Hydrocarbon Impurities in SiF₄ and SiH₄ Prepared from It

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Abstract—Using gas chromatography and high-resolution Fourier-transform IR spectroscopy, we have determined the concentrations of C_1 – C_4 hydrocarbon impurities in isotopically unmodified silicon tetrafluoride before and after fine purification and in ²⁸Si-enriched SiF₄. The concentrations of C_1 – C_4 hydrocarbon impurities in silicon tetrafluoride for SiH₄ synthesis have been shown to correlate with those in the synthesized silane.

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INTRODUCTION

Availability of polycrystalline silicon with a concentration of carbon impurity below its solubility limit (10¹⁷ cm⁻³) is essential for the ability to grow structurally perfect silicon single crystals. The carbon content of the polycrystalline silicon can then be reduced by more than two orders of magnitude by zone melting.

Several processes have been proposed to date for the preparation of silicon, in particular, isotopically pure one, using SiF₄ as a precursor [1, 2]. Devyatykh et al. [3] described a process for the preparation of high-purity isotopically pure ²⁸Si, which involved the following steps:

preparation of silicon tetrafluoride through thermal decomposition of sodium fluorosilicate;

fine purification of SiF₄ by low-temperature fractional distillation;

centrifugal separation of silicon isotopes;

conversion of isotopically pure silicon tetrafluoride to silane, followed by fine purification and thermal decomposition of the silane.

The possible sources of carbon in the final product of this process include carbon-containing impurities in silane, which in turn may originate from the starting, isotopically pure silicon tetrafluoride. A literature search revealed no data on hydrocarbon concentrations in isotopically unmodified or isotopically pure silicon tetrafluoride.

The purpose of this work was to determine the hydrocarbon concentration in isotopically unmodified silicon tetrafluoride, as-prepared and purified, and in the resulting isotopically enriched ²⁸Si. It was of interest to assess the relationship between the hydrocarbon

concentrations in silicon tetrafluoride and silane prepared from it.

EXPERIMENTAL

Since the preparation of isotopically enriched silicon tetrafluoride involves several steps, we used several samples of silicon tetrafluoride differing in purity.

Sample 1: isotopically unmodified SiF_4 prepared through thermal decomposition of pure-grade sodium hexafluorosilicate, Na_2SiF_6 , and purified by filtration through an FP fine fiber filter (Petryanov filter).

Sample 2: the same material after further purification by low-temperature fractional distillation in a middle-fed packed column [5].

Samples 3 and 4: overhead and bottom fractions, enriched in lower and higher boiling hydrocarbons, respectively, taken after 10 h of operation in withdrawal mode.

Sample 5: silicon tetrafluoride purified by fractional distillation and then isotopically enriched via centrifugation (GAZ Experimental Design Bureau) to a ²⁸Si abundance of 99.7%.

Samples 6–8: silicon tetrafluoride after purification and subsequent isotopic enrichment to a ²⁸Si abundance above 99.99% in a centrifuge cascade (Tsentrotekh EKhZ Science and Technology Center).

Hydrocarbons were determined by gas chromatography and high-resolution Fourier-transform IR spectroscopy as described by Krylov et al. [6]. The detection limits for hydrocarbons were in the range $(2-4) \times 10^{-6}$ vol %. Concentrations exceeding the detection limit by an order of magnitude were determined with an uncertainty within 10–15%. **Table 1.** Hydrocarbon impurities in samples 1 (as-prepared, isotopically unmodified SiF_4) and 2 (purified by fractional distillation) as determined by gas chromatography

Impurity	Volume percent			
mpunty	sample 1	sample 2		
CH ₄	$(1.4 \pm 0.2) \times 10^{-4}$	$(1.4 \pm 0.3) \times 10^{-5}$		
C_2H_6	$(3.4 \pm 0.5) \times 10^{-4}$	$(1.9 \pm 0.4) \times 10^{-5}$		
C_2H_4	$(7.2 \pm 0.1) \times 10^{-4}$	$(2.0 \pm 0.4) \times 10^{-5}$		
C_3H_8	$(3.1 \pm 0.6) \times 10^{-5}$	$<\!\!2 \times 10^{-6}$		
C_3H_6	$(2.2 \pm 0.3) \times 10^{-4}$	$<3 \times 10^{-6}$		
n-C ₄ H ₁₀	$(1.5 \pm 0.3) \times 10^{-5}$	$< 6 \times 10^{-6}$		
<i>i</i> -C ₄ H ₁₀	$<4 \times 10^{-6}$	$<4 \times 10^{-6}$		

Silicon tetrafluoride was determined by gas chromatography as described by Krylov and Sorochkina [7], using a setup built around a Tswett-100 chromatograph. The detection limit for C_1 – C_4 hydrocarbons was $(2-6) \times 10^{-6}$ vol %, and the error of determination was 10-20%.

IR spectroscopic determination of SiF₄ was described in detail elsewhere [8]. At typical hydrocarbon concentrations, the error of determination was within 10%. The detection limit for methane was 1×10^{-3} vol %.

The detection limits of the gas-chromatographic and IR-spectroscopic procedures differ by about three orders of magnitude. IR spectroscopy, though incapable of determining hydrocarbon impurities in highpurity samples with high sensitivity, is useful for direct

Table 2. Hydrocarbon impurities in samples 3 (overhead) and 4 (bottom) as determined by gas chromatography (GC) and IR spectroscopy

	Volume percent			
Impurity	sample 3		sample 4	
	GC	IR	GC	IR
CH ₄	$(1.4 \pm 0.1) \times 10^{-1}$	$(1.0 \pm 0.1) \times 10^{-1}$	$(2.0 \pm 0.3) \times 10^{-5}$	<1 × 10 ⁻³
C_2H_6	$(1.4 \pm 0.1) \times 10^{-2}$	$(2.0 \pm 0.2) \times 10^{-2}$	$(1.5 \pm 0.2) \times 10^{-5}$	$< 5 \times 10^{-4}$
C_2H_4	$(8.2 \pm 0.7) \times 10^{-3}$	$<5 \times 10^{-3}$	$(2.0 \pm 0.2) \times 10^{-3}$	$< 5 \times 10^{-3}$
C ₃ H ₈	$(1.0 \pm 0.1) \times 10^{-5}$	$<1 \times 10^{-3}$	$(2.5 \pm 0.4) \times 10^{-4}$	<1 × 10 ⁻³
C ₃ H ₆	$(1.0 \pm 0.1) \times 10^{-5}$	_	$(1.2 \pm 0.1) \times 10^{-3}$	-
$n-C_{4}H_{10}$	<6 × 10 ⁻⁶	-	$(2.8 \pm 0.4) \times 10^{-4}$	-
<i>i</i> -C ₄ H ₁₀	$<4 \times 10^{-6}$	_	$(4.0 \pm 0.4) \times 10^{-5}$	_

Table 3. Hydrocarbon impurities in isotopically enriched ${}^{28}SiF_4$ samples as determined by gas chromatography (GC) and IR spectroscopy

	Volume percent						
Impurity	sample 5	samj	sample 6 sample 7		ple 7	sample 8	
	GC	GC	IR	GC	IR	GC	IR
CH ₄	$(2.7 \pm 0.5) \times 10^{-5}$	$(1.9 \pm 0.4) \times 10^{-5}$	<1 × 10 ⁻³	$(5.1 \pm 0.2) \times 10^{-5}$	<1 × 10 ⁻³	$(6.3 \pm 0.9) \times 10^{-5}$	<1 × 10 ⁻³
C_2H_6	$\begin{array}{c} (2.0\pm 0.4)\times \\ 10^{-5} \end{array}$	$(7.4 \pm 0.7) \times 10^{-3}$	$(4.0 \pm 0.4) \times 10^{-3}$	$(3.4 \pm 0.3) \times 10^{-3}$	$(1.5 \pm 0.2) \times 10^{-3}$	$(8.1 \pm 0.8) \times 10^{-4}$	${}^{(4.0\pm0.4)\times}_{10^{-4}}$
C_2H_4	${}^{(1.1\pm0.2)\times}_{10^{-5}}$	$(6.3 \pm 0.6) \times 10^{-3}$	<3 × 10 ⁻³	$(3.6 \pm 0.3) \times 10^{-3}$	<3 × 10 ⁻³	$(9.4 \pm 0.7) \times 10^{-3}$	<3 × 10 ⁻³
C_3H_8	${}^{(1.6\pm0.3)}_{10^{-5}}\times$	$(2.6 \pm 0.5) \times 10^{-5}$	<1 × 10 ⁻³	$(2.1 \pm 0.5) \times 10^{-5}$	$<1 \times 10^{-3}$	<2 × 10 ⁻⁶	$<1 \times 10^{-3}$
C_3H_6	<3 × 10 ⁻⁶	$(2.7 \pm 0.7) \times 10^{-5}$	_	$(3.6 \pm 0.8) \times 10^{-5}$	_	<3 × 10 ⁻⁶	_
n-C ₄ H ₁₀	$(1.7 \pm 0.4) \times 10^{-5}$	$(3.4 \pm 0.7) \times 10^{-5}$	_	$(0.7 \pm 0.2) \times 10^{-5}$	_	<6 × 10 ⁻⁶	-
<i>i</i> -C ₄ H ₁₀	<4 × 10 ⁻⁶	$(2.0 \pm 0.4) \times 10^{-5}$	-	$(1.2 \pm 0.2) \times 10^{-5}$	-	<4 × 10 ⁻⁶	-

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Fig. 1. Absorption spectrum of sample 3 in the range 2960–3020 cm⁻¹ ($p(SiF_4) = 4.8 \times 10^3$ Pa, l = 20 cm, resolution of 0.01 cm⁻¹); asterisks mark individual components of the rovibrational band v₁₀ of C₂H₆ (0.2 vol %), overlapping with the v₃ band of CH₄.

determination of relatively high hydrocarbon concentrations in impurity-rich materials. By combining these analytical techniques, one can accurately assess the nature and concentration of impurities.

Silane was synthesized by reacting silicon tetrafluoride (samples 1, 2, 5, and 6) with calcium hydride in a flow reactor at 180°C. The diluent used was A-grade hydrogen. The silane yield was 90–92%.

EXPERIMENTAL RESULTS

Table 1 lists the hydrocarbon concentrations in samples 1 (as-prepared SiF_4) and 2 (SiF_4 purified by fractional distillation) as determined by gas chromatography.

The hydrocarbon concentrations in samples 3 and 4 are listed in Table 2. These data demonstrate that the two analytical techniques used provide comparable data.

Figure 1 presents a portion of the IR spectrum of sample 3 (2960–3020 cm⁻¹), which shows, in addition to lines of methane, the strongest lines of ethane (marked by asterisks). Comparing the gas chromatog-

raphy and IR spectroscopy results, we evaluated the detection limit of IR spectroscopy for ethane at 5×10^{-4} vol %.

Table 3 presents the gas chromatography and IR spectroscopy results for isotopically enriched SiF₄ (samples 5–8). A chromatogram of sample 6 is displayed in Fig. 2. Figure 3 shows portions of the IR spectra of samples 6–8 in the region of the strongest absorption by ethane. The ethane concentration decreases in going from sample 6 to sample 8 and also agrees well with gas chromatography results. The concentrations of C_1 – C_4 hydrocarbon impurities in the silane samples are listed in Table 4.

DISCUSSION

It can be seen from Table 1 that the concentrations of C_1-C_4 hydrocarbon impurities in the as-prepared silicon tetrafluoride are at a level of 10^{-3} vol % and drop by one to two orders of magnitude as a result of fractional distillation.

The data in Table 2 indicate that, during SiF_4 purification, the C_1 and C_2 hydrocarbons accumulate in the



Fig. 2. Chromatogram of sample 6 (${}^{28}SiF_4$): (1) methane, (2) ethane, (3) ethylene, (4) propane, (5) propylene, (6) isobutane, (7) *n*-butane.

top part of the fractional column (sample 3), and the C_3 and C_4 hydrocarbons, in the bottom part (sample 4).

From comparison of the data for samples 5 (Table 3) and 2 (Table 1), it follows that the isotopic enrichment of the SiF₄ distillate has little or no effect on the CH₄, C_2H_6 , and C_2H_4 concentrations. At the same time, the C_3H_8 and n- C_4H_{10} concentrations increase significantly, by about one order of magnitude and by a factor of 2, respectively. In samples 6–8, in addition to the higher ²⁸Si abundance, the hydrocarbon concentration is notably higher (the sum $C_1 + C_2$ attains 10^{-2} vol %). One possible reason for this is that we used undistilled silicon tetrafluoride in centrifugal separation. During cen-



Fig. 3. Portions of the rovibrational absorption band v_{10} of C_2H_6 impurity in ²⁸SiF₄ ($p(SiF_4) = 66.5 \times 10^3$ Pa, l = 20 cm, resolution of 0.1 cm⁻¹): (l) sample 6, 4×10^{-3} vol % C_2H_6 ; (2) sample 7, 1.5×10^{-3} vol % C_2H_6 ; (3) sample 8, 4×10^{-4} vol % C_2H_6 .

trifugation, these impurities were transferred through the cascade and accumulated in the light fraction, enriched in ²⁸Si. Moreover, the concentrations of

Table 4. Hydrocarbon impurities (gas chromatography data) in SiH₄ prepared from samples 1, 2, 5, and 6

Impurity	Volume percent				
	sample 1	sample 2	sample 5	sample 6	
CH ₄	$(1.9 \pm 0.1) \times 10^{-3}$	$(1.4 \pm 0.1) \times 10^{-3}$	$(3.5 \pm 0.4) \times 10^{-3}$	$(2.3 \pm 0.3) \times 10^{-3}$	
C_2H_6	$(1.3 \pm 0.1) \times 10^{-4}$	$(9.5 \pm 0.9) \times 10^{-5}$	$(3.6 \pm 0.4) \times 10^{-4}$	$(5.3 \pm 0.5) \times 10^{-3}$	
C_2H_4	$(1.4 \pm 0.1) \times 10^{-4}$	$<\!\!2 \times 10^{-6}$	$<\!\!2 \times 10^{-6}$	$(4.9 \pm 0.5) \times 10^{-3}$	
C_3H_8	$(1.2 \pm 0.1) \times 10^{-4}$	$(4.0 \pm 0.4) \times 10^{-5}$	$(5.3 \pm 0.5) \times 10^{-4}$	$(1.5 \pm 0.2) \times 10^{-4}$	
C ₃ H ₆	$(1.1 \pm 0.1) \times 10^{-4}$	$<3 \times 10^{-6}$	$<3 \times 10^{-6}$	$(2.0 \pm 0.2) \times 10^{-4}$	
$n-C_4H_{10}$	$(3.7 \pm 0.5) \times 10^{-5}$	$(2.0 \pm 0.2) \times 10^{-5}$	$(3.3 \pm 0.4) \times 10^{-4}$	$(2.1 \pm 0.3) \times 10^{-4}$	
<i>i</i> -C ₄ H ₁₀	$(1.4 \pm 0.2) \times 10^{-5}$	$<4 \times 10^{-6}$	$(6.5 \pm 0.6) \times 10^{-5}$	$(1.3 \pm 0.3) \times 10^{-4}$	

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hydrocarbon impurities in isotopically enriched silicon tetrafluoride vary from sample to sample within one batch (samples 6, 7), which seems to be due to different background concentrations of impurities in the container for the 28 Si-enriched gas.

The C₁–C₄ hydrocarbon concentrations in the silicon tetrafluoride for silane synthesis correlate with those in the resultant hydride. At the same time, the total hydrocarbon concentration in the silane is somewhat higher, primarily due to saturated hydrocarbons. According to gas chromatography data, the hydrocarbon content of the A-grade hydrogen is below 9×10^{-6} vol %, which cannot result in significant contamination of silane. The contamination seems to be the result of hydrocarbon transfer from SiF₄ to silane during synthesis and significant removal of the hydrocarbons from the calcium hydride. Moreover, the synthesis is probably accompanied by hydrogenation of the unsaturated hydrocarbons (in particular, C₂H₄) present in the silicon tetrafluoride.

CONCLUSIONS

The qualitative and quantitative compositions of hydrocarbon impurities in isotopically unmodified and isotopically enriched silicon tetrafluoride were determined for the first time by gas chromatography and IR spectroscopy, and the behavior of these impurities during the purification and isotope separation of SiF_4 was investigated.

The results demonstrate that silicon tetrafluoride is one of the sources of hydrocarbon impurities in the silane prepared from it. The other source of hydrocarbon impurities in the silane is the calcium hydride used to reduce the silicon tetrafluoride.

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