Applied Organometallic Chemistry

(Appl. Organometal. Chem.)

Featuring selected papers from JASS meeting in Hokkaido Prefectural Sapporo Institute

Guest Editor: Dr Jin
Section Editor: J. Yoshinaga

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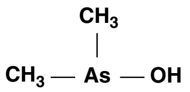
Section: Bioorganometallic Chemistry

Dimethylarsinous acid, a reduced form of dimethylarsinic acid, is detected in urine of individuals who ingest arsenic-polluted drinking water. A cytogenetic study using V79 cells revealed that dimethylarsinous acid was very toxic (LC_{50}; 1.1 μM) and induced a high rate of tetraploids (73% at 2.5 μM). Dimethylarsinous acid significantly increased sister chromatid exchange and chromosomal aberrations, most of which were gaps and breaks.



$$\begin{array}{c} CH_3 \\ | \\ CH_3 - As - OH \end{array}$$

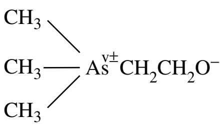
Dimethylarsinous acid

K. Kuroda*, K. Yoshida, M. Yoshimura, Y. Endo, H. Wanibuchi, S. Fukushima and G. Endo 221–225

Genotoxicity of dimethylarsinous acid: high induction of tetraploids

Section: Speciation Analysis and Environment

We have observed the first *in vivo* acute immunotoxicity of a trimethyl(2-hydroxyethyl)arsonium cation, namely arsenocholine (AsCho), which is present in seafood. A high dose of the synthetic pure AsCho was administered intraperitoneally (0.1 g kg^{-1} mouse weight) or orally (a total of 10.0 g kg^{-1}) to mice; its effect on the immune organs and immune cells was assessed. Administered AsCho showed weak and partial, but significant, *in vivo* immunotoxicity, although it did not cause any severe inflammatory responses.

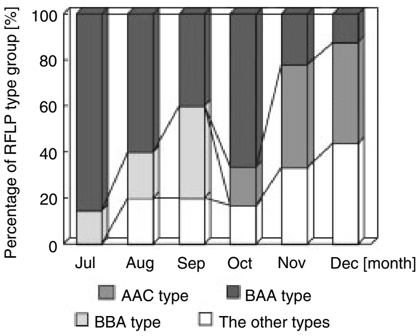


Primary structure of AsCho

T. Sakurai*, M. Ochiai, C. Kojima, T. Ohta and K. Fujiwara 226–230

Evaluation of in vivo *acute immunotoxicity of arsenocholine, a trimethyl arsenic compound in seafood*

Decomposition processes of dimethylarsinic acid (DMAA) in aquatic environments were found to depend on bioactivities of several bacterial populations, according to monitoring of the bacterial biomass involved in DMAA decomposition in Lake Kahokugata from April 2002 to January 2003. RFLP analysis and phylogenetic analysis using 16S rDNA sequences revealed that the bacterial population contributing to DMAA decomposition would be specific to the summer season or winter season.



T. Maki*, H. Hasegawa and K. Ueda 231–238

Seasonal dynamics of dimethylarsinic-acid-decomposing bacteria dominating in Lake Kahokugata

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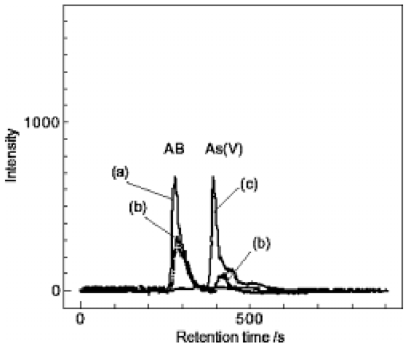
HNO_3–$HClO_4$–H_2SO_4 was the most effective mixture for decomposing AsC and AB, which are the most difficult compounds among all types of organic arsenic compounds to decompose. Complete decomposition of AB was only achieved at ≥320 °C and when the sample was evaporated to dryness. High-performance liquid chromatography combined with inductively coupled plasma atomic emission spectrometry following this treatment showed all of the arsenic present as As(V).



T. Narukawa*, T. Kuroiwa, K. Inagaki, A. Takatsu and K. Chiba 239–245

Decomposition of organoarsenic compounds for total arsenic determination in marine organisms by the hydride generation technique

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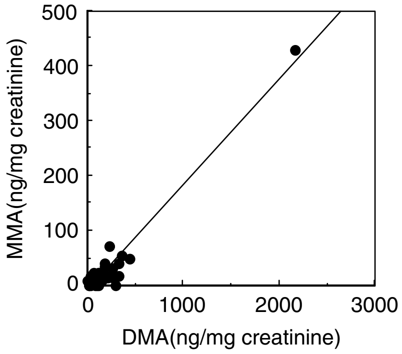
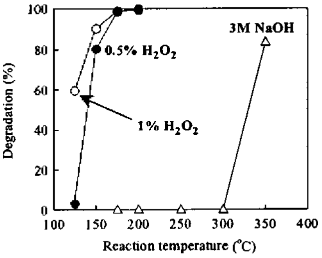
The arsenic concentrations in five shallow tubewell-waters from the Mushidabad district of West Bengal, India, ranged from 18.0 to 408.4 ppb and those in four deep tubewell-waters were from 5.2 to 9.6 ppb. The averages of arsenic(III), DMA, MMA and arsenic(V) in urine were 28.7 ng ml^{-1}, 168.6 ng ml^{-1}, 25.0 ng ml^{-1} and 4.6 ng mg^{-1} creatinine respectively. The average proportion of (MMA + DMA) to total arsenic was 86.7 ± 9.2%, (mean ± RSD, $n = 43$), except the data for one boy whose proportion was 8.0%. With this exception, there were significantly positive correlations ($p = 0.01$) between arsenic(III) and MMA, between arsenic(III) and DMA and between MMA and DMA.



H. Tokunaga*, T. Roychowdhury, T. Uchino and M. Ando 246–253

Urinary arsenic species in an arsenic-affected area of West Bengal, India (part III)

Degradation of phenylarsonic acid (PA) and its derivatives by hydrothermal treatment (HTT) was examined. When PA was subjected to an HTT with H_2O_2 at 175–200 °C, PA was almost completely degraded into arsenate, whereas an HTT with NaOH at these temperatures provided almost no degradation. The effect of the structures of PA derivatives upon the degradation susceptibility was discussed. A photocatalytic reaction using TiO_2 was also attempted for the degradation of PA derivatives.



T. Nakajima, T. Kawabata, H. Kawabata, H. Takanashi, A. Ohki* and S. Maeda 254–259

Degradation of phenylarsonic acid and its derivatives into arsenate by hydrothermal treatment and photocatalytic reaction

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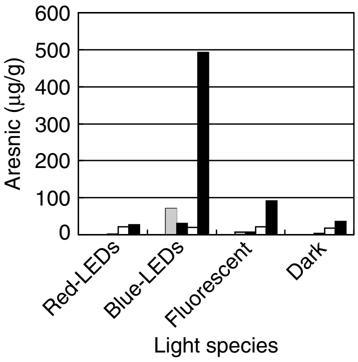
Recently, we isolated a new strain of *Thraustochytrium* sp. CHN-1 (labyrinthulids) containing a high levels of docosahexaenoic acid (C 22 : 6, DHA) and astaxanthin. The effects of various forms of light on arsenic accumulation in *Thraustochytrium* CHN-1 were investigated with regard to the quantity of arsenic accumulated and the arsenic species present.



Y. Yamaoka*, M. L. Carmona and K. Jin **260–264**

Blue light induces arsenate uptake in the protist Thraustochytrium

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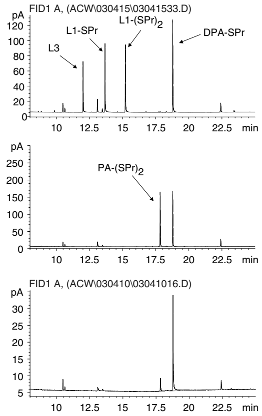
To elucidate the current extent of pollution with diphenylarsenic compounds abandoned by Japanese Imperial Forces, we have developed analytical procedures for environmental samples using gas chromatography (with/without propanethiol derivatization) and liquid chromatography. We applied this to the analysis of organoarsenic compounds from the well waters in Kamisu-cho (where the water was thought to have had deleterious effects on the inhabitants) and soils in Sagami region (where previously a naval arsenal had stood). The true magnitude of contamination became evident after these analyses.



S. Hanaoka*, E. Nagasawa, K. Nomura, M. Yamazawa and M. Ishizaki **265–275**

Determination of diphenylarsenic compounds related to abandoned chemical warfare agents in environmental samples

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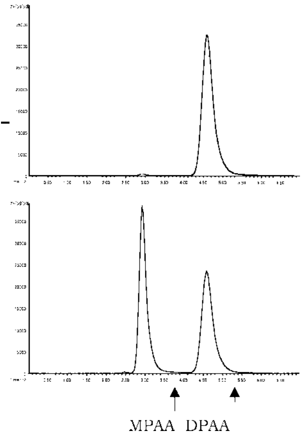
A simple, rapid and robust analytical method for determining diphenylarsinic acid in human and environmental samples is developed. Using hydrophilic polymer-based gel-permeation HPLC–ICP-MS, diphenylarsinic acid was quantified in 7 min. Two method has been applied to arsenic-contaminated groundwater in Japan.



Y. Shibata*, K. Tsuzuku, S. Komori, C. Umedzu, H. Imai and M. Morita **276–281**

Analysis of diphenylarsinic acid in human and environmental samples by HPLC–ICP-MS

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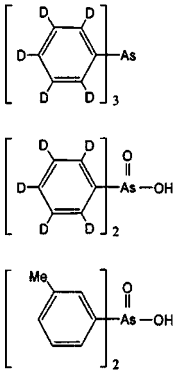
Investigation of well water contaminated with phenylarsenic acids in Ibaraki, Japan, has required the synthesis of internal analytical standards for mass spectrometric and liquid chromatographic analysis. The synthesis and characterization of deuterated and methylated standards are described.



K. Nakamiya*, Y. Shibata, H. Ito, J. S. Edmonds and M. Morita..... 282–286

Synthesis of phenyl arsenic analytical standards related to contaminated well water in Kamisu, Ibaraki, Japan

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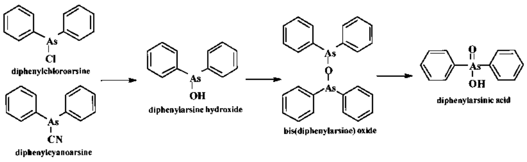
Diphenylarsinic acid (DPAA) and phenylarsonic acid, the degradation products of organoarsenic chemical warfare agents, were detected in well water by HPLC–ICP-MS. Standard material of DPAA was synthesized from arsenic acid and phenylhydrazine using a copper(II) catalyst. The DPAA showed a protonated ion at *m*/*z* 263 $[M + H]^+$ and a loss of H_2O ion at *m*/*z* 245 $[M + H - H_2O]^+$ from the protonated ion by electrospray ionization time-of-flight mass spectrometry.



K. Kinoshita, Y. Shida, C. Sakuma, M. Ishizaki, K. Kiso, O. Shikino, H. Ito, M. Morita, T. Ochi and T. Kaise* 287–293

Determination of diphenylarsinic acid and phenylarsonic acid, the degradation products of organoarsenic chemical warfare agents, in well water by HPLC–ICP-MS