

none. Column chromatography was performed using Kieselgel 60 (EM Science, 230-400 mesh) as stationary phase. Triethyl phosphite, chloromethyl methyl sulfide, chloromethyl phenyl sulfide, *n*-BuLi, N-chlorosuccinimide (NCS), and alkyl halides were obtained from commercial supplier, Aldrich and used without further purifications.

**Alkylation of Diethyl methyl (or phenyl)thiomethylphosphonate.** To a solution of diethyl methyl (or phenyl) thiomethylphosphonate (2.0 mmol)<sup>8</sup> in THF (10 mL) was added *n*-butyl lithium in hexane (2.2 mmol) at  $-78^{\circ}\text{C}$ . The reaction mixture was stirred for 10-20 min. and then alkyl halides (2.0 mmol) (methyl iodide, ethyl bromide, and benzyl bromide) was added, warmed gradually to room temperature, allowed to stand for 2 h, neutralized, and extracted into chloroform. The organic phase was dried, filtered, and evaporated. The crude product was purified by distillation (75-85% yields). Product is identical with an authentic sample.<sup>9</sup>

**Chlorination of  $\alpha$ -Sulfonyl Phosphonates with NCS.** To a suspension solution of N-chlorosuccinimide (6.2 mmol) in carbon tetrachloride (15 mL) was added diethyl methyl (or phenyl)thioalkylphosphonates (6.0 mmol) in carbon tetrachloride (50 mL) at room temperature. The reaction mixture was stirred for 4 h, filtered to remove succinimide, diluted with chloroform (10 mL) and hexane (10 mL), chilled, filtered off, and evaporated to give the crude products (**1**). The products were used without further purification.<sup>10</sup>

**General Procedure for the Formation of Vinylphosphonates (**2**).** To a solution of  $\alpha$ -chloro alkylphosphonates (**1**) (5.0 mmol) in methylene chloride (25 mL) was added Lewis acid (5.0 mmol) at room temperature. The mixture was stirred for 8-18 h, quenched with water (5 mL), and separated. The organic phase was dried, filtered, and evaporated to a pale yellow liquid. The crude product was purified by column chromatography with diethyl ether as an eluent. Products (**2a**, **2b** and **2c**) are identical with authentic samples.<sup>1</sup>

**Diethyl 1-methylthio-1-ethenylphosphonate (2a).** <sup>1</sup>H NMR  $\delta$  1.30 (t, 6H), 2.40 (s, 3H), 4.30 (dq, 4H), 5.60 (d, 1H,  $J=45$ ), 6.12 (d, 1H,  $J=25$ ); <sup>31</sup>P NMR  $\delta$  16.03; IR 1260 (P=O, s), 1060-1025 (P-O-C, vs); Mass (*m/e*, %) 109 (100), 149 (78), 155 (64), 210 ( $\text{M}^+$ , 48).

**Diethyl 1-methylthio-1-propenylphosphonate (2b).** <sup>1</sup>H NMR  $\delta$  1.30 (t, 6H), 2.12 (dd, 3H), 2.40 (s, 3H), 4.30 (dq, 4H), 7.12 (m, 1H); <sup>31</sup>P NMR  $\delta$  16.67; IR 1250 (P=O, s), 1050-1030 (P-O-C, vs); Mass (*m/e*, %) 71 (72), 135 (100), 153 (84), 191 (75), 224 ( $\text{M}^+$ , 73).

**Diethyl 1-methylthio-1-styrenylphosphonate (2c).** <sup>1</sup>H NMR  $\delta$  1.30 (t, 6H), 2.20 (s, 3H), 4.12 (dq, 4H), 7.16-8.00 (m, 6H); <sup>31</sup>P NMR  $\delta$  17.26; IR 1250 (P=O, s), 1060-1020 (P-O-C, vs).

**Diethyl 1-phenylthio-1-ethenylphosphonate (2d).** <sup>1</sup>H NMR  $\delta$  1.35 (t, 6H), 4.20 (dq, 4H), 5.85 (d, 1H,  $J=53$ ), 6.12 (d, 1H,  $J=32$ ), 7.30 (m, 5H); <sup>31</sup>P NMR  $\delta$  23.77; IR 1250 (P=O, s), 1050-1010 (P-O-C, vs).

**Diethyl 1-phenylthio-1-propenylphosphonate (2e).** <sup>1</sup>H NMR  $\delta$  1.35 (t, 6H), 2.10 (dd, 3H), 4.30 (dq, 4H), 7.20 (m, 5H), 7.40 (m, 1H); <sup>31</sup>P NMR  $\delta$  24.37; IR 1250 (P=O, s), 1060-1020 (P-O-C, vs); Mass (*m/e*, %) 115 (60), 134 (26), 147 (81), 286 ( $\text{M}^+$ , 100).

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## Determination of Trace Impurities in ULSI Grade Silane

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Many electronic specialty gases (ESG's) have been used in the process manufacturing semiconductor devices. In the dry processes of ultra-large scale integrated (ULSI) fabrication, ESG's such as SiH<sub>4</sub>, AsH<sub>3</sub>, PH<sub>3</sub>, B<sub>2</sub>H<sub>6</sub> and etc are employed as dopant and/or epitaxial gases.<sup>1</sup>

Trace impurities in ESG's should be reduced as low as possible because they introduce defects in semiconductor devices.<sup>2,3</sup> The rapid development of semiconductor industries has made the measurement of the purity of ESG's vitally important. Therefore, it is indispensable to accurately measure trace impurities in ESG's in order to improve the yield.

Recently, world-famous gas companies have established relatively well analytical techniques for ESG's<sup>4</sup>. However, they have been reluctant to distribute the technologies. Unfortunately, even though the demand of ESG's continues to increase in Korea, semiconductor manufacturers have been using these gases without any analysis, because the analytical techniques for ESG's have not been available. Accordingly, there are many problems not only in the quality certification

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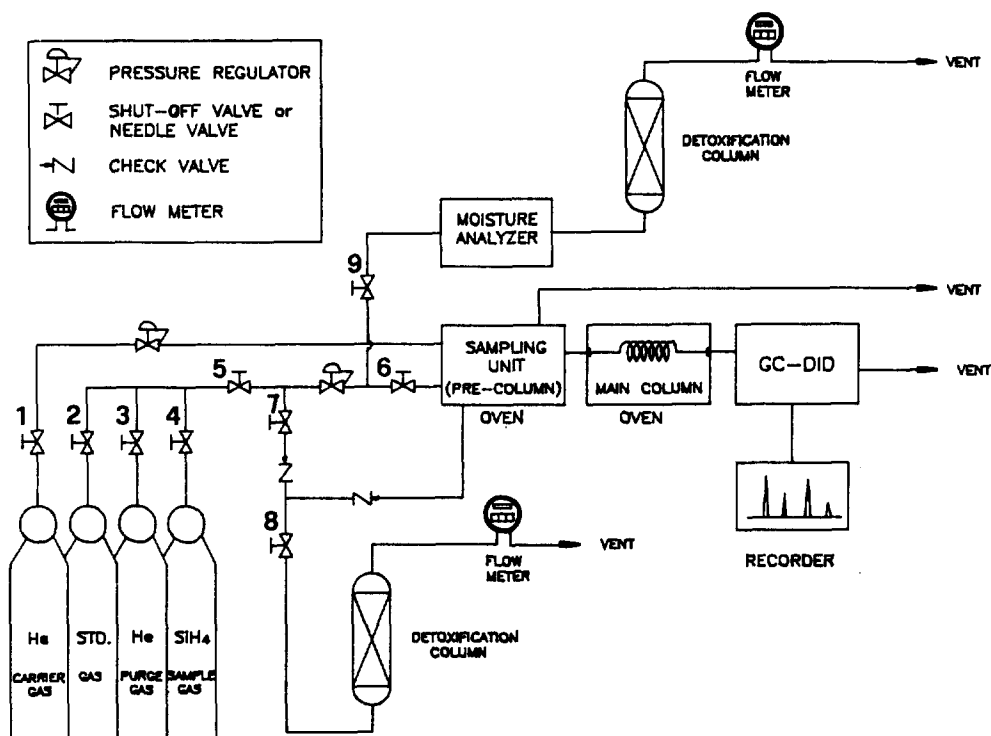


Figure 1. Schematic diagram of the analytical system.

but also in the localization of ESG's. It is necessary, despite their absence, to establish the analytical techniques for ESG's to decrease the yield loss and increase the semiconductor companies competitive power.

In ESG's analysis, the gas chromatograph-mass spectrometer (GC-MS) has been widely used<sup>5-7</sup>. The conventional GC is very useful in gas analysis, however, it does not give sufficient reliability for ESG's analysis. In order to meet this requirement, specially designed procedures and system should be prepared and installed.

The present work takes a simple approach to determine the trace impurities in ULSI grade silane by GC with a discharge ionization detector (DID). There is also, information enclosed on how to constitute the analytical procedures and system.

## Experimental

**Analytical System.** The schematic diagram of the analytical system is shown in Figure 1. Silane is pyrophoric, igniting immediately on contact with air<sup>8,9</sup>. Therefore, it should be surely kept away from discharge in air. Any leak is not allowed in all the connections of the system. A leak test is performed by a helium leak detector (Leybold, Model UL 100 PLUS).

All materials such as valves, fittings and tubings used in this system are 316L stainless steel. Bellows sealed valves and VCR fittings are employed. Packing materials of the regulators and fittings are teflon or stainless steel plate for safety.

The analytical system consists of gas cylinders, detoxification columns, a sampling unit with pre-column, analyzers and recorders.

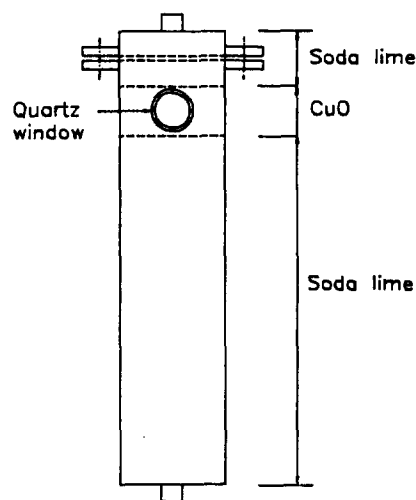
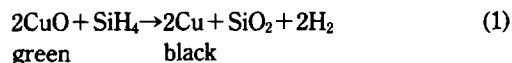


Figure 2. Detoxification column.

**Detoxification Columns.** The effluent silane after charging the sample loop is removed by detoxification columns made of 316L stainless steel. The malfunction of the filling materials can be detected by the color change through the quartz window as shown in Figure 2. Filling material in the column consists of CuO in the section of the window, and soda lime in the rest. CuO color changes from green to black in reaction with silane as follows:



By the color change, the time of replacing column is determined. The main ingredients of soda lime are  $\text{Ca}(\text{OH})_2$  and

**Table 1.** Concentration of the impurities in the standard gas

Impurity	Concentration (ppm)
H <sub>2</sub>	11.5
Ar+O <sub>2</sub>	10.1
N <sub>2</sub>	11.5
CO	8.7
CH <sub>4</sub>	2.0
Balance	He

**Table 2.** Operational conditions of the analyzer

Detector: DID

Column: Pre-column: PORAPAK Q

80/100 mesh, 3 mm ID×2 m

Main column: Molecular sieve 5A

80/100 mesh, 3 m×1/8'

Sample loop: 1 ml

Pre-column temperature: 60 °C

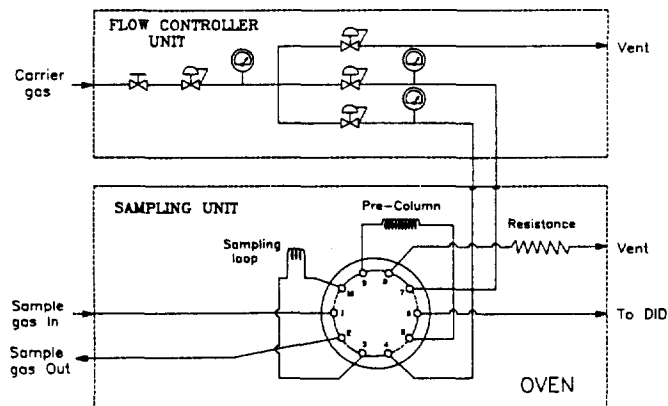
Main column temperature: 81 °C

Detector temperature: 71 °C

DC voltage: 550 mV

Current: 5.66 mA

Carrier gas: He 30 ml/min

**Figure 3.** Schematic diagram of the sampling and flow controller unit.

**Sampling Unit.** The sampling unit includes a 10-port valve, sample loop and pre-column as illustrated in Figure 3. The pre-column is utilized to protect the detector from the introduction of the great amount of silane. The pre-column plays a role of separating the impurities from silane.

The separated impurities from silane in the pre-column go to the main column, and then, they are detected. On the other hand, the effluent silane after filling the sample loop is vented through the detoxification column.

The helium carrier gas is regulated by a flow controller unit which is connected to the sampling unit as shown in Figure 3.

**Analytical Procedures.** The analytical procedures to perform safely are as follows:

1) Analytical conditions should be ready as presented in Table 2.

2) All the valves in the system except cylinders' should be fully open.

4) Open the valve on He cylinder(purge gas), and flow enough to remove air completely in the lines.

5) Close the valves (3, 4, 7, 9) and open the standard gas cylinder.

6) Determine the switching time of the 10-port valve. This should be done according to the procedures mentioned in the RESULTS AND DISCUSSION part.

7) Repeat 2)-3), and close the valves (2, 3, 7, 9).

8) Open the sample cylinder, and flow the sample gas into the line for more than 5 minutes. Control the pressure regulator to prevent from over pressure of the sample gas line. The flow rate should be 50 ml/min.

9) Switch the 10-port valve to inject the sample gas. At the same time, press the START KEY on the integrator to begin the analysis. Monitor for 10-15 minutes.

10) After the valve switching time determined at 6), switch back the 10-port valve for a pre-cut of the silane peak. Then the silane remained in the pre-column goes back the way it has entered and exits out of the column. While, the sample gas is filled in the sample loop.

For moisture analysis, after 8), open valve 9, and wait until it is stabilized.

## Results and Discussion

**Calibration.** A gas chromatogram of the standard mix-

KOH. The reaction with silane occurs as follows:



A lot of hydrogen gas is emitted from the columns as shown in equation (1) and (2). Therefore, the outlet of columns should be vented outdoors.

It is desirable to use soda lime because it is much cheaper than CuO. It is known that one kilogram of soda lime absorbs about 10-15 liters of silane.<sup>10</sup> An integrating flowmeter is connected to the detoxification column in order to calculate the replacing time of soda lime.

**Gases.** Silanes used in this experiment are ULSI grade from Matheson (USA) and TEISAN K. K. (Japan). Their purities are 99.9999%. Helium for carrier and purge gas are from DSS Co. (purity, 99.9999%). A standard gas is prepared from DSS Co., and impurity range is from 1 to 15 ppm. This standard mixture is produced by a gravimetric method<sup>11</sup>. The concentrations are presented in Table 1. If necessary, standard samples containing less than 1 ppm of impurities are employed as intermediates.

**Analyzers.** A gas chromatograph (Gow-Mac, Model 590) is used with a DID. Because of the high sensitivity, DID is very useful to determine the trace impurities in ultra-high purity(UHP) gases, compared with the conventional detector such as thermal conductivity detector (TCD) or helium ionization detector (HID). The analytical conditions of the GC are summarized in Table 2.

A moisture analyzer (Shaw, SHA-D) is employed for the measurement of the moisture in silane. A detoxification column is prepared separately for the analyzer. A moisture generator (MEECO, L'eau-Pro) is used for the calibration of the moisture analyzer.

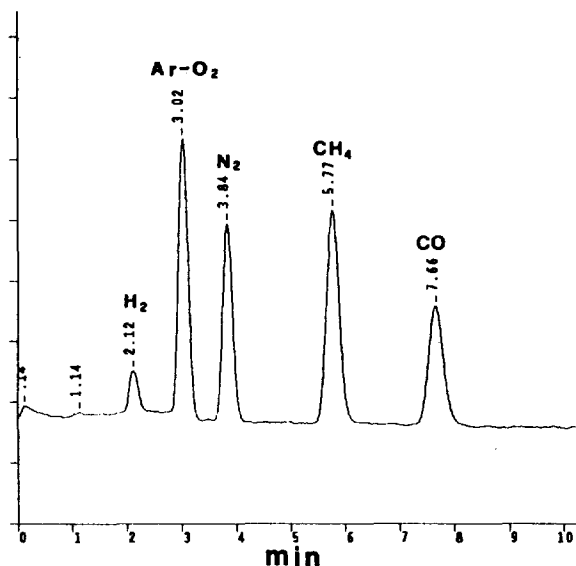


Figure 4. Chromatogram of the standard mixture.

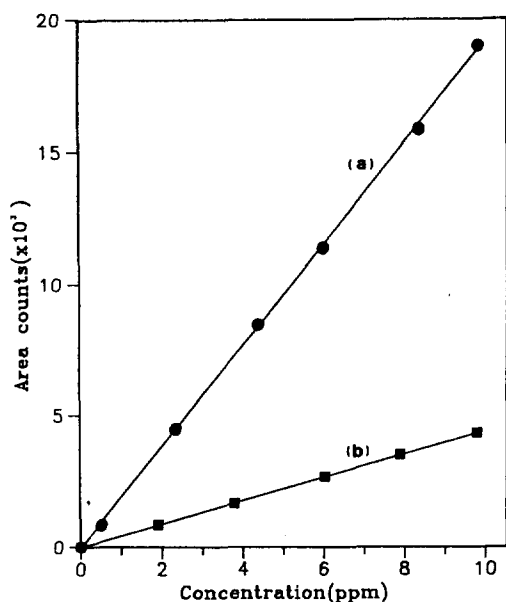


Figure 5. Calibration curves for N<sub>2</sub> (a) and H<sub>2</sub> (b).

ture in Table 1 is shown in Figure 4. It shows a good separation of the impurities.

In order to obtain calibration curves for each impurity, the same calibration system and methodology were performed as used in our previous work<sup>12</sup>. The calibration curves obtained for H<sub>2</sub> and N<sub>2</sub> are illustrated in Figure 5. They were linear in the range of 1 to 10 ppm. To measure how well the calibration curves agree with the data, the coefficients of determination<sup>13,14</sup> were obtained. It is possible to estimate the goodness-of-fit of the data to the calibration lines. The coefficients were 0.99994 for H<sub>2</sub> and 0.99977 for N<sub>2</sub>. The calibration was also carried out for N<sub>2</sub> and Ar+O<sub>2</sub> at less than 0.5 ppm. These results are shown in Figure 6. Standard samples containing less than 1 ppm were used to obtain the calibration curves in this region. The calibration curves shows a good linearity for each component in the

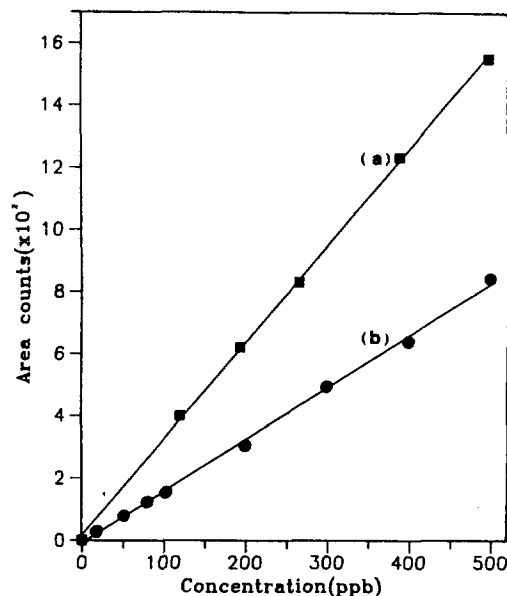


Figure 6. Calibration curves for Ar+O<sub>2</sub> (a) and N<sub>2</sub> (b).

Table 3. Response factors of DID for the impurities

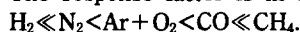
Impurity	Area counts/ppm
H <sub>2</sub>	440
Ar+O <sub>2</sub>	3,177
N <sub>2</sub>	1,977
CH <sub>4</sub>	10,583
CO	3,645

Table 4. Reproducibilities for the impurities

Impurity	N <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	Ar+O <sub>2</sub>	Ar	CO	CH <sub>4</sub>
Concentration (ppm)	9.8	2.1	10.0	0.3	1,000	2.7	2.0
RSD (%) (n=5)	1.0	5.6	0.93	7.2	0.64	3.5	0.56

range of 0 to 0.5 ppm. The coefficients of determination were also calculated from the calibration data to see the response of DID for the impurities. They were approximately equal to unity. The response was directly proportional to their concentrations in the range of 0 to 10 ppm. The response factors are summarized in Table 3.

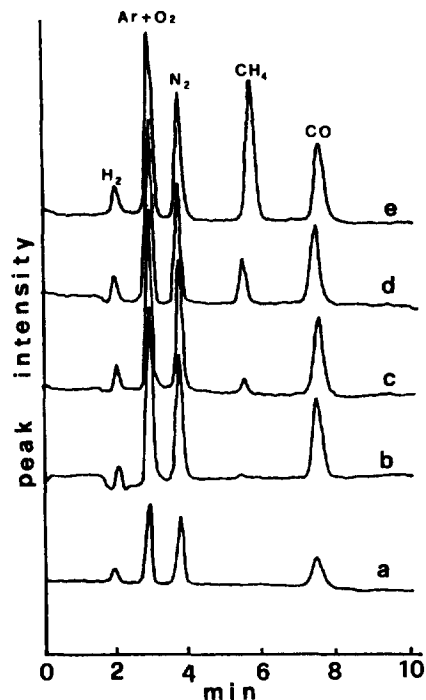
The response factor is in the following increasing order:



The factor for CH<sub>4</sub> was approximately 24 times as large as H<sub>2</sub>. The detector showed a big difference in the sensitivity according to the component.

If the concentration of impurity obtained from the calibration is in the linear range, it is possible to use a one-point calibration curve method<sup>15</sup>. However, if the difference of concentrations between the sample and standard gas is too large, this method should not be used.

**Reproducibility.** The analysis exhibits an amazingly



**Figure 7.** Chromatograms of the standard mixture according to the valve switching time: a) 70; b) 100; c) 103; d) 105; e) 120; and f) 180 seconds.

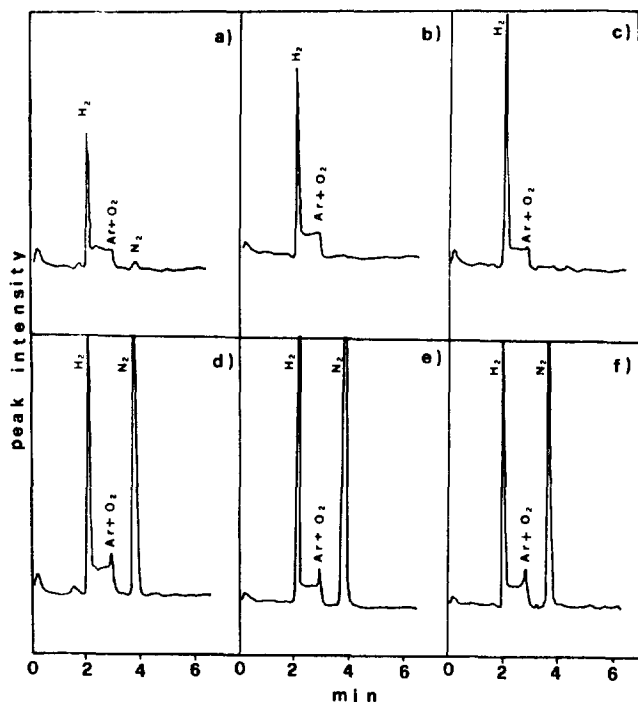
**Table 5.** Concentrations of the impurities in silanes (ppm)

Marker	Cylinder No.	H <sub>2</sub>	Ar+O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO	H <sub>2</sub> O
TEISAN	TSJ07353	17	<0.1	0.1	<0.1	<0.1	<0.2
	TSJ10046	38	<0.1	0.2	<0.1	<0.1	<0.2
	TSJ07328	7	<0.1	0.4	<0.1	<0.1	<0.2
Matheson	AS53968	33	0.5	18	<0.1	<0.1	<0.2
	AS56024	36	0.1	24	<0.1	<0.1	<0.2
	AS56254	41	0.3	25	<0.1	<0.1	<0.2

good reproducibility. As shown in Table 4, the relative standard deviations (RSD's) at the given concentration were quite low. For instance, the RSD's for N<sub>2</sub> (9.8 ppm), H<sub>2</sub> (10 ppm) and CH<sub>4</sub> (2.0 ppm) were less than 1%. However, in the lower concentration region, the RSD's were a little bit increased.

**Determination of the Valve Switching Time.** In order to prevent from the introduction of silane in the detector, it is very important to accurately determine the valve switching time.

The retention time of silane is much longer than that of the impurities in the standard mixture. Therefore, if the valve switching is performed as soon as the component, which has the longest retention time among the impurities, comes out from the pre-column, it is subsequently possible to perfectly separate silane from the impurities. From this purpose, chromatograms of the standard mixture were obtained with varying the valve switching time from 1 to 3 minutes (Figure 7). When the time was less than 100 seconds, the CH<sub>4</sub> peak did not appear (Figure 7b). However, as time went by, that peak began to increase. After 120 seconds, the peak did not



**Figure 8.** Chromatograms of the silane sample presented in Table 4: a) TSJ07328; b) TSJ07353; c) TSJ10046; d) AS53968; e) AS56254; and f) AS56024.

change any more. As a result, the valve switching time was set at 120 seconds.

It seems that the procedures mentioned above might be very tedious. The valve switching time can be decided by coupling a thermal conductivity detector (TCD) directly to the pre-column. In any case, however, because there is a certain extent of distance between the column and detector, almost all the procedures as used in the above test should be performed again to exactly determine the time.

**Analysis of Silanes.** Six of silane samples were analyzed. The concentrations of the impurities are summarized in Table 5. And the chromatograms are shown in Figure 8.

Clearly, main impurities in silanes were H<sub>2</sub> and N<sub>2</sub>. The other impurities showed very small peaks or no peaks at all. Moisture concentrations for all samples were less than 0.2 ppm.

## Conclusions

Determination of trace impurities in ULSI grade silane has been performed by GC-DID.

The response of DID for the impurities such as H<sub>2</sub>, Ar+O<sub>2</sub> and N<sub>2</sub> has demonstrated a good linearity in the range of ppb to ppm level. The RSD's for N<sub>2</sub> (9.8 ppm), H<sub>2</sub> (10 ppm) and CH<sub>4</sub> (2.0 ppm) were less than 1%. The others were below 8%. Therefore, it is possible to accurately measure the impurities in silane.

The main impurities in the samples were H<sub>2</sub> and N<sub>2</sub>. Some of them were as high as several tens of ppm. The others were less than 0.5 ppm.

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### Synthesis of Fluorescent Substrate Analogues for Mechanistic Study of Luciferase

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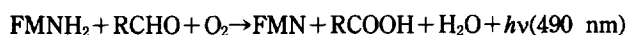
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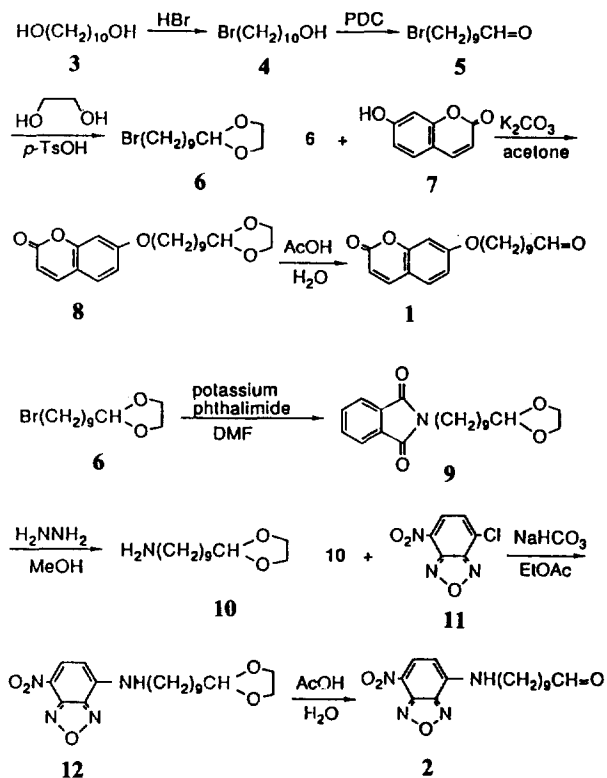
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Bacterial luciferase catalyzes the oxidation of a mixture of FMNH<sub>2</sub> and a long chain aliphatic aldehyde by oxygen to produce FMN, corresponding fatty acids, water, and bioluminescence.

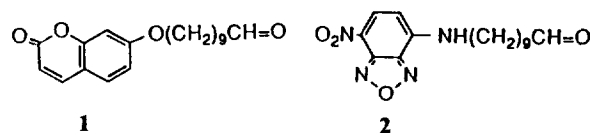


Despite many years of intensive efforts, the mechanism of the bioluminescence by bacterial luciferase has not been fully understood on the molecular level. According to mechan-



Scheme 1.

ism<sup>1-3</sup> proposed by Hastings, an excited FMN 4a-hydroxide is assumed to be the primary excited species emitting bioluminescence. However, there are some experimental evidences<sup>4-6</sup> that are inconsistent with his hypothesis and the possibility of certain other species being the primary excited state cannot be ruled out. In this report, we describe the synthesis of two fluorescent substrate analogues (1 and 2) to be used as probes for mechanistic study of bacterial luciferase.



$\lambda_{\text{max, emit}} = \text{ca. } 450 \text{ nm}^7$

$\lambda_{\text{max, emit}} = \text{ca. } 550 \text{ nm}^8$

If the oxidation of 2 gives emission with additional components (550 nm), while that of 1 does with no additional component, it could be interpreted as a supportive of the hypothesis that excited FMN 4a-hydroxide is the primary excited species. If the oxidation of both 1 and 2 give emission with additional component (450 and 550 nm respectively), it indicates that certain species other than FMN 4a-hydroxide is a primary excited species. Some reports<sup>9,10</sup> describe the usefulness of fluorescent substrate analogues similar to those in this study. However, fluorescence maxima of these analogues are either inappropriate (higher than 490 nm) or more limited (lower than 450 nm) for a mechanistic test.

The substrate analogues 1 and 2 were synthesized by the following synthetic routes.

Bromide 4<sup>11</sup> was obtained by bromination of 3 followed by separation through liquid-liquid extraction.<sup>12</sup> The product