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

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To elucidate the current extent of pollution of the environment with diphenylarsine chloride (DA, Clark I) and diphenylarsine cyanide (DC, Clark II), we have developed analytical procedures using gas and liquid chromatography and employed them to analyze water and soil samples. DA, DC, and their degradation products were extracted with water or organic solvents. Derivatization with *n*-propanethiol was adopted to achieve higher analytical reproducibility. DA and DC were unstable and decomposed into bis(diphenylarsine)oxide (BDPAO) in water, but only negligibly into diphenylarsinic acid (DPAA) during the 30 days of a stability test. Diphenylarsenic compounds afforded the same product by this derivatization, but their reaction rates varied depending on the starting materials. DPAA had to be treated under acidic conditions at 60 °C to achieve the desired conversion efficiency. Recovery of the thiol derivatives of the diphenylarsenic compounds tested was almost quantitative from water, but only about 50% from soil, reflecting the low extraction efficiency. We applied the method to the analysis of organoarsenic compounds sampled from the water of the drinking well in Kamisu-cho, Ibaraki Prefecture, where the water was thought to have had deleterious effects on the inhabitants. The high level of DPAA was identified as the causative agent. Our analyses of soil samples from Samukawa-cho and Hiratsuka City, Kanagawa Prefecture, where a naval arsenal had previously stood, succeeded in identifying intact DA, BDPAO and triphenylarsine, diphenylarsenic thiol-derivatives, as well as other substances (mustard gas, lewisite). The true magnitude of contamination became evident after these measurements.

KEYWORDS: abandoned chemical warfare agents; sternutators; diphenylarsine chloride; diphenylarsine cyanide; diphenylarsinic acid; Japanese Imperial Forces

INTRODUCTION

Diphenylarsine chloride (DA, Clark I) and diphenylarsine cyanide (DC, Clark II), classified as emetics, are known to act as sternutators and were produced and termed 'red agents' by the Japanese Imperial Forces. Red agents were loaded into shells (called red shells), red canisters, toxic smoke candles filled with powdered celluloid or as diced pumices doused with them. Red agents used as sternutators contained either DC only or a mixture of DC and DA, and were synthesized by the processes shown in Figure 1.

Documents exist indicating that the former army had stocked *ca* 1000 tons of sternutators at the Tadanoumi

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1) $2(C_6H_5)_2AsO_2H + 2SO_2 + H_2O \rightarrow [(C_6H_5)_2As]_2O + 2H_2SO_4$

DPAA **BDPAO**

2) $[(C_6H_5)_2As]_2O + 2HCl \rightarrow 2(C_6H_5)_2AsCl + H_2O$

BDPAO **DA**

3) $(C_6H_5)_2AsCl + NaCN \rightarrow (C_6H_5)_2AsCN + NaCl$

DA **DC**

Figure 1. Synthesis processes of red agents used by the Japanese Imperial Forces.

Armory, Ohkunoshima Island, Hiroshima Prefecture; further, the former navy also appears to have stocked *ca* 100 tons of sternutators at the Sagami Naval Arsenal, Kanagawa Prefecture, at the end of World War II. The majority of these kinds of material formerly on the Japanese mainland are known to have been discharged in the sea, incinerated or buried[1,2]

Presently, the recovery and destruction of chemical weapons that were abandoned in China are being carried out co-operatively by the Japanese and Chinese governments.[3] In Japan, chemical shells containing a blend of mustard gas and lewisite were recovered from Lake Kushyaro, Hokkaido Prefecture, and disposed of in 2000. Recently, further problems related to chemical weapons abandoned by the Japanese Imperial Forces have been raised at other areas in Japan. High levels of arsenic were detected in potable well waters in Kamisu-cho, Ibaraki Prefecture, where local inhabitants suffered serious health problems. Extensive surveys, including those carried out in this study, suggest that the cause is likely the chemical agents abandoned there by the Japanese Imperial Forces.

Also, at a road construction site in Samukawa-cho, Kanagawa Prefecture, where the Sagami Naval Arsenal was formerly located, beer bottles containing mustard gas, lewisite and 2-chloroacetophenone were found during excavation, causing injury to workers. Furthermore, at another construction site in Hiratsuka City, Kanagawa Prefecture, where the chemical experiments facilities of the Sagami Naval Arsenal were previously sited, a number of spherical glass bottles were unearthed, again causing injury to workmen. These incidents showed the necessity to determine the true contamination level caused by sternutators and other chemical agents.

Little has been reported on the analysis of diphenylarsenic compounds, apart from some applications of derivatization using thiol reagents.[4,5] However, these are the methodology for the analysis of diphenylarsenic compounds. And study, which applies to the degradation products of sternutators in environmental samples, is very limited.[6] We have developed an appropriate method for the analysis of individual diphenylarsenic compounds in environmental samples, and analyzed these and related compounds in water and soil in exploratory surveys of contamination caused by the Japanese Imperial Forces.

This work is of special interest as, since the end of World War II, no similar studies have been carried out in Japan. Available documentation is, in any case, in Japanese and, therefore, not immediately accessible to an international audience. Thus, the work described here should help to make current chemical weapons issues in Japan more internationally known.

EXPERIMENTAL

Reagents

As red-agent-related compounds, DA (Clark I), DC (Clark II), bis(diphenylarsine)oxide (BDPAO), and diphenylarsinic acid (DPAA) were synthesized and provided by Hodogaya Contract Laboratory Ltd (Japan). They were >98% pure by NMR. Phenylarsonic acid (PAA) and triphenylarsine (TPA) were purchased from Tokyo Kasei Chemicals Ltd (Japan), and phenylarsine oxide (PAO) from Wako Pure Chemicals Ltd (Japan). Pesticide analysis-grade solvents were used. Ultrapure water was distilled and purified using a Milli-Q system (Millipore, Bedford, MA, USA).

Authentic sample

In April 2003, 11 water samples (area A: four samples; area B: seven samples) were collected from the two wells in the different two area of Kamisu-cho, Ibaraki Prefecture, in which arsenic levels well in excess of the water quality standards had been detected, and provided by the Ibaraki Prefectural Institute of Public Health (see Fig. 2).

In November 2002, soil samples were collected from close to the sites (a and b in Figure 2) where bottles containing sulfur mustard and lewisite had been found in Samukawa-cho, Kanagawa Prefecture. Surface and core soil samples (0.5, 1.5, 2.5 and 3.5 m depth) were also collected at the construction site (c in Fig. 2) in Hiratsuka City in April 2003. And these were provided by each local office for the Ministry of Land, Infrastructure and Transport.

Preparation of standard solutions

Primary standard solutions of DA, DC, BDPAO and TPA were prepared using toluene or acetonitrile. Dilutions were prepared with hexane, dichloromethane or acetonitrile. DPAA, PAA and PAO solutions were prepared with acetonitrile or ultrapure water.

Sample preparation

Extraction

Aqueous samples (100 ml) and soil samples (*ca* 10 g) were extracted with organic solvent (20 ml). In studies of the extraction of diphenylarsine-related compounds, dichloromethane or hexane was used. Samples were extracted by either shaking (water samples) or tumbling (soil samples) twice for 5–10 min each time, and were then allowed to stand for 30 min. Soil sample extracts were centrifuged (2000 rpm,

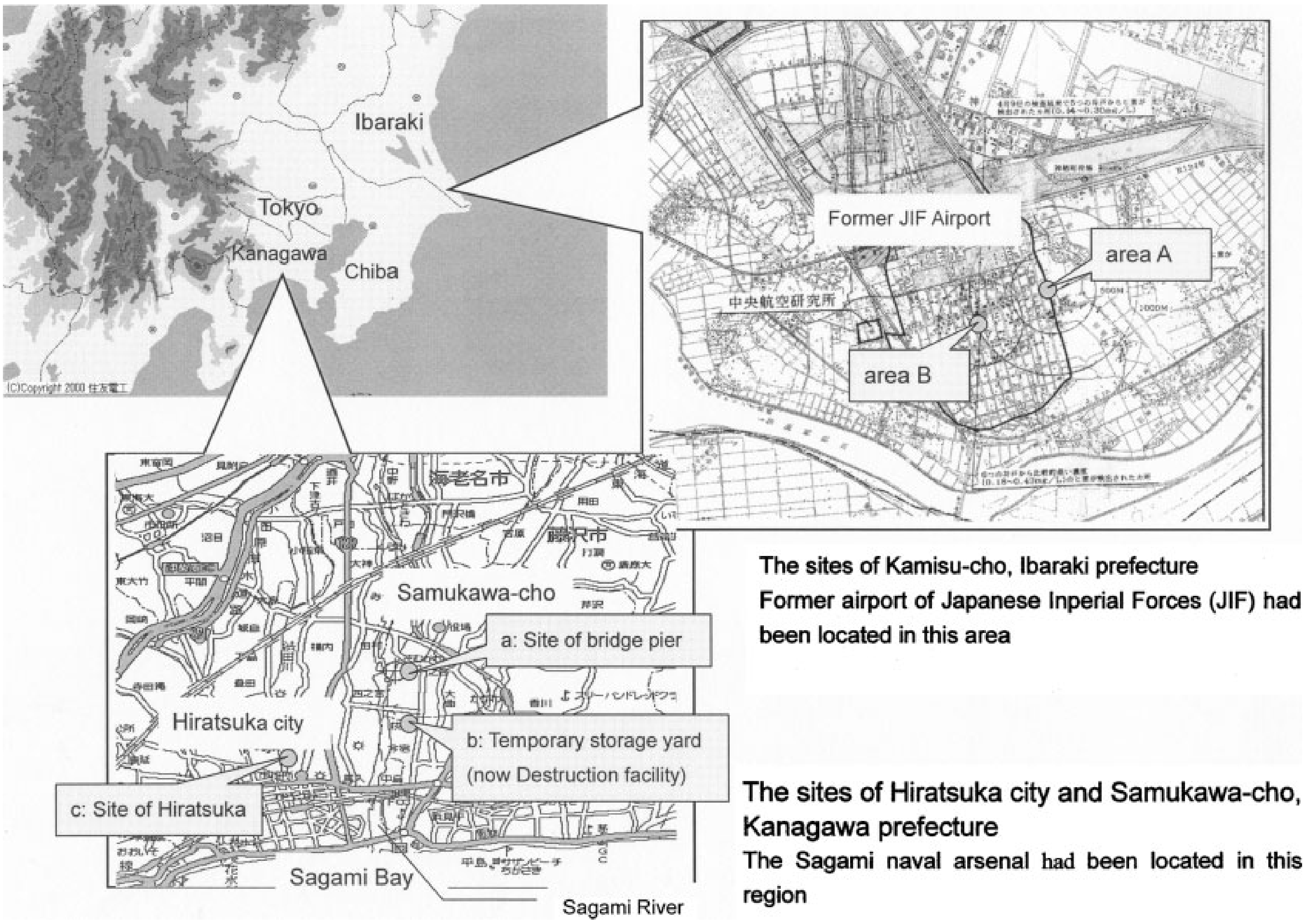


Figure 2. Location of controversial abandoned chemical weapons sites in Japan.

5 min) when necessary. The organic phase collected was dehydrated over anhydrous sodium sulfate and filtered through a No. 2 filter paper (Advantec, Tokyo, Japan). The mixed extract was then concentrated by rotary evaporation to a few milliliters, then purged with nitrogen to 1 ml, and analyzed by gas chromatography (GC) and GC–mass spectrometry (MS).

Soil samples (10 g) were also extracted with 20 ml of ultrapure water twice and used in the thiol derivatization described below.

Thiol derivatization

Water samples or aqueous layers (40 ml portions) after dichloromethane extraction were poured into 50 ml screw-cap vials. HCl solution (1 ml; 2 mol l^{-1}) and 50 μl of *n*-propanethiol were added to the sample vials and mixed. The derivatization reaction (Fig. 4) was completed at ambient temperature or 60 °C for 20 min. Hexane (5 ml) was added to the vials by pipette and vigorously shaken twice. A total of 10 ml of the hexane layer was recovered. Some of the extracts were occasionally evaporated to 1 ml and used for GC–flame ionization detection (FID) and/or GC–MS analysis.

In this study, conditions such as the pH and reaction temperature were compared in establishing the optimal derivatization technique.

Extracts of soil samples with ultrapure water were treated in the same way as aqueous samples.

Chromatographic instruments and conditions

Chromatographic analyses of the relevant substances were conducted using a quadrupole mass spectrometer (GC–MS; Agilent 5973, Agilent Technologies), and DB-5ms (30 m × 0.32 mm, 0.25 μm film thickness; J&W) was used as the column in the analysis. The column oven temperature was increased linearly from 60 °C (hold for 1 min) to 280 °C (hold for 10 min) at 10 °C min^{-1}. The injection port temperature was 280 °C (MS, FID) for the splitless injection (purge-on time: 1 min), and the column temperature plus 3 °C for on-column injection. A 50 cm retention gap was attached for on-column injection. The flow of carrier gas (99.999% helium) was 1.5 ml min^{-1} in constant-flow mode. Positive electron ionization (ionization energy 70 eV) was used as the ionization mode, and the acquisition mass range was m/z 20 to 600. Quantitative analysis was conducted with GC–FID or GC–mass-selective detection (selective ion mode) (Agilent 6890N, Agilent Technologies) under the GC conditions set for GC–MS.

For the analysis of DPAA, PAA, and BDAO, a high-performance liquid chromatograph mass spectrometer (LCMS-2010, Shimadzu Corporation) and UV detector (SPD-10A Shimadzu Corporation) equipped with an L-column ODS (4.6 mm × 15 cm, Chemical Evaluation and Research Institute, Japan) was used. The oven temperature, injection volume, and flow rate were adjusted to room temperature, 10 µl, and 0.8 ml min^{-1} respectively, and the mobile phase of acetonitrile/0.05% trifluoroacetic acid aqueous solution was used with a gradient program (5 : 95 to 95 : 5 in 15 min). Atmospheric-pressure chemical ionization (APCI) (+) was used as the ionization mode for the mass spectrometer. For the UV detector, the measurement wavelength was 225 nm.

Recovery test

Test solutions of DA, DC, and TPA (50 µg ml^{-1} each) were prepared by spiking acetonitrile stock solutions appropriately into ultrapure water. Each test solution was extracted 30 min after spiking, as per the method given above, and analyzed using GC–MS and GC–FID. Residual aqueous layers were analyzed by liquid chromatography (LC)–MS and/or LC–UV.

In the recovery test using derivatization, a acetonitrile standard solutions of DA, DC, BDPAO, and DPAA were prepared by adding to 40 ml of ultrapure water and approximately 10 g of soil to concentrations of about 10 µg ml^{-1} and 10 µg g^{-1} respectively. Each was derivativized with propanethiol 30 min after spiking, according to the method given above, and then GC analysis was conducted.

Experiment on the stability of diphenylarsine compounds in water

Two concentrations (50 and 0.5 µg ml^{-1}) of each DA and DC test solution were prepared by adding acetonitrile standard solution to 20 ml of ultrapure water in a closed glass tube. Each test solution was extracted twice with hexane (5 ml) after 30 min, 1, 3, 7, 14, 21 and 30 days; extracts were gently concentrated by nitrogen purge and then analyzed by GC–FID. Each residual aqueous layer was analyzed by LC. The remaining residual aqueous layer (10 ml) was used for propanethiol derivatization and analyzed by GC–FID. The test solutions prepared were refrigerated (*ca* 4 °C) during the test period.

RESULTS AND DISCUSSION

GC analysis of diphenylarsenic compounds without derivatization

Diphenylarsenic compounds hydrolyze relatively easily or react with alcohols to produce hydrolysates or diphenylarsenic alkyl esters, since the reactivity between arsenic and the chlorine radical or cyanogen is high. For the analyses of DA and DC, derivatization with thiol reagents has been applied, but it is impossible to analyze individual compounds. Accordingly, for DA, DC, BDPAO, and TPA we have attempted to conduct GC analyses without derivatization. Calibration curves from 0.5 to 20 µg ml^{-1} for DA, DC, BDPAO, and TPA by GC–FID are shown in Fig. 3. On-column injection was used to avoid thermal decomposition of the non-derivatized substances.

Although all four compounds are fairly stable during GC analysis and show good linear calibration curves, the presence of the arsenic–chlorine bond in DA brings about some instability on sample preparation and instrumental analysis.

During dehydration and filtering using anhydrous sodium sulfate, DC, TPA, and BDPAO were recovered almost entirely, but about 20% of DA was recovered as BDPAO, and recovery rates varied widely. Even in the relatively gentle processes of concentration by a rotary evaporation or by nitrogen purge, the recovery rate of DA was lower than for the other compounds.

In GC analysis, the sensitivity of DA was drastically decreased at lower concentrations and varied widely. Decomposition into BDPAO occurred on some occasions, especially when using split/splitless injection.

Therefore, for the analysis of DA, DC and BDPAO, we used the on-column injection technique and attempted to control memory effects by repeated analysis of the solvent blank when analyzing the samples.

Work on BDPAO was the most frustrating, as its solubility in solvents or water was relatively poor. Furthermore, both GC and LC analyses of BDPAO showed wide variability and its standard solution was relatively unstable.

It is suggested that quantitative analysis of intact diphenylarsenic compounds is possible, but that extreme care and detailed knowledge of the individual systems are necessary for success.

There are advantages to determining individual diphenylarsenic compounds, especially for environmental surveys on the fate or dispersion of diphenylarsenic contaminants, but it should be kept in mind that quantification can be imprecise. We suggest, therefore, conducting analyses both with and without thiol derivatization.

Study of thiol derivatization

Although, as demonstrated above, direct GC analysis of DA, DC and BDPAO is possible, quantitative analysis of low concentrations or impure samples should be carried out only after thiol derivatization.

Thiol derivatization of compounds like lewisite, DA, DC and some related compounds with several different reagents has already been reported[4–6]

In order to study the applicability of thiol derivatization to environmental samples, in this study we have compared the reactivity of DA, DC and their related compounds (BDPAO,

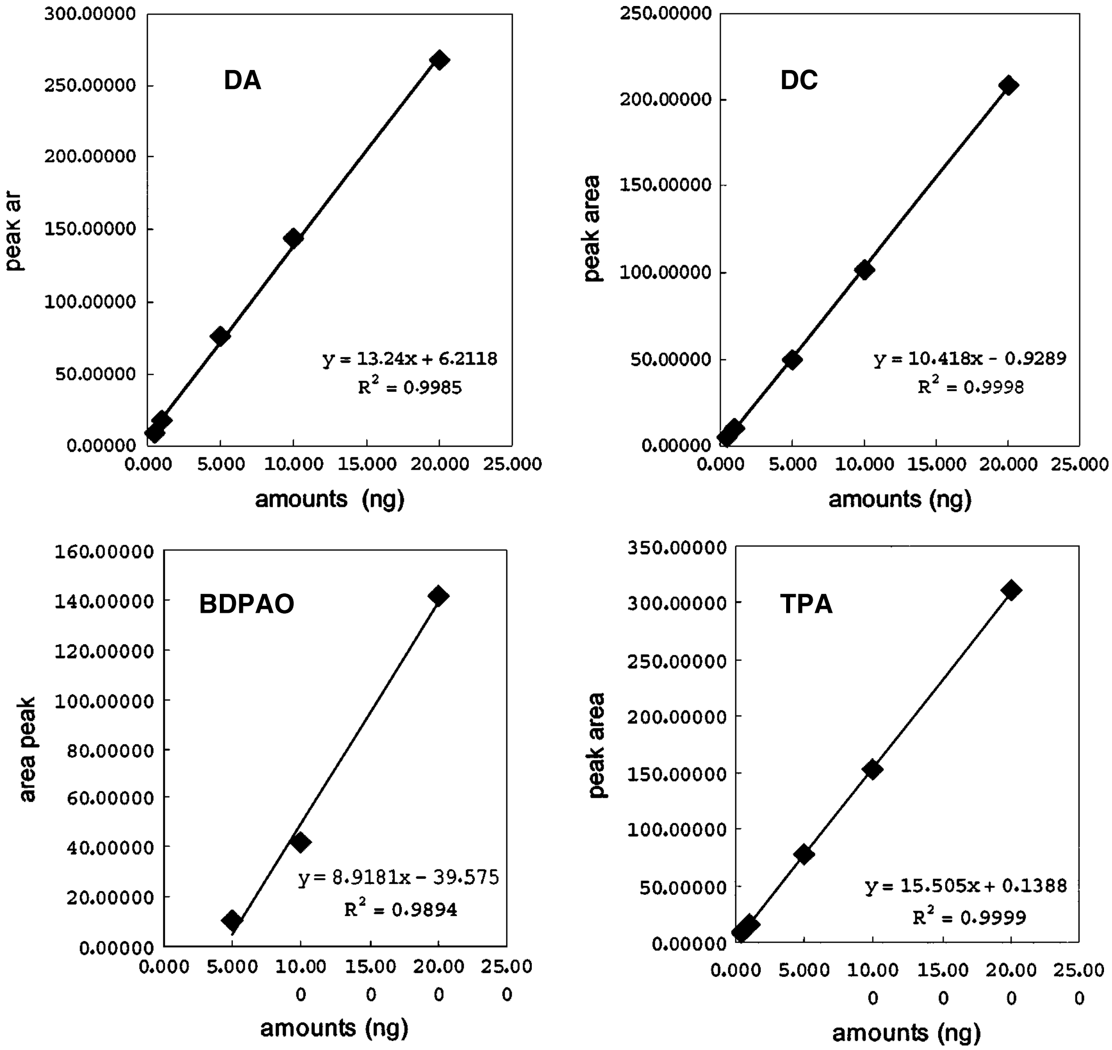


Figure 3. Calibration curves of DA, DC, BDPAO, and TPA, measured by GC–FID.

DPAA, PAA) towards propanethiol and the efficiency of the recovery of their derivatives from aqueous solution.

The derivatization reaction is shown in Figure 4. BDPAO and DPAA, as well as DA, DC and their alkyl esters, generate the same derivative: diphenylarsine-thiopropane. Monophenylarsonic acid and PAO also produced the identical product: phenylarsine-bis(thiopropane). Although thiol derivatization was indeed effective for the analysis of diphenylarsenic compounds in environmental samples, the reaction rates differed among the compounds. Whereas in the method of Haas and co-workers[5,6] the derivatization was carried out at 20 °C, Schoene *et al.*[4] recommend a reaction temperature of 60–70 °C. The reaction efficiency of each diphenylarsenic compound under different conditions is shown in Table 1. Derivatizations were carried out at two different concentrations under neutral and acidic (HCl) conditions, and the reaction efficiencies were compared based on the peak area of the GC–FID chromatograms. DA, which has a chlorine–arsenic bond, reacted easily even under neutral conditions. Unlike DA, derivatization of DC, BDPAO and DPAA was not sufficient under neutral conditions, and an acidic milieu was needed.

The recovery rates in cases where DA, DC, BDPAO, and DPAA were added to ultrapure water and derivatized in the presence of HCl are shown in Table 2. DA, DC, and BDPAO were derivatized relatively easily, and recovery rates reached almost 100% at room temperature in the presence of HCl. However, the recovery rate of DPAA was only about 12.2%. The latter, however, could be raised to almost 100% by heating the reaction mixture to *ca* 60 °C.

In addition, in order to examine of the quantitative aspects of the technique, test water samples were derivatized in the same way after spiking with different amounts of the diphenylarsenic compounds. Figure 5 shows the linearity of the thiol derivatization for the four individual diphenylarsenic compounds in the range 0.5 to 20 $\mu g\ ml^{-1}$ during GC–FID analysis (coefficient of correlation: 0.999).

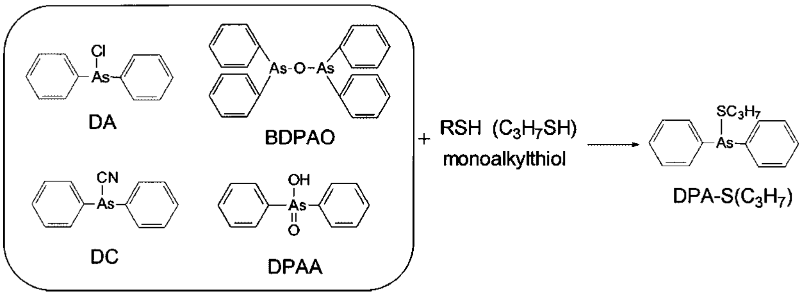


Figure 4. Derivatization of diphenylarsenic compounds with thiol reagents.

Table 1. Comparison of reaction efficiency of each diphenylarsenic compound with propanethiol (normalized with DA-SC_3H_7 in acidic condition)

	Reaction efficiency[a]			
	Acidic[b]	Neutral[b]	Acidic[c]	Neutral[c]
DA	1.0[d] (3.0)	1.01 (1.1)	1.0[d] (3.5)	1.03 (3.2)
DC	0.95 (2.6)	0.64 (38.9)	1.03 (1.6)	0.52 (78.6)
BDPAO	0.88 (3.3)	0.74 (7.8)	0.97 (2.9)	0.89 (0.9)
DPAA	0.95 (9.7)	0.46 (3.8)	0.82 (1.7)	0.60 (6.6)

[a] Coefficient of variation (%, $n = 3$) in parentheses.
[b] 0.5 μg ml^{-1} chemicals added.
[c] 10 μg ml^{-1} chemicals added.
[d] Normalized with recovery rate of DA with propanethiol derivatization under acidic conditions.

Table 2. Recovery of diphenylarsenic compounds as the propanethiol derivatives

	Mean recovery[a] (%)	
Chemical	Water[b]	Soil[b,c]
DA	113.1 (9.6)	52.1 (19.4)
DC	116.0 (3.7)	53.5 (6.5)
BDPAO	108.5 (1.4)	48.6 (10.5)
DPAA	12.2 (7.4)	54.3 (4.9)
DPAA[d]	106.1 (13.5)	–

[a] Coefficient of variation (%) in parentheses. $n = 3$.
[b] Concentration of test sample: water, 20 μg ml^{-1}; soil, 20 μg g^{-1} (wet). Derivatization reaction at room temperature.
[c] Wet rubble collected at the site of Hiratsuka City.
[d] Derivatization carried out at 60 °C.

The lowest limit of detection ($S/N = 5$) by GC–FID was 0.5 ng for each substance.

The recovery rates of the respective diphenylarsenic compounds from soil through derivatization are also shown in Table 2. Whereas the recovery rates of DA, DC, and BDPAO from the water samples tested were almost 100%, the recovery rates of the same compounds from soil through water extraction were only about 50%. The recovery rate of lewisite from the same soil was almost 100% in our study.

LC analysis

For water samples, LC analysis for DPAA, BDPAO, and PAA is possible without troublesome derivatization. Figure 6 shows the calibration curves of DPAA and PAA in the high-performance LC (HPLC)-UV analysis. In this case, the lowest limit for detection was about 1 μg ml^{-1}.

We also conducted analysis by LC-APCI(+)–MS and analyzed DPAA with a sensitivity of about 0.5 μg ml^{-1}. But its detection range was narrow, and low ionization efficiency of DPAA and poor linearity were observed.

As we observe in a later study, electron spray ionization (ESI) will probably allow a more sensitive and quantitative DPAA analysis. It is most probable that diphenylarsenic compounds are present as DPAA in environmental water samples. Accordingly, a more sensitive LC analysis would be expected to analyze specific polar decomposition products such as DPAA and PAA.

Recovery test

Recovery tests of DA, DC and TPA in water were conducted to elucidate the forms present in water. DA, DC, and TPA concentrations of 50 μg ml^{-1} in ultrapure water were prepared and the extraction performed within 30 min. The recoveries of DA, DC, and TPA as individual compounds are shown in Fig. 7. DA was not detected intact even when extraction was carried immediately after preparation of the solution; it was recovered as BDPAO. This result is not entirely surprising, as the As–Cl bond is apparently easily hydrolyzable. That is, the possibility of detecting such chemicals in water in their original chemical forms is quite small. On the other hand, regarding DC, whereas about half was detected as BDPAO, about half could be recovered as intact DC. TPA was relatively stable, with no significant decomposition being observed.

Stability of DA and DC in water

Figure 8 shows the results of the stability test for DA and DC conducted over a period of 30 days. The test was conducted on two samples in parallel. No significant dispersion was

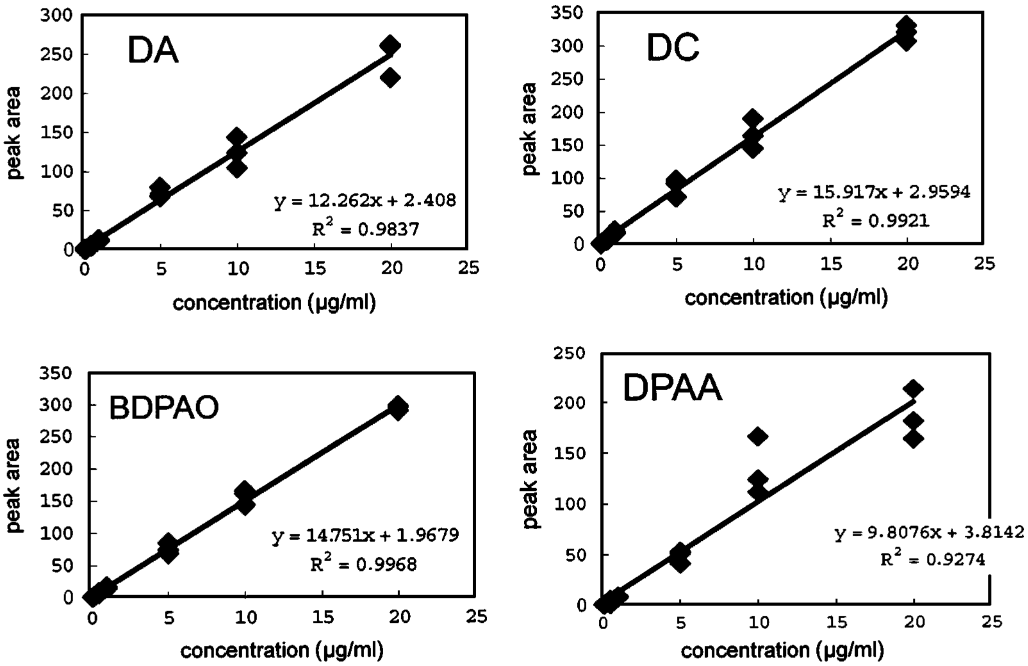


Figure 5. Linearity of derivatization reaction of DA, DC, BDPAO, and DPAA with propanethiol.

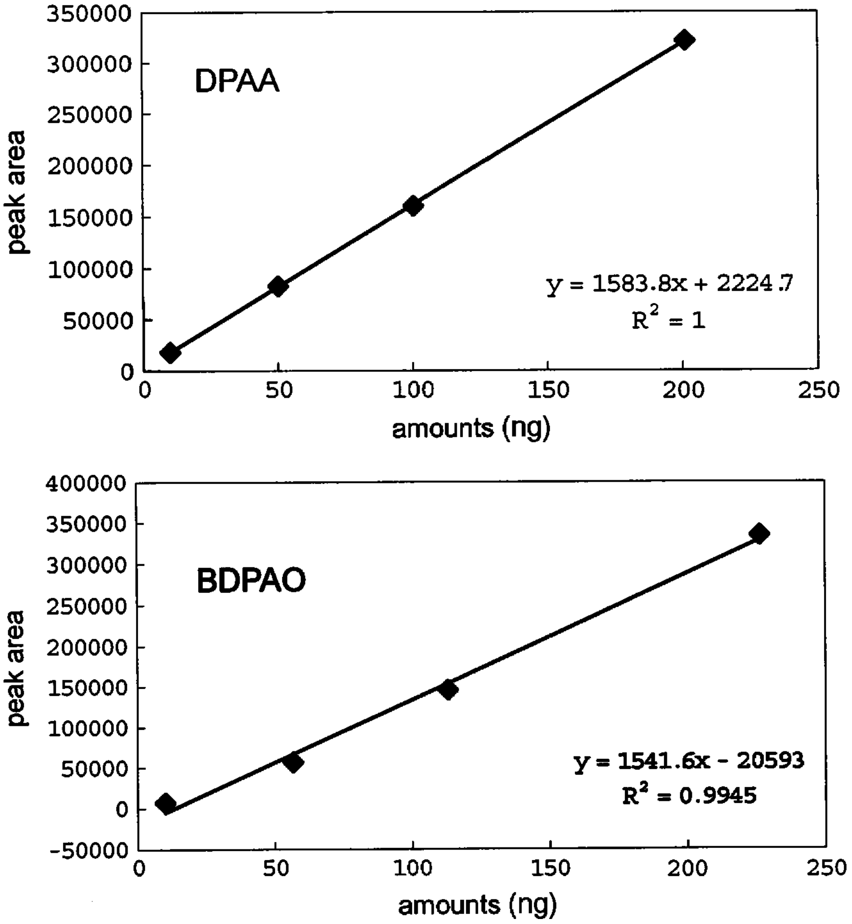
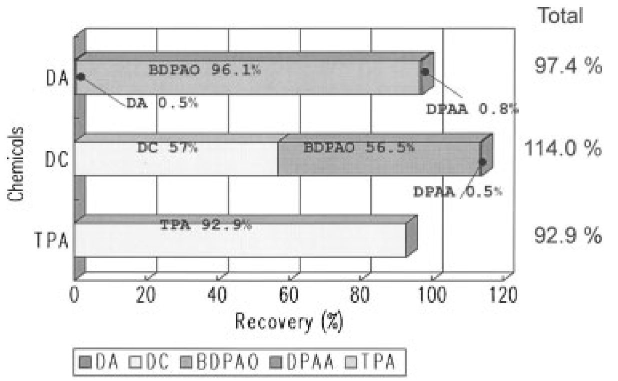


Figure 6. Calibration curves of DPAA (above) and PAA (below), measured by HPLC.



Extracted within 30 min after adding chemicals
% Conc. % % % μg/ml % n=3(CV % 0.1-1.9%)

Figure 7. Recovery of individual diphenylarsenic-related compounds after adding DA, DC, and TPA into ultrapure water.

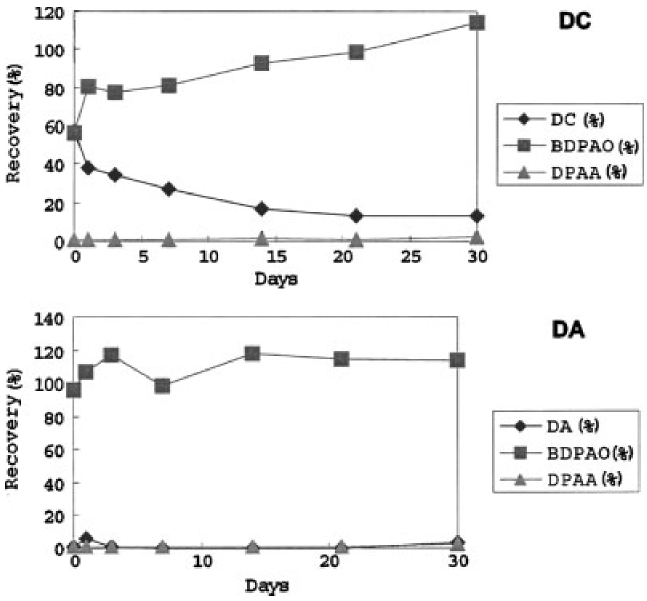


Figure 8. Stability of DC and DA in test water.

observed in the reproducibility of the data, and the coefficient of variation was within 0.1.

Concurrently, in a stability test at low concentration, although similar tendencies were observed, the quantitative results showed appreciable scatter.

In aqueous solution both DA and DC were unstable and decomposed into BDPAO. The decomposition rate of DC is much lower than that of DA, and even after 30 days about 13% could still be recovered unaltered. This suggests that DC may be partly detected together with BDPAO if the time elapsed after contamination is short. Decomposition from BDPAO to DPAA is relatively slow. In the test, only a few percent of DPAA was detected on the 30th day, and no conspicuous decomposition from BDPAO to DPAA was observed.

Water samples were acidic ($pH = 2$) and stored in refrigerator at 4 °C. Under basic conditions or at higher temperature, even DC would be decomposed into BDPAO and subsequently into DPAA.

APPLICATION TO AUTHENTIC CONTAMINATED SAMPLES

Determination of diphenylarsenic compounds in environmental samples

Although DPAA and TPA are relatively stable during the analysis, DA, DC, and BDPAO suffer effects such as hydrolysis, oxidative destruction or reaction with solvents in the sample preparation, thermal effects during GC analysis, adsorption, and residue at the inlet or column and causing a short column life. As also seen from the results of the stability test, the possibility of the presence of DA or DC itself in environmental water is low. For quantitative analysis of diphenylarsenic compounds in environmental samples, therefore, three analytical procedures (i.e. GC analysis through solvent extraction, GC analysis through thiol derivatization, and direct LC analysis of water samples) were applied to the authentic contaminated samples.

The lowest determination limits for diphenylarsine compounds in this study were from 0.005 to 0.01 $\mu g\,ml^{-1}$ for aqueous samples and from 0.05 to 0.1 $\mu g\,g^{-1}$ for soil samples.

Diphenylarsenic compounds detected in contaminated well water

A health problem, evidently different from that caused by inorganic arsenic, was observed in inhabitants who had drunk well water in Kamisu-cho, Ibaraki Prefecture, in which a high concentration of arsine (4.5 $mg\,l^{-1}$, 450 times higher than the environmental quality standards for groundwater) was detected. With the aim of specifying the causative agent, we conducted analyses for organoarsenic compounds in the water of two wells from two areas; one (area A) is highly contaminated with arsine and the other (area B), also with relatively high observed arsine concentrations, is 1 km west of area A (see Fig. 2). Figure 9 shows the chromatogram of an extract after propanethiol derivatization.

Although diphenylarsenic derivatives were detected in all samples, monophenylarsenic derivatives were only present in some. GC analysis of dichloromethane extracts (Fig. 10) revealed neither the ingredients of sternutators (DA, DC) nor their common impurity, TPA. Hence, it is expected that the origin of the diphenylarsenic derivative is DPAA. The latter was identified and determined by LC analysis. Typical concentrations were from 6.0 to 10 $\mu g\,ml^{-1}$ (Table 3 and Fig. 11).

In the C18 solid-phase extract of the sample provided by Ibaraki Prefectural Institute of Public Health, trace amounts of BDPAO were detected after 1000-fold concentration.

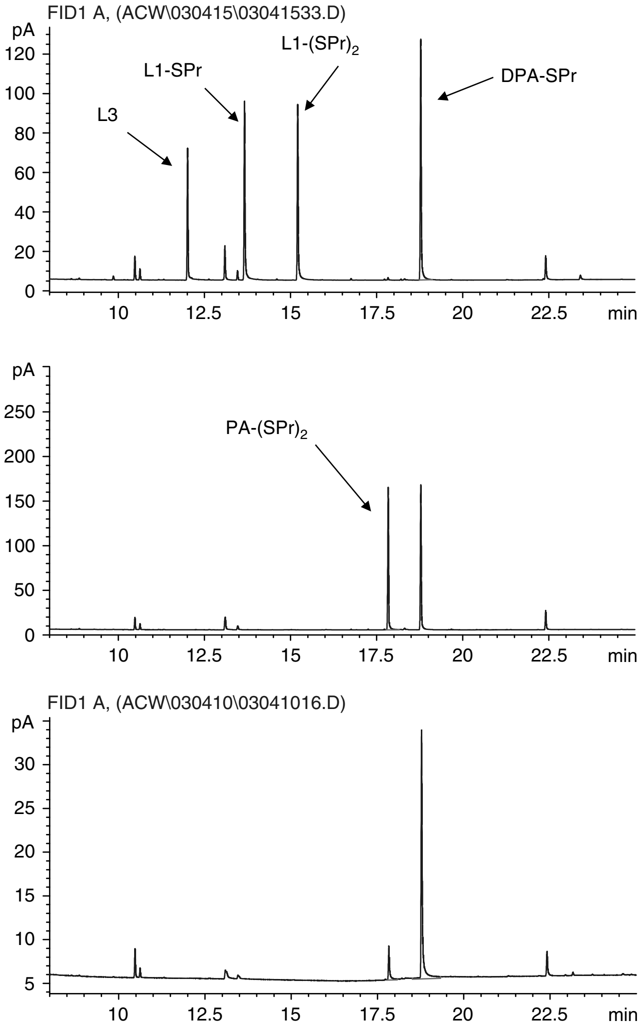


Figure 9. GC–FID chromatograms of standard solution (top: lewisite and DPAA; middle: DPAA and PAA) and the well water sample collected at Kamisu-cho (bottom) after propanethiol derivatization. SPr = SC_3H_7.

Although the causal relationship with the Japanese Imperial Forces of this district is unclear, it is also not known either whether diphenylarsenic compounds were produced or used for purposes other than sternutators. Accordingly, it is quite probable that diphenylarsenic compounds were detected as decomposition products of the intermediate substance (DPAA) for producing DA or DC, although the possibility that these compounds are derived from other chemical substances is not completely deniable. Thus, it has become clear that the causative agent of the inhabitants' ill health was DPAA.

PAA was also detected along with diphenylarsenic compounds in some well water samples. Regarding monophenylarsine compounds, phenyldichloroarsine (PD), which is classified as a vesicant, is known. It is presumed that this chemical also decomposes into PAA in water. But no document indicating that the Japanese Imperial Forces produced PD has been found. Regarding monophenylarsine compounds, arsanilic acid and sodium arsanilate have been used overseas since the mid-1940s as food additives to prevent the spread of diseases and to facilitate weight increase in swine and poultry.[7] It is expected that the PAA detected is related to diphenylarsenic compounds as an impurity.

Table 3. Concentration of diphenlyarsenic compounds in well water

	Concentration (mg l^{-1})		
Sample[a]	DPAA[b]	Diphenyl-arsenic derivatives[c]	Monophenyl-arsenic derivatives[d]
Area A	8.3	6.6	ND
Well water (27 March 2003)	10	7.4	ND
Well water (2	6.0	4.7	1.1
April 2003)	7.0	5.3	0.8
Area B		0.50 (0.82–0.31)	
Well water (8 April 2003) ($n = 7$)	ND		–
Quantification limit	1	0.01	0.5

Arsine concentration calculated based on the concentration of DPAA. The well in area B is 1 km west of the well in area A.

[a] Sampling date in parentheses.

[b] Analysis by HPLC-UV.

[c] Concentration as DA (by GC–FID analysis after thiol derivatization).

[d] Concentration as PAA (by GC–FID analysis after thiol derivatization).

As the results of the stability test also indicate, these polar organic arsenic compounds are expected to reside in well water for a relatively long period and, if groundwater is contaminated, the occurrence of a serious toxicity problem is to be feared. Only very limited study was reported.[8]

It is known that the former Japanese Imperial Forces' airport had been located in this area, but no evidence related to red agents has been discovered yet. The surveys to elucidate the source of this pollution are continuing.

Diphenylarsenic compounds detected in contaminated soil

Beer bottles containing mustard gas and lewisite abandoned by Japanese Imperial Forces were discovered at the bridge pier construction site in Samukawa-cho, Kanagawa Prefecture. Investigations were conducted into soil close to these bottles and the surface soil around the temporary storage yard for the excavated soil transferred from the construction site. In this investigation, 16 $\mu g\ g^{-1}$ (wet) of DA and 13 $\mu g\ g^{-1}$ (wet) of BDPAO were detected from one of the soil samples collected by the temporary storage yard

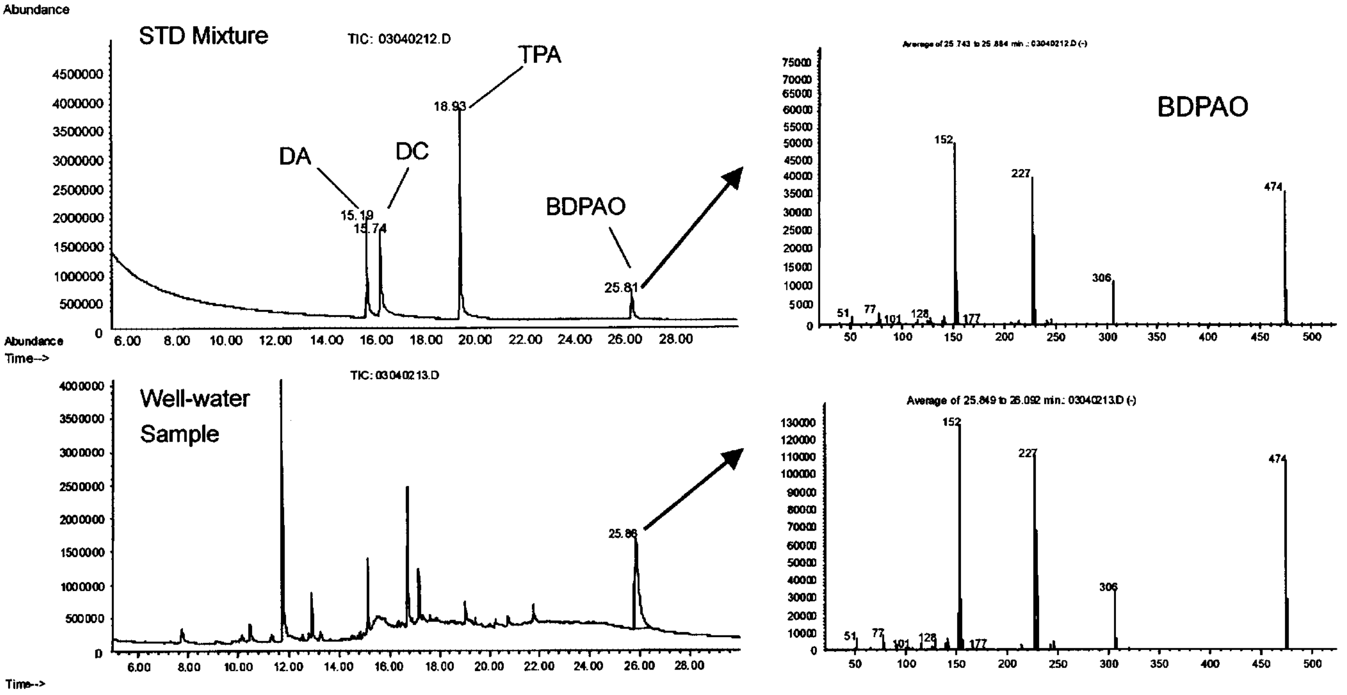


Figure 10. Total ion chromatograms and BDPAO mass spectra of standard solution and extracted solution of the well water sample collected at Kamisu-cho.

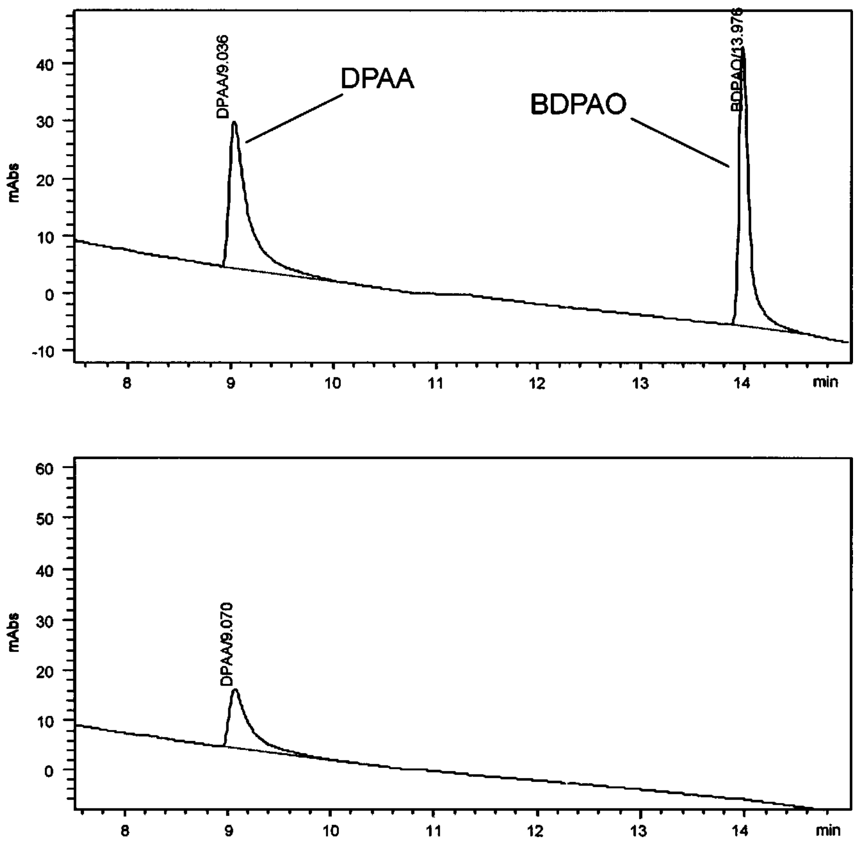


Figure 11. HPLC-UV (210 nm) chromatograms of DPAA and BDPAO standard solution (top) and the well water sample collected at Kamisu-cho (bottom).

Table 4. Concentration and frequency of the diphenylarsenic-related compounds detected from the contaminated soil sample collected at the site in Hiratsuka City

Sampling depth (m)	Triphenylarsine		Diphenylarsenic compounds	
	Concentration range (mg kg^{-1} (wet))	Frequency	Concentration range (mg kg^{-1} (wet))	Frequency
0.5	<0.05	4/26	ND	0/26
1.5	<0.05–1.4	6/26	<0.05–0.16	7/26
2.5	<0.05–0.38	4/26	<0.05–0.12	12/26
3.5	0.26	1/26	<0.05–0.53	10/26

Soil samples were collected at every 6 m point (26 points) in the site (30 m × 30 m square). <0.05: lower than quantification limit (0.05 mg kg^{-1} (wet)), but a peak was detected and identified by GC–MS.

(where contamination seems to have occurred in an isolated manner), and at the construction site of the bridge pier the propanethiol derivative of diphenylarsenic compounds was detected within the range from trace level (<0.1 μg g^{-1} (wet)) to 0.53 μg g^{-1} (wet).

Although no bottles, etc. containing red agents (DA, DC) have been found, there is evidence documenting[2] the production of red agents at the Sagami Arsenal of the former Japanese Navy. Contamination by red agents is, therefore, not unimaginable. There is a report stating that TPA and BDPAO were detected in the bottom sediment of Skagerrak, leading to the Baltic Sea.[9] This suggests that red-agent-related compounds can possibly be detected in the case of soil samples.

The other case occurred at the construction site in Hiratsuka City, where the chemical experiments facilities of Sagami Naval Arsenal had been located. Diphenylarsinic propanethiol derivatives and TPA were also detected from soils collected at a depth between 0.5 and 1.5 m, where hundreds of suspicious glass bottles, most containing an unidentified liquid, have been found. Since DA, DC, or BDPAO were not detected in the soil samples, the diphenylarsenic compounds detected are assumed to be present as DPAA. Furthermore, thiol derivatives of diphenylarsenic compounds were detected in soil collected in a relatively deep stratum (3.5 m), suggesting their downward motion by way of interstitial water in the soil. Table 4 shows the diphenylarsenic-related compounds detected from the site at Hiratsuka.

TPA may be identified, by proxy, by its DA and DC impurities. Furthermore, as TPA is more stable and less mobile in the environment than either DA or DC, we can expect to detect TPA close to the pollution source even if DA and DC are decomposed on their passage through soil (e.g. to DPAA).

At present, the actual source of contamination by diphenylarsinic acid in Kamisu-cho has not been elucidated. Diphenylarsenic compounds are unusual substances, and their physical/chemical properties and details regarding their toxicity and environmental behavior are insufficiently known. In order to identify the point of release and the causative agents, a comprehensive survey is required. Since in general, chemical warfare agents decompose relatively rapidly in the environment, the effects of toxicity due to their decomposition products will need to be investigated. Now that the effects of decomposition products, such as DPAA, on health have become more evident, more work on the toxicity and the environmental behavior of such compounds is required.

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