**Figure S1. Representative HPLC-AFS chromatograms.** (A) Representative HPLC-AFS chromatogram of blank. (B) Representative HPLC-AFS chromatogram of the standards, with concentrations recorded as As at 10 ng/mL (As$^{III}$, DMA$^V$, MMA$^V$, and As$^V$ concentrations are all 10 ng/mL).
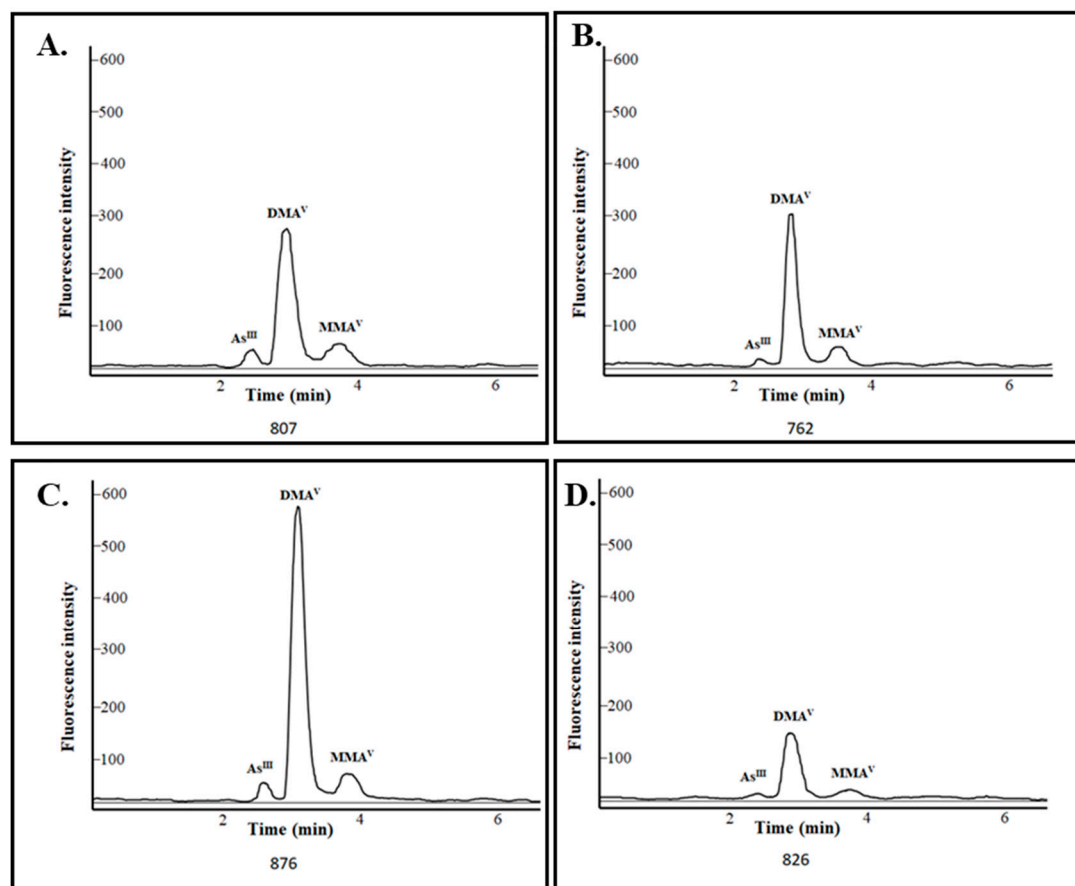
**Figure S2. Representative HPLC-AFS chromatograms.** (A) Representative HPLC-AFS chromatogram of urine sample #807. (B) Representative HPLC-AFS chromatogram of urine sample #762. (C) Representative HPLC-AFS chromatogram of urine sample #876. (D) Representative HPLC-AFS chromatogram of urine sample #826.
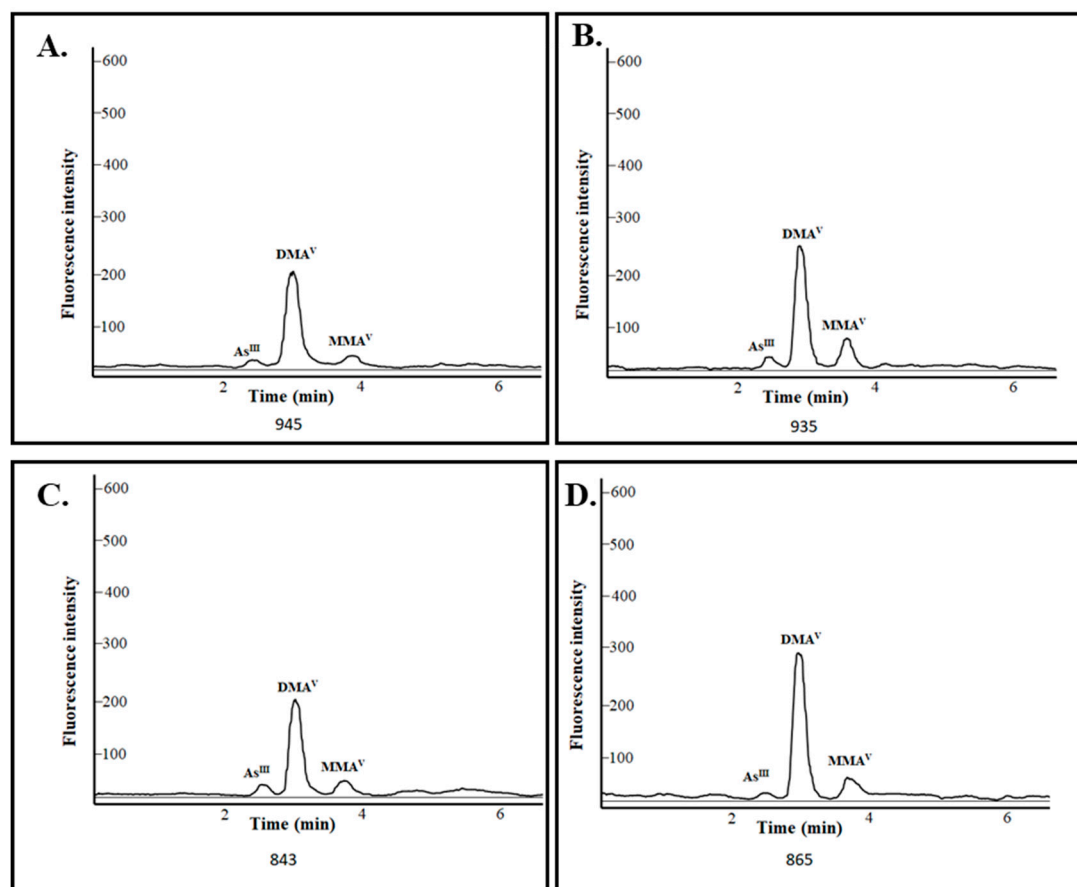
**Figure S3. Representative HPLC-AFS chromatograms.** (A) Representative HPLC-AFS chromatogram of urine sample #945. (B) Representative HPLC-AFS chromatogram of urine sample #935. (C) Representative HPLC-AFS chromatogram of urine sample #843. (D) Representative HPLC-AFS chromatogram of urine sample #865.

**Figure S4. Representative HPLC-AFS chromatograms.** (A) Representative HPLC-AFS chromatogram of urine sample #866. (B) Representative HPLC-AFS chromatogram of urine sample #914. (C) Representative HPLC-AFS chromatogram of urine sample #816. (D) Representative HPLC-AFS chromatogram of urine sample #896.
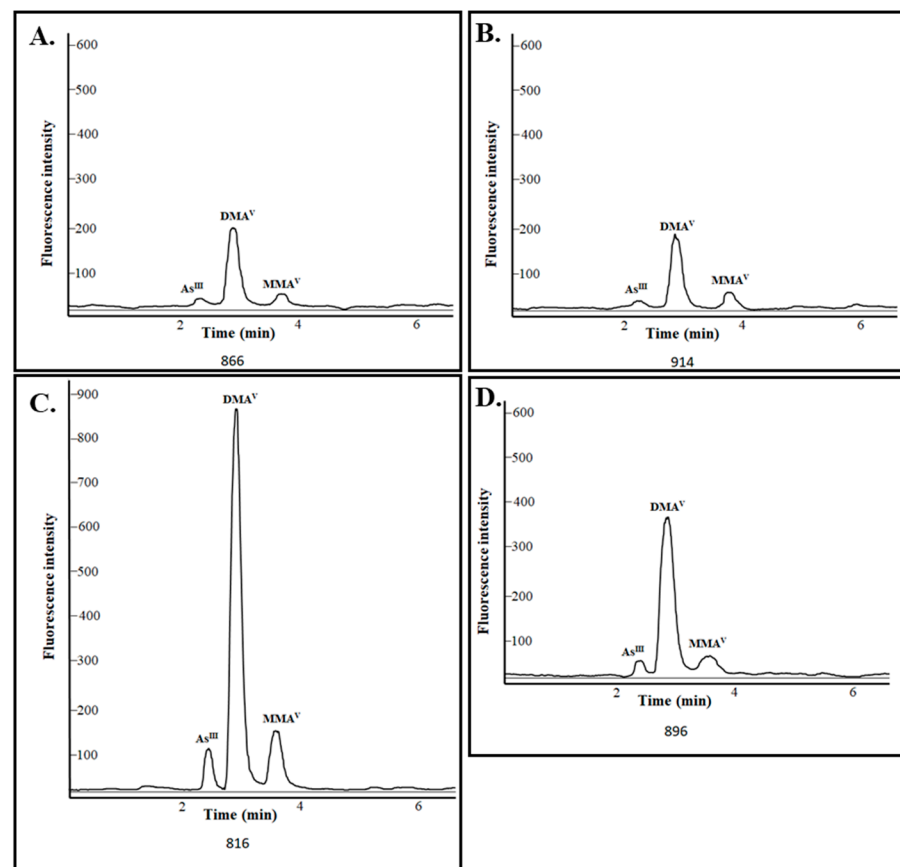
**Figure S5. Representative HPLC-AFS chromatograms.** (A) Representative HPLC-AFS chromatogram of urine sample #835. (B) Representative HPLC-AFS chromatogram of urine sample #811. (C) Representative HPLC-AFS chromatogram of urine sample #796. (D) Representative HPLC-AFS chromatogram of urine sample #858.
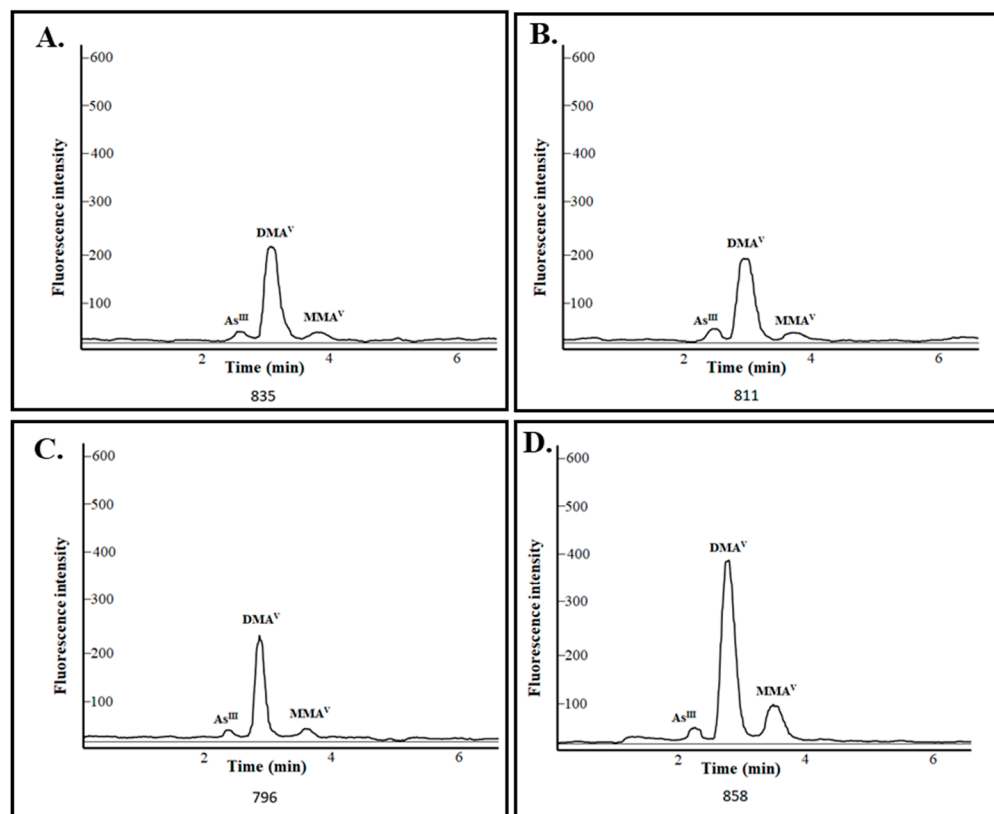
**Figure S6. Representative HPLC-AFS chromatograms.** (A) Representative HPLC-AFS chromatogram of urine sample #830. (B) Representative HPLC-AFS chromatogram of urine sample #832. (C) Representative HPLC-AFS chromatogram of urine sample #872. (D) Representative HPLC-AFS chromatogram of urine sample #918.
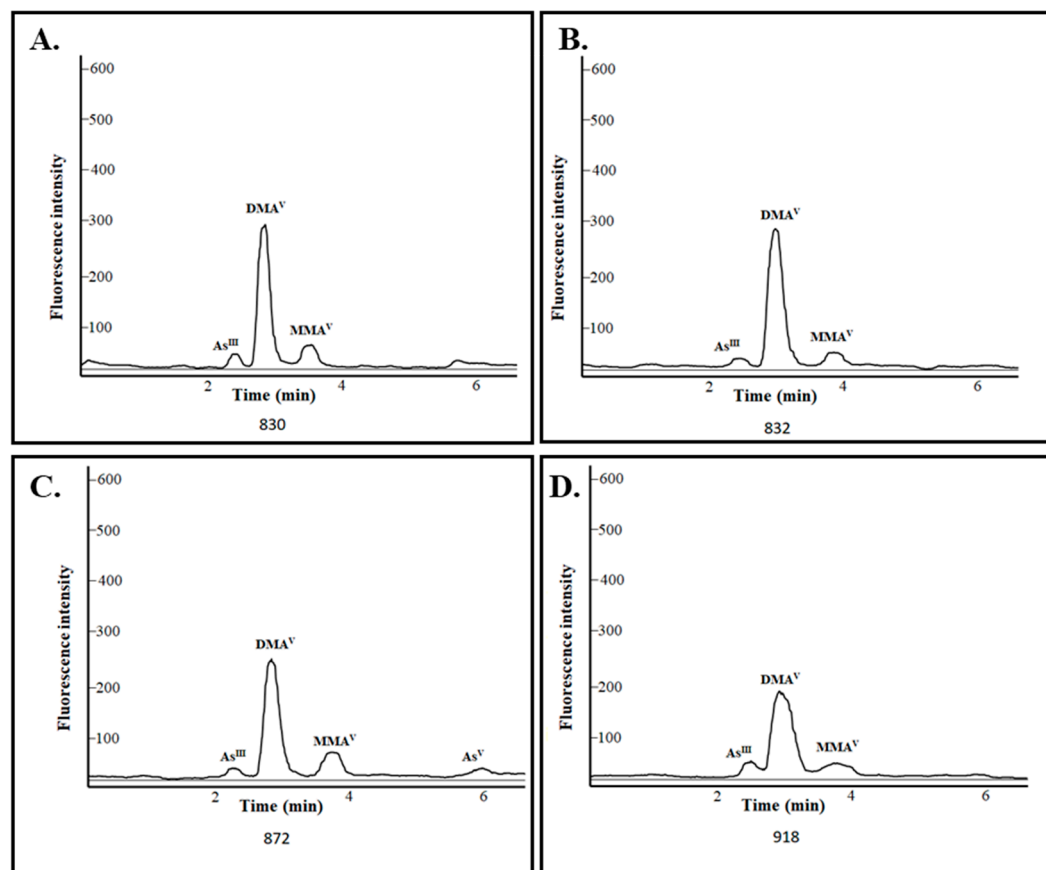
**Figure S7. Representative HPLC-AFS chromatograms.** (A) Representative HPLC-AFS chromatogram of urine sample #902. (B) Representative HPLC-AFS chromatogram of urine sample #916. (C) Representative HPLC-AFS chromatogram of urine sample #828. (D) Representative HPLC-AFS chromatogram of urine sample #807.

**Figure S8. Representative HPLC-AFS chromatograms.** (A) Representative HPLC-AFS chromatogram of urine sample #861. (B) Representative HPLC-AFS chromatogram of urine sample #922. (C) Representative HPLC-AFS chromatogram of urine sample #856. (D) Representative HPLC-AFS chromatogram of urine sample #885.
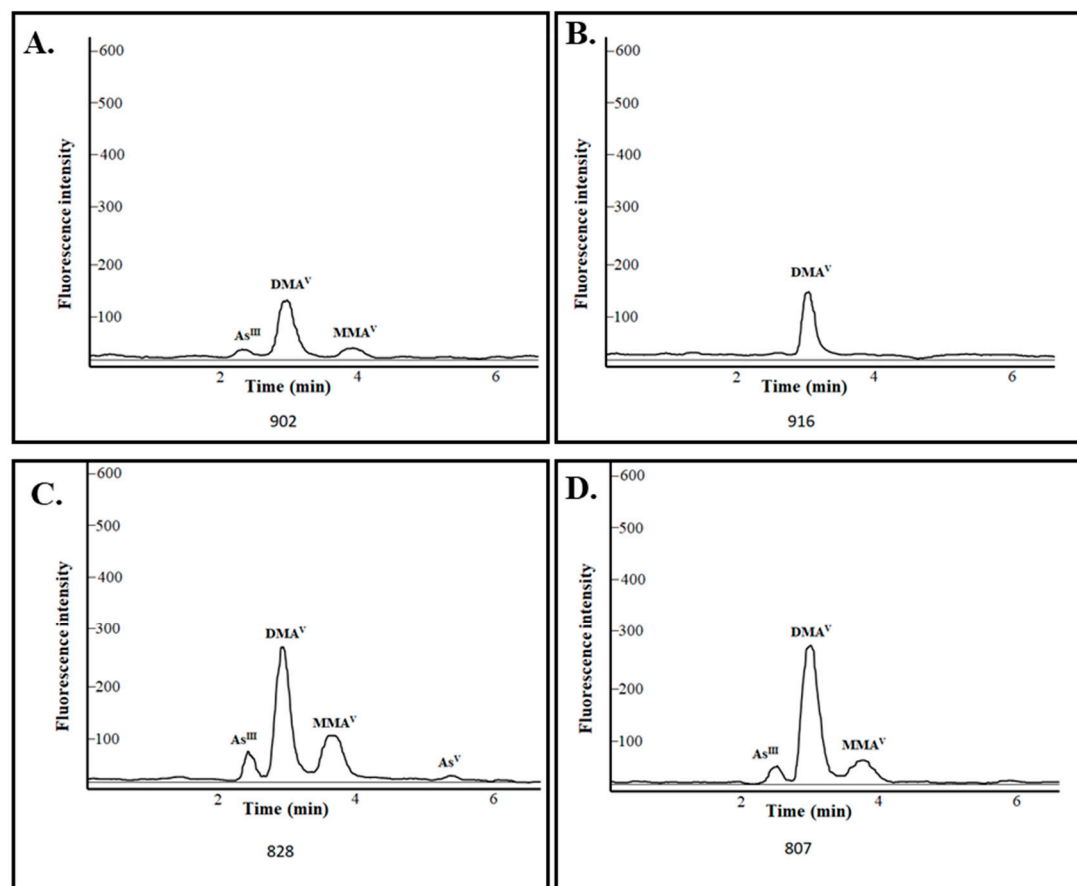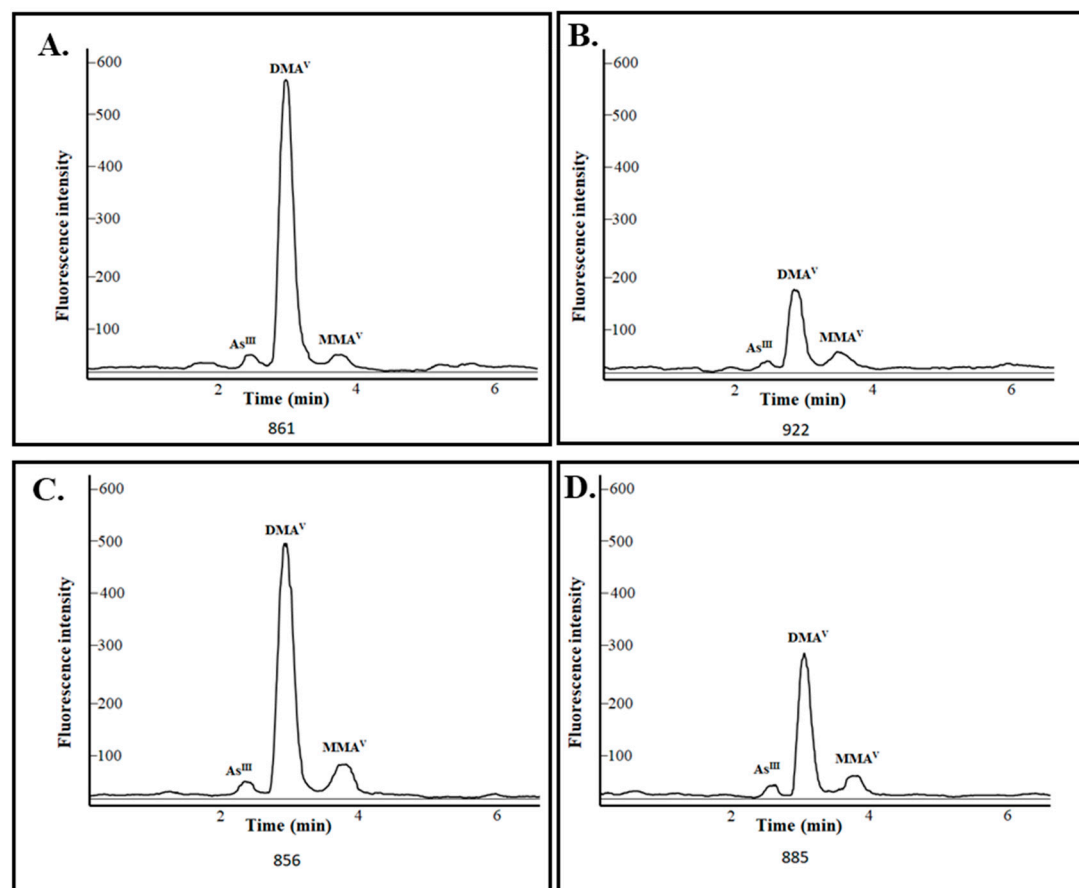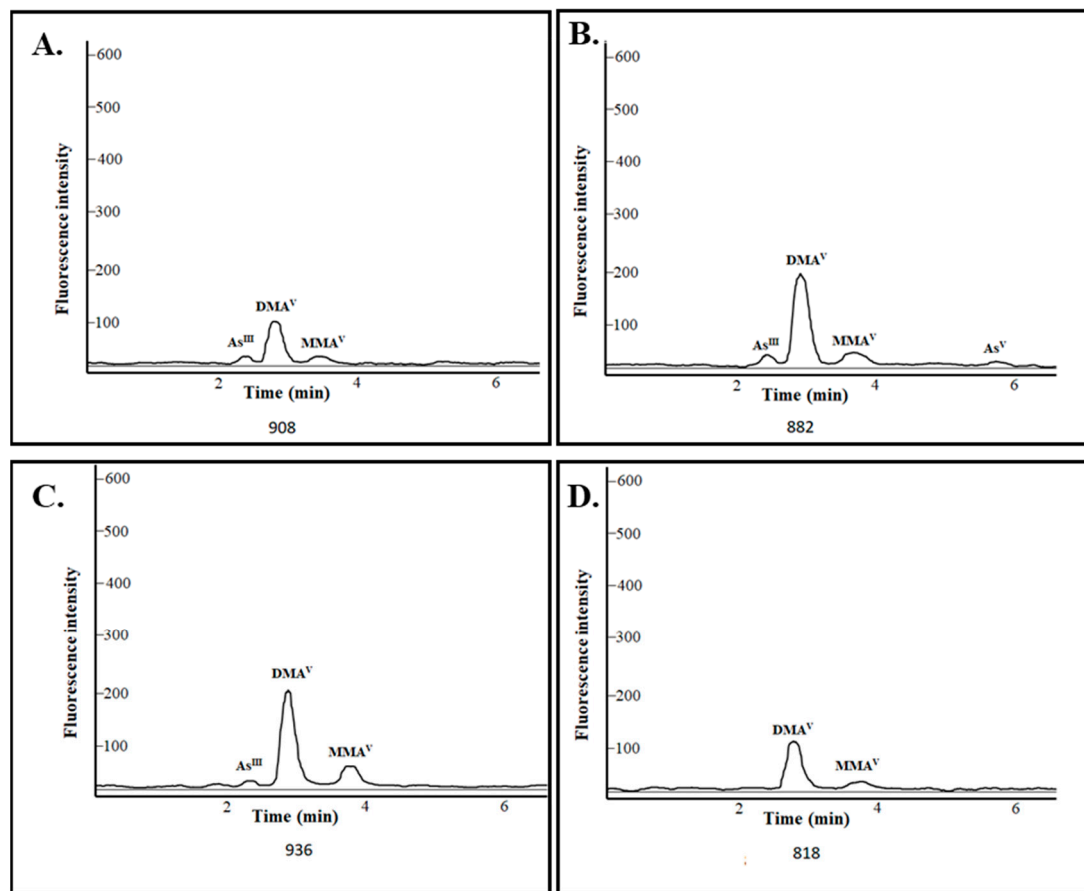
**Figure S9. Representative HPLC-AFS chromatograms.** (A) Representative HPLC-AFS chromatogram of urine sample #908. (B) Representative HPLC-AFS chromatogram of urine sample #882. (C) Representative HPLC-AFS chromatogram of urine sample #936. (D) Representative HPLC-AFS chromatogram of urine sample #818.

**Table S1 Population's characteristics description of the normal group and vitamin D excess group**

| Variables | Normal group | Vitamin D excess group | t/χ2/z | *P-Value* |
|---|---|---|---|---|
| | Mean ± SD/median (P25-P75)/n (%) | | | |
| Age, years, mean ± SD | 57.58 ± 10.80 | 59.47 ± 10.79 | -1.709 | 0.088 |
| BMI, kg/m2, mean ± SD | 25.88 ± 3.70 | 25.16 ± 5.48 | 1.763 | 0.078 |
| Gender, n (%) | | | | |
| Male | 175 (23.1) | 81 (10.7) | 86.83 | **< 0.01** |
| Female | 469 (62.0) | 31 (4.2) | | |
| Skin hyperkeratosis | | | | |
| No | 426 (56.3) | 63 (8.3) | 4.093 | **0.043** |
| Yes | 218 (28.8) | 49 (6.6) | | |
| Education, n (%) | | | | |
| Primary and below | 221 (29.2) | 44 (5.8) | 1.083 | 0.582 |
| Junior high school | 353 (46.7) | 56 (7.4) | | |
| Senior high and above | 70 (9.3) | 12 (1.6) | | |
| Occupation, n (%) | | | | |
| Farmer | 551 (72.8) | 101 (13.4) | 1.716 | 0.190 |
| Others | 93 (12.3) | 11 (1.5) | | |
| Milk consumption, n (%) | | | | |
| >1/week | 256 (33.9) | 32 (4.2) | 5.057 | **0.025** |
| ≤1/week | 388 (51.3) | 80 (10.6) | | |
| Urinary tAs, μg/L, median (P25-P75) | 66.94 (24.98-132.63) | 84.38 (37.59-152.59) | -2.430 | **0.015** |
| Urinary iAs, μg/L, median (P25-P75) | 3.19 (0.83-14.35) | 6.57 (0.83-17.47) | -1.793 | 0.073 |
| Urinary MMA$^V$, μg/L, median (P25-P75) | 4.33 (0.32-15.07) | 6.84 (0.32-19.11) | -1.490 | 0.136 |
| Urinary DMA$^V$, μg/L, median (P25-P75) | 48.59 (17.96-100.88) | 70.85 (32.13-122.89) | -2.555 | **0.011** |

| Blood glucose, mmol/L, median (P25-P75) | 5.80 (5.10, 7.35) | 5.70 (5.10, 6.70) | -1.088 | 0.276 |

**Table S2 Population's characteristics description of the normal group and skin hyperkeratosis group**

| Variables | Normal group | Skin hyperkeratosis group | t/χ2/z | P-Value |
|---|---|---|---|---|
| | Mean ± SD/median (P25-P75)/n (%) | | | |
| Age, years, mean ± SD | 58.25 ± 11.08 | 57.30 ± 10.26 | 1.150 | 0.250 |
| BMI, kg/m2, mean ± SD | 25.59 ± 4.19 | 26.09 ± 3.63 | -1.620 | 0.106 |
| Gender, n (%) | | | | |
| Male | 166 (21.8) | 90 (11.8) | 0.002 | 0.962 |
| Female | 329 (43.2) | 177 (23.2) | | |
| Education, n (%) | | | | |
| Primary and below | 185 (24.3) | 84 (11.0) | 4.347 | 0.114 |
| Junior high school | 252 (33.1) | 157 (20.6) | | |
| Senior high and above | 58 (7.6) | 26 (3.4) | | |
| Occupation, n (%) | | | | |
| Farmer | 423 (55.5) | 234 (30.7) | 0.698 | 0.404 |
| Others | 72 (9.5) | 33 (4.3) | | |
| Milk consumption, n (%) | | | | |
| >1/week | 185 (24.3) | 106 (13.9) | 0.398 | 0.528 |
| ≤1/week | 310 (40.7) | 161 (21.1) | | |
| Urinary tAs, μg/L, median (P25-P75) | 57.49 (19.92-122.79) | 80.04 (41.42-149.22) | -3.917 | **< 0.01** |
| Urinary iAs, μg/L, median (P25-P75) | 3.19 (0.83-14.47) | 5.28 (0.83-15.10) | -0.836 | 0.403 |
| Urinary MMA$^V$, μg/L, median (P25-P75) | 3.58 (0.32-15.34) | 6.85 (0.32-17.30) | -1.700 | 0.089 |
| Urinary DMA$^V$, μg/L, median (P25-P75) | 45.32 (14.08-95.58) | 66.70 (32.70-119.50) | -4.044 | **< 0.01** |
| Blood glucose, mmol/L, median (P25-P75) | 5.80 (5.10, 6.70) | 5.60 (5.10, 6.60) | -1.687 | 0.092 |
| 25(OH)D, ng/mL, mean ± SD | 72.79 ± 21.14 | 76.34 ± 25.15 | -2.064 | **0.039** |