

Measurement of As, P, and S in the Waste Gases and Water Emitted from Semiconductor Processes by High-Temperature Hydrogen Reduction Gas Chromatography

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Abstract

A quick, sensitive, and accurate method, high-temperature hydrogen reduction gas chromatography (GC) (1,2), for measuring arsenic (As), phosphorus (P), and sulfur (S) in the waste gases and water emitted from semiconductor processes is proposed in this paper. A high-temperature hydrogen reduction system that changes As, P, S, and their compounds into hydrides by atomic hydrogen has been designed. It is convenient to detect these elements in solid, liquid, and gaseous samples by high-temperature hydrogen reduction GC without pretreating samples. The lower detection limits of As, P, and S by this method are 0.01, 0.003, 0.02 mg/L, respectively, and the values of relative standard deviation are 6.2%, 8.6%, and 0.3%, respectively. Results determined by high-temperature hydrogen reduction GC are primarily accordant to those by conventional methods such as colorimetry and ion chromatography. The error statistics of this analysis method also show that high-temperature hydrogen reduction GC can be successfully used to determine trace As, P, and S in waste gases and wastewater emitted from semiconductor processes.

Introduction

It is well known that the semiconductor industry is a new multi subject trade. In the waste gases and wastewater emitted from many factories and labs, there are lots of poisonous materials containing arsenic (As), phosphorus (P), and sulfur (S) elements and their other compounds such as AsH₃, PH₃, SO₂, SO₃, H₂SO₄, H₃PO₄, and H₃AsO₄.

Conventionally, titration, colorimetry, atomic emission spectroscopy, atomic absorption spectrometry, inductively coupled plasma-mass spectroscopy, ion chromatography (IC), gas chromatography (GC), and so on have been adopted for measuring As, P, and S. Of these methods, colorimetry (3), IC, and GC are commonly used. However, colorimetry requires a long process of sample pretreating. As for IC (4–6) and GC (7), the former needs

liquid samples and must exist in an ionized state. The latter requires gaseous samples, and if there are solid samples, they must be pyrolyzed into a gaseous state before measurement. Thus, it is significant to propose a method for measuring As, P, and S directly, quickly, and sensitively in the waste gases and wastewater emitted from semiconductor processes without pretreatment. In this work, we report a quick, sensitive, and accurate method for measuring As, P, and S in the waste gases and water emitted from semiconductor processes. A high-temperature hydrogen reduction system is designed. The concentrations of As, P, and S are determined by the high-temperature hydrogen reduction GC.

Principle

In the waste gases and wastewater emitted from the semiconductor processes, only As, P, S, and their compounds can be reduced to hydrides by atomic hydrogen under high temperature in the reduction furnace. These hydrides can be determined directly with GC. However, other impurities in the waste gases and wastewater cannot be reduced to hydrides. Therefore, the interference with analysis can be ignored.

Take phosphate for an example:



where P⁰ refers to the atomic P, H⁰ refers to the atomic hydrogen, and M refers metal atoms.

Through the calculation of thermodynamics of P-H₂-KBH₄ (2), the dependence of partial pressure of PH₃, P₂, P₄, B, and K on temperature in the system of P-H₂-KBH₄ is shown in Figure 1.

Figure 1 shows that P_{PH₃} → P_{P₂} → P_{P₄} under high temperature, so the concentration of PH₃ is far higher than that of P₂ or P₄, and the greatest part of P can be changed into PH₃. Moreover, P_{PH₃} → P_K or P_B, thus boron (B) or potassium (K), also scarcely interfered with measuring P. Meanwhile, it is safe and cheap to use KBH₄ as the reagent producing atomic hydrogen.

Experimental

Apparatus and operating condition

The high-temperature hydrogen reduction GC system used in this experiment is shown in Figure 2.

The operating condition of the determining system in this

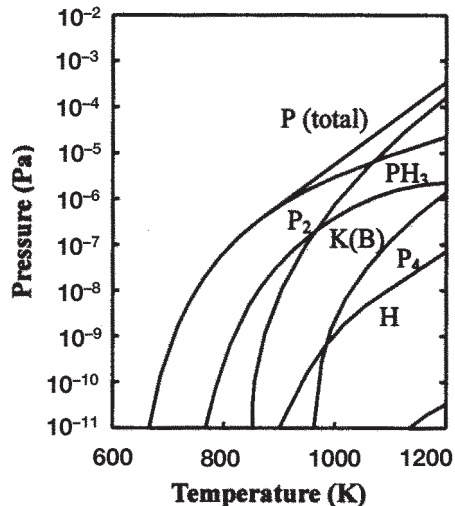


Figure 1. Dependence of partial pressure of PH_3 , P_2 , P_4 , B, and K on temperature in the system of P- H_2 -KBH.

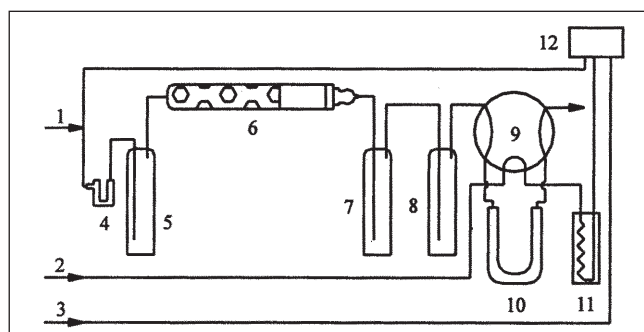


Figure 2. The high-temperature hydrogen reduction GC system: (1) H_2 , (2) N_2 , (3) air, (4) sample entrance, (5) counter mixer, (6) reduction tube, (7) separator with NaOH, (8) dehydrator, (9) six-way valve, (10) collector (-80°C or 90°C), (11) separator, and (12) double flame photometric detector. Gaseous samples can be entered into the system through (4). Liquid samples should be evaporated to dry, then mixed with KBH_4 , and put into (6). Solid samples that are directly mixed with KBH_4 , put into (6).

experiment is shown in Table I.

Standard curves

Diluted to 100 mL with high-purity hydrogen as the standard gas were 1 mL 2.5% AsH_3 and PH_3 , respectively. Respectively, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mL standard gases were sampled and placed into the analytic system and plotted with the peak height and concentration of AsH_3 or PH_3 so that the standard curves were obtained. For high concentrations of P, 2.0, 4.0, 6.0, 8.0, and 10.0 mL standard gas of PH_3 were sampled, and the standard curve with peak height and concentration of PH_3 was plotted. With hydrogen, 1 mL 90% H_2S , obtained by the reaction of Na_2S and H_2SO_4 , was diluted to 100 mL as standard gas, and the standard curve with the square root of peak height ($h^{1/2}$) and concentration of H_2S was plotted.

Sampling procedure

There are two different ways to sample, according to phases of species containing As, P, and S in waste gases. If there are several different phases of species containing As, P, and S in waste gases, they can all be sampled by absorbing with solutions. A sampling tube containing absorbing solution (1% NaOH+ H_2O_2) was connected to a sampling apparatus for sampling waste gases emitted from semiconductor processes. The gas flow rate was 0.3 L/min and the sampling time was 20 min. The absorbing solution was then transferred into a quartz crucible and evaporated under an IR lamp in a ventilator. If there is only gaseous arsenide, phosphide, and sulphide in the waste gases, the best way to sample them is to concentrate under low temperature. A U-pipe containing chromatography silica gel was sunk into a cooling trap (liquid nitrogen was added into ethanol and stirred until the temperature went down to -80°C), and its one side was connected to the air-sampling apparatus. The gases were taken into the sampling tube from its other side. Thus, AsH_3 , PH_3 , SO_2 , H_2S , etc. were enriched. The gas flow rate was 0.4 L/min, and the sampling time was 30 min. Wastewater can be sampled directly.

Analysis procedure

If the analyte is solid, it must be milled and mixed with dried KBH_4 (or NaBH_4). The mixture was transferred into a quartz crucible, and then the quartz crucible was put into the high temperature reduction furnace, in which the reduction reaction happened. If the analyte is liquid, it can be evaporated to dry under an IR lamp. After that, the analyte was mixed with KBH_4 and then measured with the same procedure as P. If the analyte is a gas, it can be detected directly by GC.

The preceding samples do not need chemical pretreatment, and they can be directly reduced with atomic hydrogen decomposed from KBH_4 in the reduction furnace. The As, P, and S impurities in the samples were reduced to AsH_3 , PH_3 , and H_2S , respectively. They were carried into the collector in a cooling trap (-80°C) by H_2 . The sampling tube was connected to the GC; synchronously, the six-way valve was located at the "Sampling" position. After the carrying gas, N_2 , purged for approximately 1–2 min, the six-way valve was located at the "Feeding" position. The

Table I. Operating Condition for High-Temperature Hydrogen Reduction GC System

GC system		Reduction system	
Flow rate of flame H_2 (mL/min)	180	Flow rate of reduction H_2 (mL/min)	200
Flow rate of air (1) (mL/min)	80	Temperature of furnace ($^\circ\text{C}$)	950 (As), 1000 (P), 850 (S)
Flow rate of air (2) (mL/min)	170	Time of sampling (min)	8
Flow rate of N_2 (mL/min)	50	Flow rate of effluent N_2 (mL/min)	80
Temperature of separator ($^\circ\text{C}$)	130		
Temperature of detector ($^\circ\text{C}$)	100		

sampling tube was then put into boiling water. The absorbed gas was deabsorbed and entered into the GC. Signals were detected by a double flame photometric detector at 526 nm, amplified, and recorded. Thus, the concentrations of As, P, or S in analyte can be obtained according to the standard curves or extrapolation of standard curves.

Error statistics

The detectability of high-temperature hydrogen reduction GC

The relationship $D = Rn/S$ is used to calculate the detectability, where Rn refers to the noise and S refers to the size of the signal produced by a detector when the smallest amount of analyte enters the detector. The lower detection limits of AsH₃, PH₃, H₂S, and solid or liquid As and P are 0.013, 0.0031, 0.02, 0.0088, and 0.0031 mg/L, respectively.

Ten parallel experiments with 0.025% AsH₃ and PH₃ and 0.9% H₂S were carried out to check the accuracy, precision, and repeatability of this method. The results are shown in Tables II, III, and IV.

Tables II, III, and IV show that the values of the relative standard deviation are 6.2%, 8.6%, and 0.3% for As, P, and S, respectively,

which are small enough to satisfy the requirement for trace analysis and demonstrate that this method has good repeatability.

Recovery experiment

In order to check the authenticity of results, certain amounts of AsH₃, PH₃, and H₂S (calculated as SO₄²⁻) were added to the flask absorbing waste gases, and certain amounts of AsO₃⁻, HPO₃⁻, and SO₄²⁻ were added to wastewater. The recovery was determined according to the aforementioned analysis procedure. The results are shown in Table V.

It is clear from Table V that recovery is high and the results are accurate and authentic when analyzing trace impurities of As, P, and S emitted from the semiconductor processes by the method of high-temperature hydrogen reduction GC.

Results and Discussion

Results of measuring waste gases

Results of measuring waste gases discharged after treatment by a scrubber for As, P, and S pollutants are shown in Table VI (sampled at outlets of the 42-m high emitting gas pipes) and Table VII (sampled at 20-m away from outlets of emitting gas pipes).

It can be seen from Tables VI and VII that the concentrations of As, P, and S in gaseous samples discharged after treatment by a scrubber for As, P, and S pollutants are very low, normally < 0.1 mg/m³, which is less than those of discharged standards.

Results of measuring wastewater

Results of measuring wastewater discharged after treatment by methods of coagulation and settlement are shown in Table VIII.

From Table VIII, it can be seen that the concentrations of As, P, and S in wastewater samples discharged after treatment by methods of coagulation and settlement in the process of the semiconductor are approximately 0.08, 0.05, and 0.34 mg/L, respectively, which are also less than those of discharge standards.

Tables VI, VII, and VIII show waste gases and wastewater treated by using the preceding methods in the process of the semiconductor; As, P, and S are in trace quantities, but they could be determined by this high-temperature hydrogen reduction GC directly and accurately.

Comparison of different methods for determining As, P, and S

In order to check further the veracity of results measured by the method of high-temperature hydrogen reduction GC, As, P, and S in different samples were analyzed using different analytic methods such as colorimetry and IC, shown in Tables IX and X.

Table II. Repetition of Analysis of AsH₃ (0.025% AsH₃ as Standard Gas)

Peak height (h, mm)	Mean deviation	Relative deviation	Standard deviation	Relative standard deviation
40.0, 44.0, 41.5, 44.0, 48.0, 46.0, 48.0, 47.0, 45.0	0.00119	4.8%	0.00155	6.20%

Table III. Repetition of Analysis of PH₃ (0.025% PH₃ as Standard Gas)

Peak height (h, mm)	Mean deviation	Relative deviation	Standard deviation	Relative standard deviation
39.5, 36.0, 42.0, 40.0, 44.0, 45.0, 41.5, 44.0, 48.0, 46.0	0.0017	6.9%	0.00214	8.56%

Table IV. Repetition of Analysis of H₂S (0.9% H₂S as Standard Gas)

Square root of peak height (h ^{1/2} , mm ^{1/2})	Mean deviation	Relative deviation	Standard deviation	Relative standard deviation
125.73, 126.49, 126.49, 126.49, 125.98, 126.49, 126.74, 126.24, 126.49, 126.75	0.002	0.2%	0.0027	0.3%

Table V. Recovery Experiment of Waste Gases and Wastewater

Tested impurities	Waste gases			Wastewater		
	AsH ₃	PH ₃	SO ₄ ²⁻	AsO ₃ ⁻	HPO ₃ ⁻	SO ₄ ²⁻
Added quantity (ng)	10.0	10.0	6.0	5.0	10.0	10.0
Recovery (%)	95.8	109.2	99.0	98.2	96.0	108.7

Table VI. Concentration of Gaseous Impurities after Absorbed by a Scrubber for As, P, and S Pollutants

Impurities	Arsenide	Phosphide	SO ₄ ²⁻
Concentration (mg/m ³)	0.080	0.045	0.082
State standards	0.3*	0.3*	70 [†]

* TJ36-79 (Hygienic Standards for the Design of Industrial Enterprises).
[†] GB16297-96 (integrated emission standard of air pollutants).

Table VII. Concentrations of Gaseous Impurities Sampled at 20-m Away from Outlets of Emitting Pipes

Impurities	As (mg/m ³)	P (mg/m ³)	SO ₄ ²⁻ (mg/m ³)
Sample I	0.016	0.003	0.090
Sample II	0.040	0.014	0.092
Sample III	0.011	0.006	0.080
Sample IV	0.025	0.004	0.082

Table VIII. Concentrations of Impurities in Wastewater Treated by Coagulation and Settlement

Impurities	AsO ₄ ³⁻ (mg/L)	HPO ₃ ⁻ (mg/L)	SO ₄ ²⁻
Treated sample A	0.08	0.04	0.39
Treated sample B	0.09	0.05	0.24
State standards	0.5*	2.0*	1.0 [†]

* GB8978-88 (integrated wastewater discharge standard).
[†] CJ18-86 (discharged standards for municipal wastewater).

It can be seen from Tables IX and X that the results determined by these methods agree with each other very well, which shows that the results of determining trace As, P, and S by high-temperature hydrogen reduction GC are accurate.

Conclusion

The high-temperature hydrogen reduction furnace has been designed, and the method of low temperature (−80°C) collecting and sampling is introduced in this experiment. Only As, P, S, and their compounds can normally be reduced to hydrides by atomic hydrogen at high temperatures, and hydrides can be determined directly with GC. Though, other impurities cannot be reduced to hydrides. So, the interference with analysis would be ignored. KBH₄ was chosen as the reducer and used as the ideal material of producing atomic hydrogen. High-temperature hydrogen reduction GC is a new method for determining trace As, P, S, and their compounds in the solid, liquid, or gaseous states quickly, sensitively, accurately, and directly without pretreating samples.

Table IX. Comparison of Different Methods of Determining As and P

Number of samples	High-temperature hydrogen reduction GC		Colorimetry	
	As	P	As	P
1. Gas sample (mg/m ³)	0.02	0.03	0.02	0.04
2. Solid sample (mg/L)	0.12	1.50	0.12	1.20
3. Liquid sample (mg/L)	0.18	0.14	0.20	0.15

Table X. Comparison of Different Methods of Determining S

Number of samples	High-temperature Hydrogen reduction GC	IC
	SO ₄ ²⁻ (mg/m ³)	SO ₄ ²⁻ (mg/m ³)
1. Sample A (gas)	0.10	0.10
2. Sample B (gas)	0.10	0.12
3. Sample C (gas)	1.00	0.90

The error of analysis satisfies the requirement for trace elements; the recovery is also high. The lower detection limits of As, P, and S by this method are 0.01, 0.003, and 0.02 mg/L, respectively, and the values of relative standard deviation are 6.2%, 8.6%, and 0.3%, respectively.

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