# 行政院國家科學委員會專題研究計畫成果報告

## 半導體業員工作業環境金屬暴露—離子植入機台維修工程師之砷暴露

## Occupational Metal Exposure Among Workers of Semiconductor Industry – Engineers' Arsenic Exposure During Ion Implanter Maintenance

**計畫編號：**NSC 87-2314-B-002-348
**執行期限；**86 **年** 8 **月** 1 **日至** 87 **年** 7 **月** 31 **日**
**主持人：黃耀輝　臺灣大學公共衛生學院職業醫學與工業衛生研究所**

**中文摘要**

**本研究目的在釐清維修工程師於維護離子植入機台時的砷暴露。共有 21 名維修工程師及 10 名電腦程式設計師分別作為暴露組及非暴露組的研究對象。空氣、擦拭及尿液樣本，以及使用過的擦拭布及手套都被收集來當作砷的暴露樣本。結果顯示，除了部份擦拭樣本、擦拭布及手套有較高砷含量外，一般工作環境中的砷暴露相當低。但維修期間工程師的尿中砷濃度平均上升 4.4 μg/g creatinine，可能是因未適當使用防護具及不小心接觸砷粉塵而造成暴露。此外，本研究採用的連續性尿中砷監測可取代環境採樣用來評估此項特殊行業的低濃度砷暴露。**

**關鍵詞：砷、砷化氫、尿、離子植入機台維修**

**Abstract**

The purpose of the present study was to delineate the potential arsenic exposure for engineers during the ion implanter maintenance. A total of 21 maintenance engineers and 10 computer programmers were recruited as exposed and non-exposed group, respectively. Air, wipe, urine samples, used cleaning cloth and gloves were collected for the characterization of arsenic exposure. Results showed that arsenic levels were very low in environmental samples except some episodes of high arsenic contents in wipe samples, used cleaning cloth and gloves. However, an average elevation of 4.4 μg/g creatinine in urinary arsenic level was estimated among maintenance engineers without adequate and effective personal protection, probably due to the inadvertent contact with dust arsenic around the work areas. Also, it is concluded that a series of urine samples with self-reference is good enough to monitor such low-level arsenic exposure in this industry.

Keywords: Arsenic, Arsine, Urine, Ion Implanter Maintenance.

**Introduction**

Among various potential occupational hazards in the clean room, arsenic is a site specific health hazard for maintenance engineers regularly assigned to cleaning the ion implanter and disposing of the wastes.[1-3] The process involved in doping silicon wafers to produce conducting circuit using arsine gas or elemental arsenic leaves arsenic residues on equipment such as ion implanter, ion source housings, beam line. The activities of maintenance or source changing would produce airborne arsenic and residues on nearby work surface, which maintenance engineers working in these areas might be exposed to. A previous study has shown that the airborne arsenic levels were very low in ion implanter area, except when the maintenance work at the beam line area was conducted.[1] Though lack of published data verifying the perceived risk, arsenic exposure of maintenance engineers around the ion implanter remained a concern. In order to identify the possible impact of arsenic exposure, the purpose of the present study was to use a series of urine samples as an alternative to delineate the potential arsenic exposure during ion implanter maintenance.

## Materials and Methods

Three ion implanters of two fabrication companies were included in the present study. Each ion implanter area was under one week investigation. In this study, a total of 21 maintenance engineers on duty were recruited as exposed group as well as 10 designated computer programmers working in office as non-exposed group. Since arsenic contaminant may be in the forms of aerosol and/or of residues on the surface of work area, air samples, wipe samples, used cleaning cloth and used gloves as well as urine samples were collected for exposure assessment. Area samples were collected at the work sites, e.g. source housing, beam line, end station, hoods, nearby area of ion implanter, and administration office. Personal samples were obtained from all recruited maintenance engineers. Arsenic in air sample, wipe sample, used cleaning cloth, used gloves, and urine sample were analyzed on hydride generation atomic absorption spectrometer [4] while air arsine samples were analyzed on graphite furnace atomic absorption spectrometer.[5] Urinary creatinine was measured with a colorimetric method.[6] If a sample contained an abnormally low or high level of creatinine, i.e., less than 0.5 g/l or greater than 3.0 g/l, the urinary arsenic result was excluded from analysis.[7] The analytical method for the urinary arsenic was based on the direct analysis of the urine sample, which accounted for the total four major metabolites of inorganic arsenic in urine, i.e., $As^{3+}$, $As^{5+}$, MMA(monomethyl-arsonic acid) and DMA (dimethylarsinic acid).[8] Detailed description of the study protocol and QA/AC process can be found elsewhere.[9] In addition, individual information of study subjects was collected by administration of questionnaires, including demographic and behavioral information, work history, work-related syndrome and symptoms, general environmental conditions related to potential arsenic exposure, consumption of seafood, and drinking water, etc.

## Results

Among 21 maintenance engineers recruited in the present study, 10 were from the Facility A, 5 were from the Facility B, and 6 were from the Facility C, respectively.

In Table 1, of the total 93 air samples, arsenic contents were undetectable in 46 samples. Relatively high levels of airborne arsenic were found in the areas of source housing, inside-hood, outside-hood, while no arsenic was detectable in the office area. Other than four samples, no airborne arsenic level in the study areas exceeded the recommended occupational exposure limit of 10 $\mu g/m^3$.[10] Regarding personal airborne arsenic exposure, 21 out of 31 samples did not have arsenic detected. Of those 11 samples with detectable arsenic, the geometric mean was 1.66 $\mu g/m^3$(GSD =2.2) and there was no extraordinary high level arsenic exposure. The ranges and the geometric standard deviation presented in Table 1 for both area and personal samples indicated that the airborne arsenic was distributed variously in space and in time.

For arsine exposure, only 22 out of

45 area samples had detectable arsine contents ranging from 0.01 to 0.49 ppb. For personal exposure, only 15 out of 35 samples had detectable arsine, ranging from 0.01 to 1.66 ppb (GM=0.07 ppb, GSD=4.3). All these arsine levels were well below the occupational exposure limit of 50 ppb recommended by the ACGIH[6].

Arsenic contents on work surface, used cleaning cloth, and used gloves were presented in Table 2. Dust arsenic loading on work surfaces varied from non-detectable level to 146 $\mu g/cm^2$, with the high geometric means of arsenic contents found in the hood and the beam line areas, i.e., 10.1 $\mu g/cm^2$(GSD=4.0) and 6.0 $\mu g/cm^2$ (GSD=13.9), and indicated that arsenic contents on the work surface of these two areas were generally higher than the other areas. For used cleaning cloth, the highest arsenic contents were found in the samples collected from the source housing area (GM=201 $\mu g/cm^2$, GSD=3.6), where element arsenic was used as source for ion implantation and need to be changed during the maintenance. Furthermore, gloves used in the processes of dismounting the major parts of ion implanter and of cleaning arsenic residues on these parts were found with high level arsenic residues, ranging from 24 to 7215 µg/piece with a geometric mean of 681 µg/piece (GSD=3.4).

Table 3 is the arsenic results of a total of 98 urine samples from all the participating study subjects. The average level of urinary arsenic for the 10 computer programmers was 3.8 µg/g creatinine, not significantly different from the maintenance engineers' average urinary arsenic level of the first day, 3.6 µg/g creatinine. Also Table 3 elucidates that the daily average urinary arsenic levels of the Facility A engineers increased steadily and reached the highest average level of 8.5 µg/g creatinine in the fifth-day morning, then declined slowly in the later days. On the other hand, the urinary arsenic levels of those engineers of Facilities B and C, around 3.4-4.5 µg/g creatinine, did not deviate much from their own self-reference and showed no similar elevation trend as that in Facility A.

Individual urinary arsenic levels of 7 maintenance engineers from the Facility A were plotted in Figure 1, who provided with at least four successive days' urine samples. In the first three days, all urinary arsenic concentrations leveled around 4 µg/g creatinine. Then, urinary arsenic levels of four maintenance engineers, i.e., $A_1$, $A_2$, $A_4$, $A_6$, climbed up steadily to 6-8 µg/g creatinine since the fourth day. These elevations were strong supporting evidence in time sequence to attribute the increase of excreted urinary arsenic to the exposure at their first two-day's maintenance work.

**Discussion**

The baseline of urinary arsenic levels of the study subjects, both computer programmers or maintenance engineers, was comparable to the previous studies. Comparison in Table 4 indicated that the mean baseline of the present study, i.e., 3.7 µg/g creatinine, was not significantly different from other study groups. This was consistent with our assumption that these study subjects, in addition to the possible occupational exposure due to the ion implanter maintenance, did not expose to unusual arsenic sources during the study period.

Results shown in Table 3 and Figure 1 clearly indicated the elevation of urinary arsenic levels of these maintenance engineers, even though this increase was slight. As shown in Figure 1, urinary arsenic levels of each maintenance engineer on the third and the fourth days of the maintenance work significantly increased by 1.0~7.8 $\mu$g/g creatinine compared to their own urinary arsenic level of the first day, the self-reference. In average, these maintenance engineers experienced an increase of 4.4 $\mu$g/g creatinine. Such results demonstrated the potential arsenic exposure in clean room, in which, with relatively low airborne arsenic level, dust arsenic resulting from the ion implanter maintenance work might play an important role as exposure source.

Positive results of arsenic loading on used cleaning cloth and gloves implied that there were important alternative sources other than airborne arsenic particulate for the maintenance engineers' arsenic exposure. This exposure during the ion implanter maintenance might be primarily through ingestion as well as inhalation. This can be further demonstrated by assuming that the elevation of urinary arsenic was totally attributable to the uptake through inhalation and comparing the expected airborne arsenic concentration with the really measured one. Using the maintenance engineers of Facility A as an example, the average increase of urinary arsenic level was 4.4 $\mu$g/g creatinine after their most polluting maintenance work, which approximately accounted for 12.1 $\mu$g extra arsenic excreted in urine per day, given an average urinary creatinine of 1.96 g/l and an average urinary excretion of 1.4 liters per day.(11) If this increased 12.1 $\mu$g/day urinary arsenic were all attributed to work-related exposure through inhalation, the time weighted average air arsenic concentration was conservatively estimated to be as high as 5.3-8.0 $\mu g/m^3$ by assuming a tidal volume of 0.5 liters, breathing frequency of 18/min, a 7-hour work shift without respiratory protection, and 40-60% of inhaled arsenic excreted in urine.(12,13) However, only 11 out of 31 samples had detectable arsenic contents with an geometric mean of 1.66 $\mu g/m^3$ (Table 2). The aforementioned estimation implies that the arsenic in the work environment might be exposed to the maintenance engineers through some important alternative pathways other than inhalation, most probably through ingestion.

Since the purpose of occupational health is to prevent any potential hazard from the work environment, a series of urine arsenic monitoring with self-reference becomes a helpful tool to measure the recent low level occupational arsenic exposure due to the short half-life of arsenic in the human body. Furthermore, the work loading for collection and analysis of daily first morning voided urine samples will be much less than that for environmental exposure monitoring. Therefore, from the occupational hygiene point of view, urinary arsenic levels of a series of work shifts, which reflect the comprehensive exposure in the body burden, is a better exposure monitoring than other measures to evaluate the low level, potential occupational arsenic exposure. Also, results shown in Table 3 and Figure 1 demonstrated that use of appropriate personal protection equipment, such as full face-piece respirator with supplied-air, the maintenance engineers would effectively eliminate arsenic exposure and have their urinary arsenic levels hold stable without elevation. Without adequate and/or effective personal protection, such as those engineers of Facility A, an inadvertent arsenic exposure would occur and be reflected in the elevation of urinary arsenic level. Based on these observations, it is strongly recommended that an increase of 4~5 $\mu$g/g creatinine for urinary arsenic following a series of work shift monitoring could be used as a criteria to verify the necessity of further improvement in working environment, personal protection or person hygiene.

In general, average arsenic level in

the ion implanter area was found low, implying no evident and imminent threat of adverse health effect on workers in this work environment. However, elevated excretion of arsenic was still demonstrable and warranted further attention to reduce their exposure to arsenic since arsenic has been recognized as human carcinogen by IARC.(14) Any unnecessary exposure should be eliminated to reduce the risk of potential adverse health effect. Use of a series of urine samples as arsenic monitoring during the work shifts would facilitate their efforts more efficiently.

**Reference**


1. Ungers LJ, Jones JH. Industrial hygiene and control technology assessment of ion implantation operations. Am Ind Hyg Assoc J 1986;47(10):607-614.
2. Harrison M. Semiconductor manufacturing hazards. In: Sullivan Jr. JB, Krieger GR, eds. Hazardous materials toxicology, clinical principles of environmental health. Baltimore, Maryland: Williams and Wilkins, 1992;472-504.
3. Peyster A, Silvers JA. Arsenic levels in hair of workers in a semiconductor fabrication facility. Am Ind Hyg Assoc J 1995;56:377-386.
4. NIOSH. Manual of analytical methods, Method No. 7900 - Arsenic & compounds. 4th ed. Cincinnati, Ohio; US National Institute for Occupational Safety and Health, 1994.
5. NIOSH. Manual of analytical methods, Method No. 6001 - Arsine. 4th ed. Cincinnati, Ohio; US National Institute for Occupational Safety and Health, 1994.
6. Henry RJ. Clinical chemistry: principles and technic. 3rd ed. New York; Harper and Row, 1965.
7. ACGIH. Threshold Limit Values (TLVs) for chemical substances and physical agents and Biological Exposure Indices (BEIs), 1995-1996. Cincinnati, Ohio; American Conference of Governmental Industrial Hygienists, 1995.
8. Norin H, Vahter M. A rapid method for the selective analysis of total urinary metabolites of inorganic arsenic. Scan J Work Environ Health 1981;7:38-44.
9. Chen SC. Workers' exposure to arsenic in the maintenance of ion implanters in semiconductor fabrication facilities[master thesis]. Taipei, Taiwan; National Taiwan University, 1998. (in Chinese)
10. NIOSH. Pocket guide to chemical hazards. Cincinnati, Ohio; US National Institute for Occupational Safety and Health, 1990.
11. Guyton AC. Human physiology and mechanisms of disease. 5th ed. Philadelphia; Sauders, 1992.
12. Pinto SS, Varner MO, Nelson KW, et al. Arsenic trioxide absorption and excretion in industry. J Occup Med 1976;18:677-680.
13. Vahter M, Friberg L, Rahnster B, Nygren A, Nolinder P. Airborne arsenic and urinary excretion of metabolites of inorganic arsenic among smelter worker. Int Arch Occup Environ Health 1986;57:79-91.
14. IARC. Evaluation of carcinogenic risks to humans, Supplement 7. Lyon; International Agency for Research on Cancer, 1987:100-106.
15. Farmer JG, Johnson LR. Assessment of occupational exposure to inorganic arsenic based on urinary concentrations and speciation of arsenic. Brit J Ind Med 1990;47:342-348.
16. Buchet JP, Lauwerys R, Roels H. Comparison of urinary excretion of arsenic metabolites after a single oral

dose of sodium arsenite, monomethylarsonate, or dimethylarsinate in man. Int Arch Occup Environ Health 1981;48:71-79.
17. Foa V, Colombi A, Maroni M, Buratti M, Calzaferri G. The speciation of the chemical forms of arsenic in the biological monitoring of exposure to inorganic arsenic. Sci Tot Environ 1984;34:241-259.
18. Vahter M. Environmental and occupational exposure to inorganic arsenic. Acta Pharmacol Toxicol 1986;59:31-34.

**Table 1. Concentrations of airborne arsenic and arsine during the ion implanter maintenance.**

| Sample Types | Chemical | # of Sample | # of Samples with Concentration > DL* | GM (GSD)** As, $\mu$g/m$^3$ $AsH_3$, ppb | Range** As, $\mu$g/m$^3$ $AsH_3$, ppb |
|---|---|---|---|---|---|
| Area Sample | | | | | |
| Source Housing | Arsenic | 26 | 16 | 0.67(6.5) | 0.12-440 |
| | Arsine | 10 | 7 | 0.04(4.0) | 0.01-0.49 |
| Inside Hood | Arsenic | 19 | 14 | 4.62(14.3) | 0.24-560 |
| | Arsine | 13 | 9 | 0.04(3.2) | 0.02-0.41 |
| Outside Hood | Arsenic | 7 | 5 | 0.72(3.5) | 0.20-4.45 |
| | Arsine | 3 | 0 | ND | ND |
| Beam Line | Arsenic | 9 | 4 | 0.46(2.2) | 0.19-0.90 |
| | Arsine | 5 | 3 | 0.03(1.9) | 0.02-0.06 |
| End Station | Arsenic | 9 | 4 | 0.13(4.6) | 0.05-1.30 |
| | Arsine | 4 | 0 | ND | ND |
| Work Table | Arsenic | 4 | 1 | 0.32(-) | 0.32 |
| | Arsine | -*** | - | - | - |
| Passageway | Arsenic | 8 | 3 | 0.20(3.0) | 0.09-0.72 |
| | Arsine | 6 | 3 | 0.04(2.0) | 0.02-0.08 |
| Office | Arsenic | 11 | 0 | ND | ND |
| | Arsine | 4 | 0 | ND | ND |
| Subtotal | Arsenic | 93 | 47 | 0.92(9.2) | 0.05-560 |
| | Arsine | 45 | 22 | 0.04(2.9) | 0.01-0.49 |
| Personal Sample | | | | | |
| Maintenance | Arsenic | 31 | 11 | 1.66(2.2) | 0.50-7.00 |
| Engineers | Arsine | 35 | 15 | 0.07(4.3) | 0.01-1.66 |

* Detection Limit --- Arsenic: 0.01 μg/m$^3$, Arsine: 0.01 ppb.

** Only samples with concentration greater than detection limit were included.

*** Datum not available.

**Table 2. Arsenic loading on the work surface, cleaning cloth and gloves.**

| Sample Types | Number of Sample | GM (GSD)* | Range |
|---|---|---|---|
| Work Surface ($\mu$g/cm$^2$) | | | |
| Source Housing | 18 | 0.86(471) | ND* - 146 |
| Inside Hood | 18 | 10.1(4.2) | 0.01-103 |
| Beam Line | 6 | 6.00(13.9) | 0.48-19.9 |
| End Station | 5 | 0.28(3.1) | 0.02-8.56 |
| Work Table | 4 | 0.06(2.2) | ND*-4.00 |
| Floor | 2 | 2.67(1.1) | 2.53-2.81 |
| Cleaning Cloth ($\mu$g/cm$^2$) | | | |
| Source Housing | 7 | 201(3.6) | 15.0-832 |
| Hood | 7 | 13.1(6.4) | 0.37-117 |
| End Station | 3 | 24.2(1.4) | 16.3-34.7 |
| Gloves of Maintenance Engineers ($\mu$g/piece) | 36 | 681(3.4) | 24-7215 |

* Detection limit of wipe sample arsenic loading was 0.0005 μg/cm$^2$, which was used in the calculation of geometric mean & GSD for the value under detection limit.

**Table 3. Arsenic levels of the first morning voided urine during the week of ion implanter maintenance, μg/g creatinine.**

| Facility | Computer Programmer | | Maintenance Engineers | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1st* | | 2nd | | 3rd | | 4th | | 5th | | 6th | | 7th | |
| | N | Mean | N | Mean | N | Mean | N | Mean | N | Mean | N | Mean | N | Mean | N | Mean |
| A | 4 | 4.0 (2.5-4.6)** | 7 | 3.7 (2.8-4.7) | 7 | 3.7 (2.3-5.8) | 7 | 3.8 (2.5-5.2) | 7 | 5.5 (3.0-8.5) | 4 | 8.5 (5.1-10.6) | 2 | 5.9 (4.9-6.8) | 2 | 6.1 (4.3-8.0) |
| B | 4 | 4.4 (3.5-5.7) | 3 | 3.97 (2.8-5.6) | 4 | 4.3 (2.4-6.6) | 4 | 3.6 (2.6-5.6) | 4 | 4.2 (3.0-7.0) | 5 | 4.3 (3.0-6.4) | 5 | 4.8 (2.6-7.1) | 5 | 4.4 (3.3-6.6) |
| C | 3 | 2.7 (2.2-3.1) | 6 | 3.4 (2.0-6.0) | 6 | 3.7 (1.8-8.6) | 5 | 3.5 (1.3-6.6) | 2 | 4.4 (1.6-7.3) | - | - (-) | 2 | 8.0 (1.9-14.2) | - | - (-) |
| Total | 11 | 3.8 (2.2-5.7) | 16 | 3.6 (2.0-6.0) | 17 | 3.8 (1.8-8.6) | 16 | 3.7 (1.3-6.6) | 13 | 4.9 (1.6-8.3) | 9 | 6.2 (2.0-10.6) | 9 | 5.8 (1.9-14.2) | 7 | 4.9 (3.3-8.0) |

* The day urine samples were collected.

** Numbers in parenthesis indicate the range of urinary arsenic levels.

**Table 4. Referential urinary arsenic levels in five previous and the present studies.**

| Reporters | Number of Sample | Mean Concentration |
|---|---|---|
| Farmer & Johnson, 1990[15] | 40 | 4.4 μg/g creatinine |
| Buchet et al., 1981[16] | 16 | 4.7 μg/L |
| Foa et al., 1984[17] | 148 | 5.9 μg/L |
| Vahter, 1986[18] | 6 | 6.0 μg/L |
| Present Study | 31* | 3.7 μg/g creatinine |

* Include urine samples of both the computer programmers and the maintenance engineers, the first day urine samples, to establish the baseline data of urinary arsenic level.

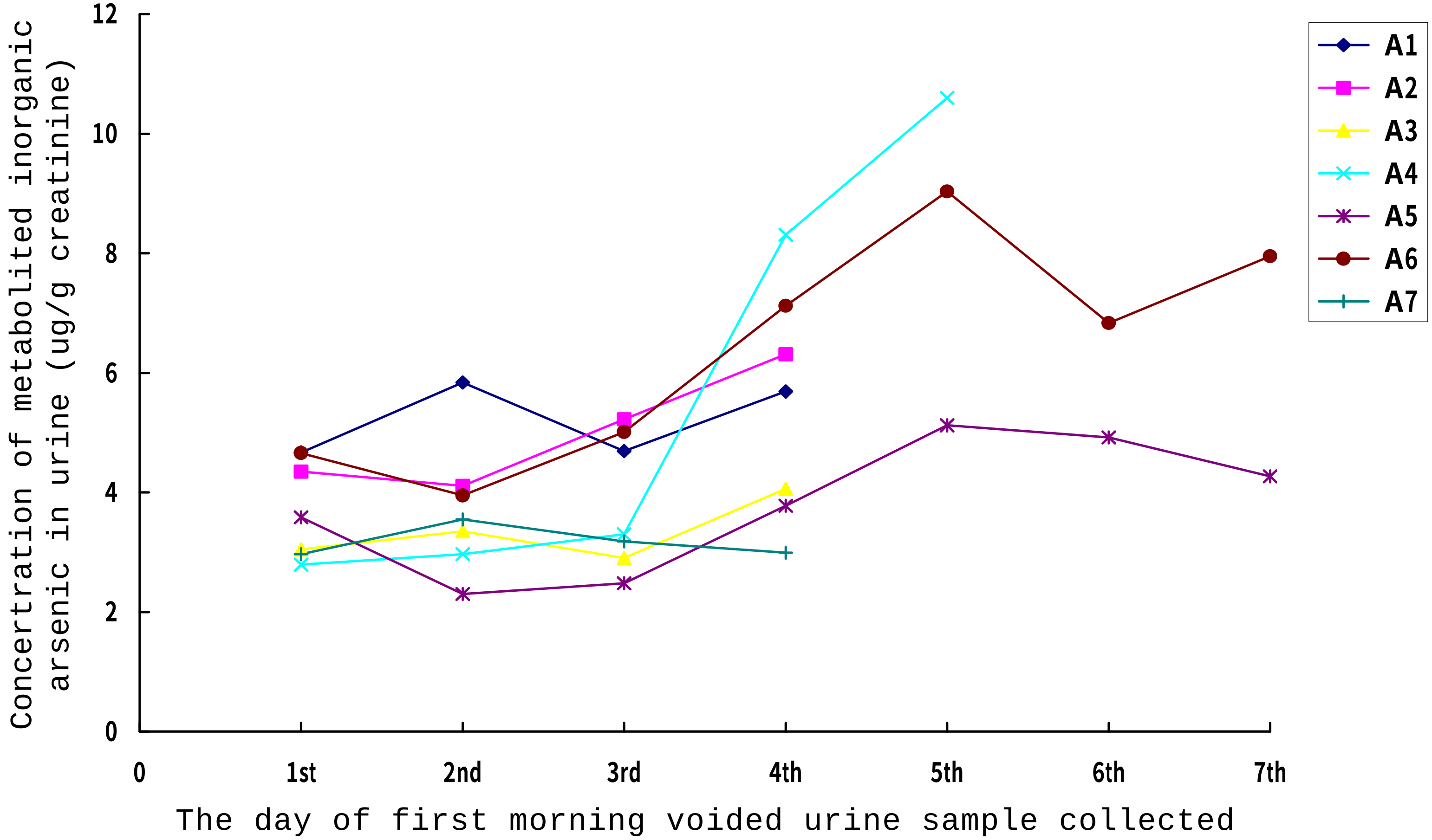

Figure 1. Urinary arsenic levels of seven maintenance engineers in Facility A during the one-week ion implanter maintenance.