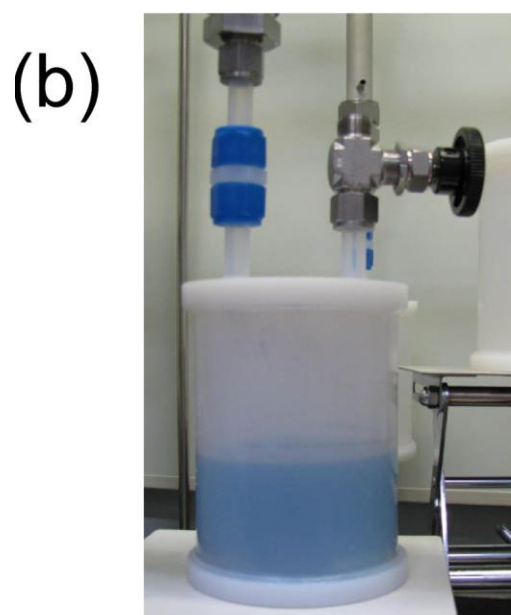
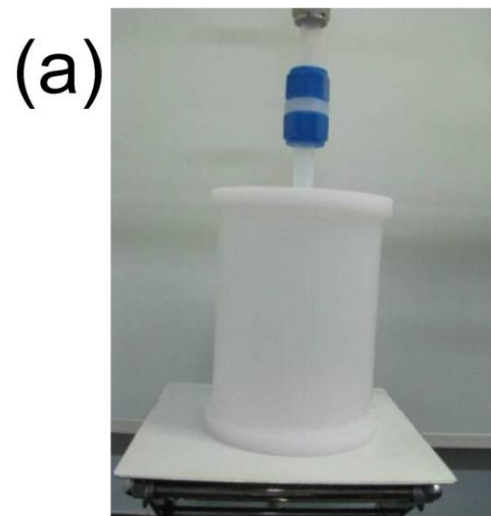
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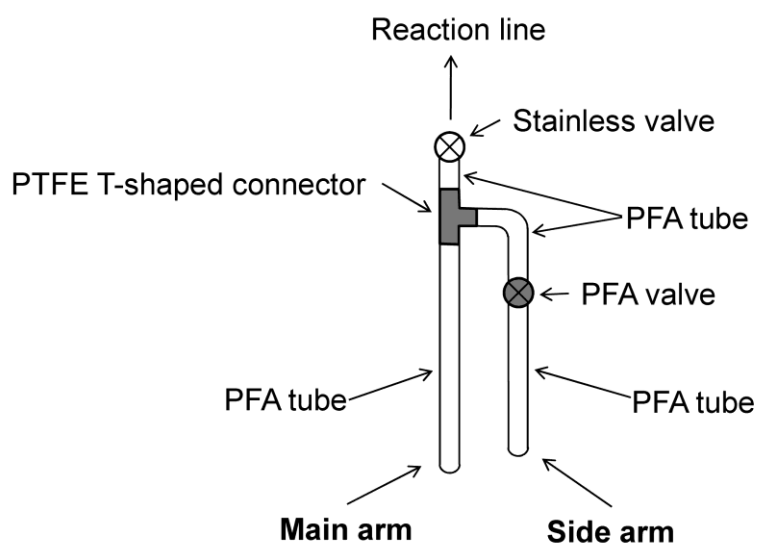
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**Fig. S1** Photographs of PFA reactors for (a) Reactor A or C and (b) Reactor B in Fig. 2. The reactor in the photograph (b) contains ~500 mL of HF with  $\text{AgFAsF}_6$ .



PTFE: poly(tetrafluoroethylene)  
PFA: poly(tetrafluoroethylene-co-perfluoro(alkyl vinyl)ether)

**Fig. S2** An h-shaped PFA reactor used for preliminary examination.