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Identification and quantitative determination of diphenylarsenic compounds in abandoned toxic smoke canisters

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Abstract

Knowledge of the exact nature of the constituents of abandoned chemical weapons (ACW) is a prerequisite for their orderly destruction. Here we report the development of analytical procedures to identify diphenylchloroarsine (DA/Clark I), diphenylcyanoarsine (DC/Clark II) and related substances employed in one of the munitions known as "Red canister". Both DA and DC are relatively unstable under conventional analytical procedures without thiol derivatization. Unfortunately however, thiol drivatization affords the same volatile organo-arsenic derivative from several different diphenylarsenic compounds, making it impossible to identify and quantify the original compounds. Further, diminishing the analytical interference caused by the celluloid powder used as a stacking material in the weapons, is also essential for accurate analysis. In this study, extraction and instrumental conditions have been evaluated and an optimal protocol was determined. The analysis of Red canister samples following this protocol showed that most of the DA and DC associated with pumice had degraded to bis(diphenylarsine)oxide (BDPAO), while those associated with celluloid were dominantly degraded to diphenylarsinic acid (DPAA).
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Keywords: Abandoned chemical weapon; Diphenylarsenic compound; Sternutators; Red canister; Chromatographic analysis

1. Introduction

Tons of chemical weapons abandoned by the Japanese Imperial Forces were stored and remain buried in China. Approximately 23,000 Red canisters were recovered and stored at the temporary storage facility in Nanjing as of April 1998 [1–3]. These agents were produced at the Tadanoumi manufacturing plant on Okuno Island in the Seto inland sea during WWII. At the end of WWII, the chemical weapons stored on Okuno Island were destroyed by incineration and disposed of by dumping in the sea. However, nine large-size Red canisters were discovered there in 1999 and disarmed in 2001.

More recently, chemical weapons abandoned by the Japanese Imperial Forces at the end of WWII are becom-

ing a growing social problem in certain areas of Japan [4]. For example, a serious health problem occurred in Kamisu, Japan in 2004. Compounds related to sternutators (diphenylarsinic acid) were detected in drinking well water [5].

The safe destruction of these chemical weapons is a political and environmental issue of primary importance. However, before destruction can begin, the nature of the substances contained in aged weapons must be ascertained.

Based on this premise, we pursued experiments to develop an analytical procedure suitable for the compounds in one class of abandoned chemical weapons (ACW) known as Red canister, in which Red agent, diphenylchloroarsine (DA/Clark I) and diphenylcyanoarsine (DC/Clark II), classified as sternutators were the main C.W. constituents.

These toxic agents were packed in chemical munition shells either directly and/or fused with ingredients like cel-

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Table 1
Type and contents of Red canisters manufactured by the Japanese Imperial Forces, according to surviving documents

Type of Red canister	Matrices	Contents	Amounts
98 Type small-size	Celluloid	DA, DC 35% celluloid powder[a] 65% MgO[b]	90 g of Red agent per canister
99 Type medium-size	Celluloid	DA, DC 50% celluloid powder[a] 47% MgO[b] 3%	456 g of Red agent per canister
Trial 1 type large-size	Celluloid	DA, DC 47% celluloid powder[a] 50% MgO[b] 3%	4000 g of Red agent per canister
97 Type medium-size	Pumice	DA, DC 60% diced pumice 40%	500 g of Red agent per canister

[a] Celluloid: 75% nitrocellulose and 25% camphor as plasticizer.
[b] MgO as catalyst.

luloid powder and diced pumice. The former is known as Red shell and the other, Red canister. We can see the type and the original components of Red canister from surviving documents (Table 1). According to the surviving document, 97 type Red canisters were produced by adsorbing a fused Red agent into pumice, which was pre-purified by ignition under reduced pressure. On the other hand, 99 type Red canisters were produced by adding a fused Red agent (at 30–50 °C) into celluloid powder (10–30 mesh, less than 1% water content) at ca. 30 °C, and mixed magnesium oxide with stirring.

Studies on samples of real munitions are limited [6], however, and very few studies are available on the determination of diphenylarsenic compounds. Most of the analytical studies on these compounds adopted thiol derivatization techniques [7–9] and are limited in laboratory examination. They were not useful enough to obtain the information on decomposed products that were expected to be present in such Red canister samples. Analytical protocols for the safe and precise analysis of these ACW samples prior to destruction are thus desperately required.

DA and DC are relatively unstable in solutions used in conventional analytical procedures. Their main degradation products are bis(diphenylarsine)oxide (BDPAO) and diphenylarsinic acid (DPAA), with triphenylarsine (TPA) being present as an impurity. For the quantitative chromatographic analysis of these compounds, derivatization with thiols can be used under certain circumstances. However, its use is limited, as reaction occurs not only with intact DA and DC but also with their degradation products, affording identical derivatives. Quantification and identification of individual components of munitions is therefore rendered impossible using this procedure.

In this study, we developed an analytical procedure consisting of a combination of techniques suitable for identification and for quantification of Red agent and its related compounds.

Identification is performed by GC/MS and/or LC/MS/MS comparing the retention indexes with those of authentic specimens, and quantification by GC/AED. In addition, HPLC is used for quantification of non-volatile compounds.

Conventional wet analytical procedures, e.g. macro analysis, allowing a mass balance of the components of munitions were also employed.

2. Experimental

2.1. Chemicals

As Red agent related compounds, DA, DC, BDPAO and DPAA were provided from Hodogaya Contract Laboratory (Japan). They were >98% pure by NMR.

Camphor, TPA, phenylarsonic acid (PAA) and diphenyl were purchased from Aldrich (Japan). Pesticide analysis-grade solvents were used. Water was distilled and purified using a Milli-Q system (Millipore, Bedford, MA, USA). Details of DA, DC and other related compounds used in this study are listed in Table 2.

2.2. Materials

Twenty-seven Red canisters were selected from four types of Red canisters stored at Nanjing, China in October 1999. Three types contained Red agent fused on celluloid *idest*. (i) 98 type small-size, (ii) 99 type medium-size and (iii) 100 type small-size. The fourth type contained Red agent absorbed into diced pumice (97 type medium-size).

All of the munitions were incrusted with rust, and most of them were seriously damaged. The contents were open in some of them, suggesting that they may have been exposed to water after abandoned.
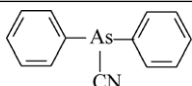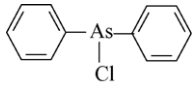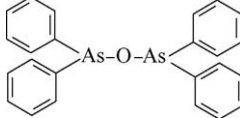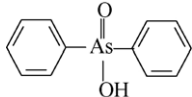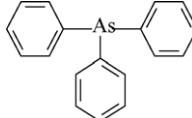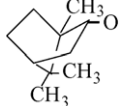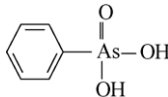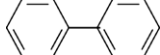
The selected canister shells were cut open, their contents removed and transferred into plastic bags, and frozen at −20 °C overnight. These frozen samples were quickly crushed using an electronic mill, and mixed with a pestle and mortar to give a homogeneous sample. Two typical types of middle-size Red canisters containing Red agents mixed with either celluloid or pumice which, judging from their outward appearance seemed to be stored under better conditions, were selected for this study.

Another group of samples were prepared from the contents taken from each of three large-size Red canisters that were a part of nine canisters recovered at Okuno Island, Japan in 1999. These contents were mixed with celluloid in shells, which were highly damaged and exposed their contents.

2.3. Preparation and stability analysis of standard solution

To select an organic solvent for the analyses, the stability of the related compounds in various organic solvents was

Table 2
List of compounds related to Red agent

Compound no.	Name	CAS re. no.	Molecular form (MW)	Structure
1	Diphenylcyanoarsine (DC)	23525-22-6	$C_{12}H_{10}AsCN$ (255)	
2	Diphenylchloroarsine (DA)	712-48-1	$C_{12}H_{10}AsCl$ (264)	
3	Bis(diphenylarsine) oxide	2215-16-9	$C_{24}H_{20}AsO$ (474)	
4	Diphenylarsinic acid	4656-80-8	$C_{12}H_{13}AsO_2$ (262)	
5	Triphenylarsine	603-32-7	$C_{18}H_{15}As$ (306)	
6	Camphor	464-49-3	$C_{10}H_{16}O$ (152)	
7	Phenylarsonic acid	98-05-5	$C_6H_7AsO_3$ (202)	
8	Diphenyl	92-52-4	$C_{12}H_{10}$ (154)	

examined. Standard solutions were prepared by dissolving each of the four compounds (DA, DC, BDPAO and TPA) in five different solvents (acetone, dichloromethane, acetonitrile, hexane and toluene) at concentrations of ca. 100 μg/ml. Each solution was sealed in crimp vials and stored in a refrigerator (ca. 4 °C) until GC analysis. To avoid the thermal degradation in the injection port, GC measurements were performed by on-column injection.

2.4. Extraction of samples

To select a solvent for extraction, ca. 0.5 g of each Red canister sample was extracted 2–4 times (20 ml each) by 10–20 min ultrasonication with several organic solvents. Acetone, dichloromethane, toluene, hexane and acetonitrile were tested, and the recovery of each sample was evaluated by measuring the corresponding peak area in its GC or HPLC chromatogram.

2.5. Chromatographic instruments and conditions

A gas chromatograph (Agilent Technologies Model HP5921) equipped with an atomic emission detector (AED)

in carbon and arsine-selective mode was used for all measurements. The following conditions were employed; column: fused-silica capillary column (DB-5; 30 m × 0.32 mm I.D., 0.25 μm film thickness), He (99.999%) flow: 1.5 ml/min, injection port (splitless) temperature: 250 °C, and oven temperature: 80 °C (0–1 min), 80–280 °C linear gradient (10 °C/min), and 280 °C (5 min).

A Hewlett-Packard model HP5973 MSD equipped with a same column as GC/AED was used for all GC/MS determinations under the following conditions; GC conditions: He flow: constant pressure mode (head pressure 50 kPa), injection port (splitless) temperature: 250 °C, oven temperature: 100 °C (0–5 min) and linear gradient 100–280 °C (10 °C/min), MS conditions: ion source temperature: 230 °C, ionization: EI (70 eV), ionization current: 60 μA, mass scanning: 40–550 m/z and 0.66 scan/s acquisition was started 4 min after injection.

LC separations were performed using a HPLC (Shimadzu 10AD×2) equipped with UV detector (Shimadzu SPD-10A) and an Inertsil CN-3 (25 cm × 4.6 mm I.D.) column. The eluate was monitored at 210 nm. The mobile phase consisted of 20 mmol/l KH_2PO_4 in water (pH 2.6) (solvent A) and acetonitrile (solvent B); elution was performed with 5% B

for 20 min, and 85% B for over 20 min, at a flow rate of 1.0 ml/min. Injections (10 μl) were carried out using an auto-injector (SIL-10A).

GPC separations were performed with a HPLC (Shimadzu 9A) equipped with RI detector (Shimadzu RID-6A) and a KF-803 (30 cm × 8.0 mm I.D.) column. Elution was performed with tetrahydrofuran (THF), at a flow rate of 1.0 ml/min. Injection volumes were 20 μl.

LC/MS/MS, using Micromass QuatroII (Manchester, UK) equipped with an electrospray interface, was performed for identification of DPAA and PAA—the hydrolysis products of DA and DC. The conditions for LC were identical to those for HPLC-UV analysis.

2.6. Macro analysis

To clarify the mass balance of the contents of Red canisters, elemental analysis, measurements of moisture and combustion test were also performed.

Water contents of the samples were measured by Karl Fischer's titration (instrument: KF-06, Mitsubishi, dehydration solvent: GEX (methanol 80–90%)). All concentrations are given on a dry weight basis. Extracts and residues were measured gravimetrically, and their elemental analysis by ICP-AES and CHN analysis were also employed in the macro analysis. The amounts of total arsenic, which were especially determined to clarify the mass balance of analytical portions in original samples, and their extracts and residues, were measured by ICP-AES (Shimadzu ICP-1000 III) after acidic degradation with nitric acid and sulfuric acid. The analytical conditions were as follows; high frequencies was maintained at 1.2 kW and torch height was 15 mm. Current, plasma, carrier and purge gas flow were maintained at 14, 1.2, 1.0 and 3.5 l/min, respectively. CHN measurements were performed on some of the extracted residues to estimate the amounts of organic compounds in them.

3. Results and discussions

3.1. Chromatographic analysis

The stability test, which was performed to select appropriate solvents to be employed in the analysis without thiol derivatization, DA, DC and BDPAO in three solvents, acetonitrile, hexane and toluene showed better stability of the solutes, up to 30 days after preparation, than the others. Degradation of DC to BDPAO in acetone and reaction product peak in dichloromethane was slightly observed, especially these peaks were more markedly observed by using splitless injection mode than using a on-column injection mode. Apparently, this results from the joint effect of solvents and high temperature at injection port and tends to induce thermal degradation. For the quantification of such compounds, on-column injection was basically shown to provide more reliable results than split/splitless injection. Additionally, it

should be taken into account that solutions of low concentration (ca. 10 μg/ml) in all solvents were less stable.

The solutions in other solvents such as chloroform and THF, were also examined, and revealed that DA and DC were seriously degraded to DPAA. TPA was stable in all of the solvents examined, as was DPAA in polar organic solvents. From the discussion above, we recommend hexane and toluene for the analysis of DA, DC and their related compounds. As an alternative, acetonitrile could also be used.

Another major problem is that for reliable analysis, it is essential to recover DA, DC and related compounds efficiently from samples containing both kinds of matrix, i.e. celluloid and pumice.

The presence of a matrix, celluloid in this case, made it particularly difficult to analyze diphenylarsenic compounds in Red canisters. The on-column injection technique that was effective for standard solutions failed to avoid the interference caused by the matrix. The extracts from samples impregnated with nitrocellulose interfered with GC analysis in this mode by critically reducing the sensitivity, especially when acetone was used for extraction, due to its higher solubility of celluloid matrix (Table 3). Otherwise, this negative effect is much less when splitless injection is applied.

In this study, we examined a gel permeation chromatography (GPC) to separate the nitrocellulose fraction form other low molecular fractions in which DA, DC and other related compounds occurred, but unsuccessful.

The recovery of DC from GPC was approximately 96% when dichloromethane was used as a developing solvent, and 77% when acetone was used, while DPAA was quantitatively recovered in both solvents. The other chemicals, DA and BDPAO were hardly recovered because of adsorption on the column and degradation to DPAA. GPC was suitable only for the analysis of DC, therefore, we did not adopt this method in the established procedure for the sample analysis.

Based on the discussion described above, splitless injection was applied to the sample analysis.

3.2. Extraction efficiency from the sample matrices

The extraction efficiencies of Red agent and the related compounds in celluloid samples were examined using three different solvents (hexane, toluene and acetonitrile). We found that three-fold extractions were required to extract all relevant substances sufficiently. Quantitative analysis gave slightly different results depending on the solvents used for extraction. Extracts of the celluloid samples with either hexane or toluene led to a drastic decrease of sensitivity in GC analysis and/or a lower efficiency for the extraction. (BDPAO with toluene: 34.4%, BDPAO with hexane: 5.0% and DPAA with hexane: 37.7% comparing with acetnitrile) For that reason, these solvents could not be applied to their extraction from celluloid matrices.

Acetonitrile has the advantage to induce less affinity than other two solvents. Otherwise, although acetonitrile was less efficient for the extraction of DPAA, the low recov-

Table 3
Comparison of effect of sample preparation on macro analysis

Macro components after extraction with different organic solvents

Sample type	Extraction solvents[a]	Water content (%)	Proportion of extract (%)	Proportion of residue (%)	Total (%)	As (%) in residues	CHN Conc. in residues (%)
99-Medium A-2 (celluloid)	Acetone	40.2	45.3	15.8	101.3	3.6	C: 36.4, H: 4.0, N: 5.3
	Dichloromethane		28.5	28.2	96.9	2.6	C: 30.0, H: 3.6, N: 8.0
	Acetonitrile + 0.01 MHCl		–	23.2	–	3.4	C: 38.6, H: 4.0, N: 5.8
	Tetrahydrofuran		58.6	5.3	104.1	–	
	Hexane		–	51.4	–	–	
	Toluene		–	41.8	–	–	
	Acetone[b]		41.0	17.4	58.4	–	
97-medium B-2 (pumice)	Acetone	28.8	31.8	45.4	106.0	0.9	C: 2.3, H: 0.3, N: <0.2
	Dichloromethane		29.3	43.5	101.6	1.1	C: 2.2, H: 0.3, N: <0.2
	Acetonitrile + 0.01 MHCl		–	46.0	–	0.9	C: 1.9, H: 0.3, N: <0.2
	Hexane		–	52.8	–	–	
	Toluene		–	48.6	–	–	
	Acetone[b]		27.0	45.6	101.4		

Macro components by ignition test

Sample type	Condition	Ignition loss (%)		Ignition residue (%)	As (%) in residues	Other metals in ash (%)
		Water	Organics[c]			
99-Medium A-2 (celluloid)	600 °C with N$_2$ reflux	40.2	56.8	3.0	45.9	Mg: 32.4, Fe: 2.8
97-Medium B-2 (pumice)	600 °C with N$_2$ reflux	28.8	29.9	41.3	0.7	Si: 73.6, Fe: 2.0

[a] Extraction method: ultrasonication (10 min).

[b] Extraction method: soxhlet (12 h).

[c] Organics% = 100.0% − (water% + ignition residue%).

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ery (67.4%) of DPAA by triple acetonitrile extraction was improved and brought about a reduction in time by successive extraction with 0.01 M HCl aqueous solution after the initial acetonitrile extraction.

The other sample matrix, pumice, did not cause us any serious problems. Both on-column injection and non-polar solvents could be applied in GC analysis of the extracts from samples impregnated with pumice. In the standardized final analytical procedure for the samples, however, both types of samples were subjected to the same established procedures.

3.3. Macro analysis for sample preparation

To investigate the mass balance for the contents of Red canisters, macro analyses were carried out for both pumice and celluloid samples. The results are shown in Table 3.

The water contents of pumice and celluloid samples were 27.4–28.8% and 21.8–40.2% respectively. In the case of pumice matrices, there are no significant differences in the ratios (%) of extracts and residues, among the solvents. The results of CHN analyses and the presence of SiO_2 (73.6%) in the ignition ash, indicate that the residue after extraction (>40%) was mostly pumice. Apart from the low arsine contents, we conclude that the organic arsine-containing compounds are quantitatively extracted.

In celluloid matrices, the amounts of the extracted residues significantly varied depending on the solvents used even after triple extraction.

This difference could result from the solubility of nitrocellulose in these solvents. Its solubility in THF is highest and the residue was as low as 5%. CHN measurements of the residues from celluloid matrices suggested that the principal constituent was nitrocellulose, and organic arsine-containing compounds remaining in the matrix was low. This suggested that most of the organic arsine-containing compounds were extracted. The small differences between the arsine contents in the extracted residues and the ignited residue of the celluloid sample support this argument.

Magnesium was detected in the extracted residue of celluloid samples, agreeing with information in the surviving document that magnesium oxide (3%) was present in Red agents as a catalyst.

3.4. Quantitative analysis applied to the Red canister samples

Based on the experiments described above, optimal protocols for the analysis of Red canister samples were determined. A flow chart of the scheme is shown in Fig. 1.
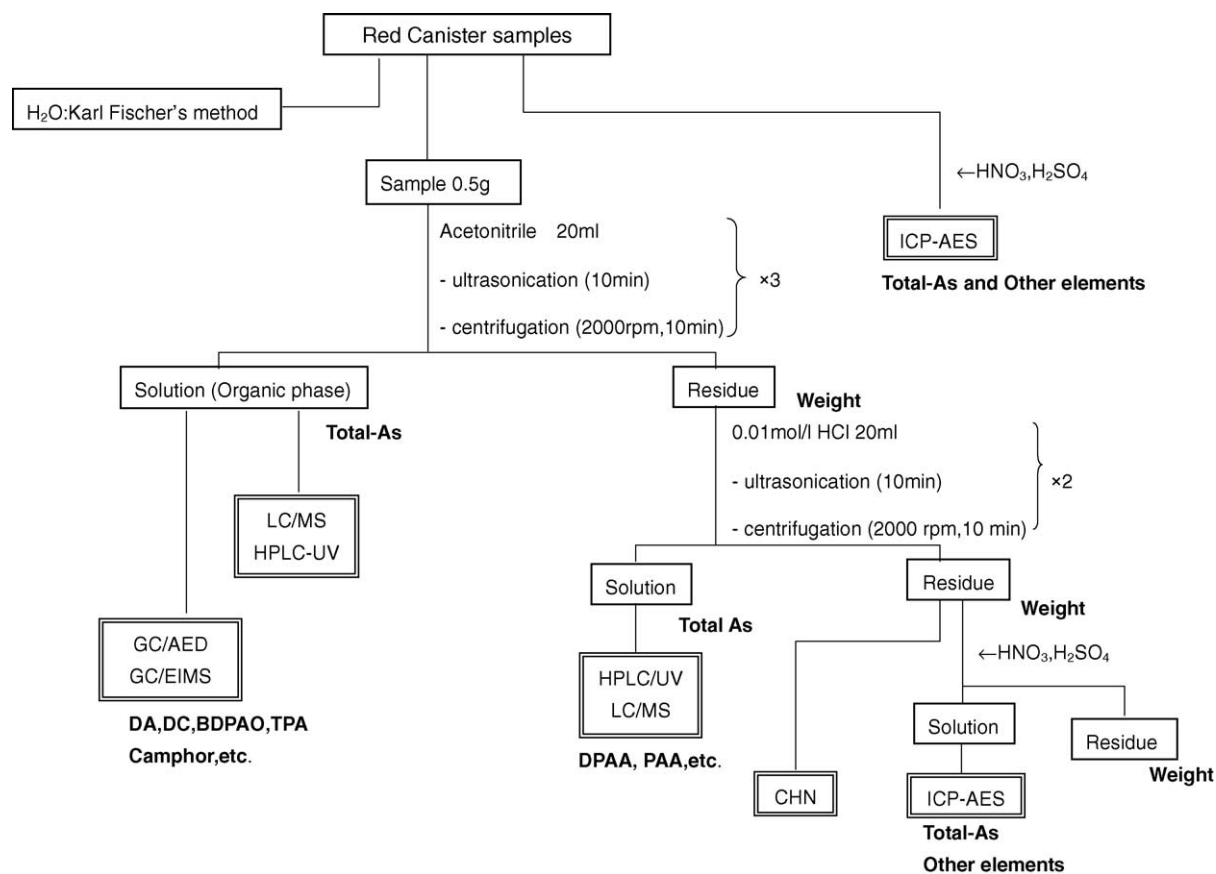

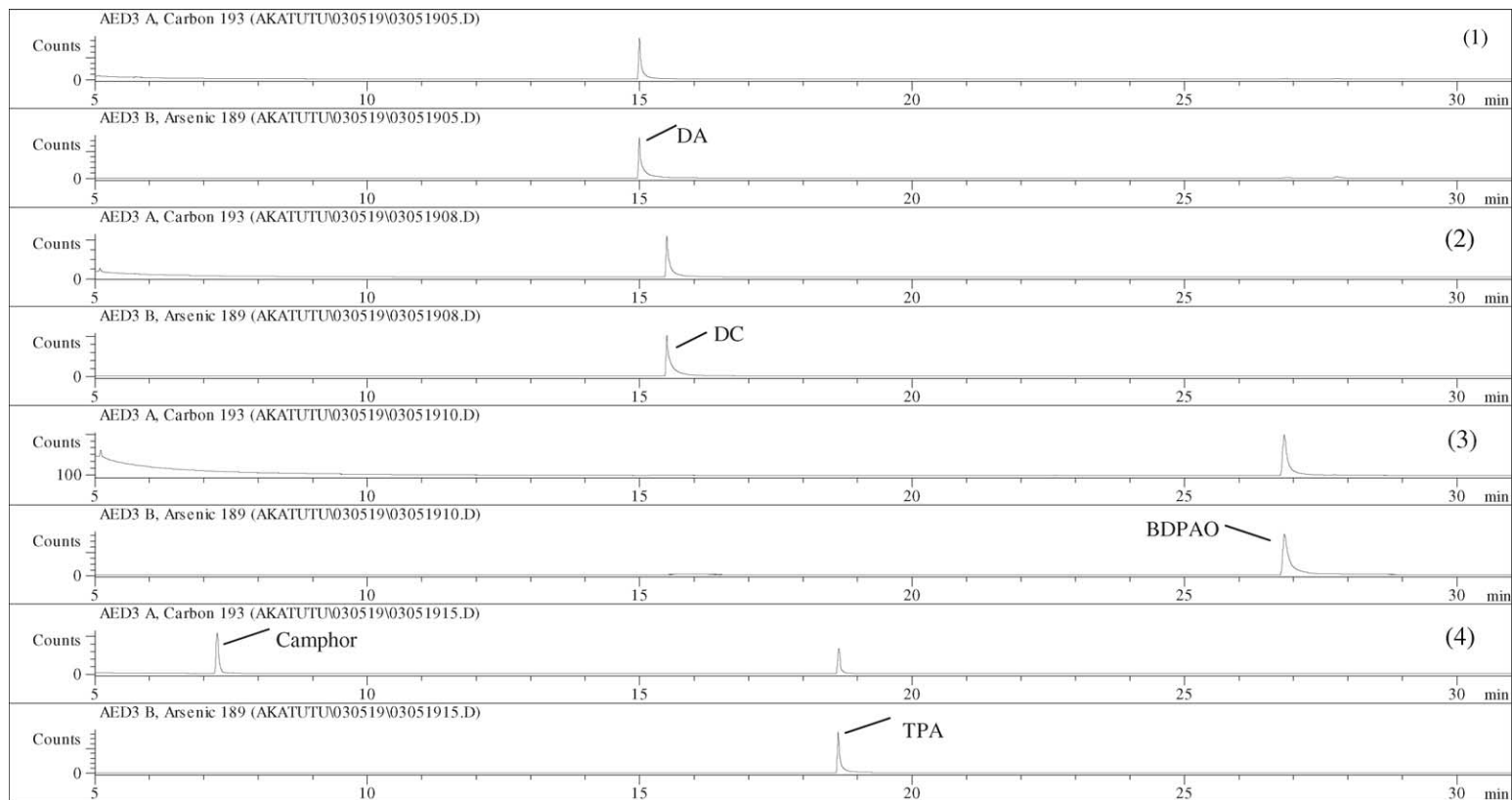Fig. 1. Analytical flow chart for Red agent related compounds in abandoned toxic smoke canisters.

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Fig. 2. (A) GC/AED elemental chromatogram (above: carbon, below: arsine) of DA (1), DC (2), BDPAO (3), TPA and camphor (4) asetonitrile standard solutions (concentration: 100 μg/ml for DA, camphor and TPA, 50 μg/ml for DC and BDPAO), injection volume was 1 μl, and splitless injection mode was applied. Standard solution of camphor and TPA was prepared for mixture. (B) GC/AED elemental chromatogram (carbon and arsine mode) of acetonitrile extracts from the Red canister samples (1) 99-medium (A-2: celluloid matrix), (2) 97-medium (B-2: pumice matrix) 0.5 g of sample were extracted with acetonitrile (20 ml × 2) and diluted 1 ml of these extracts to 40 ml with asetonitrile.
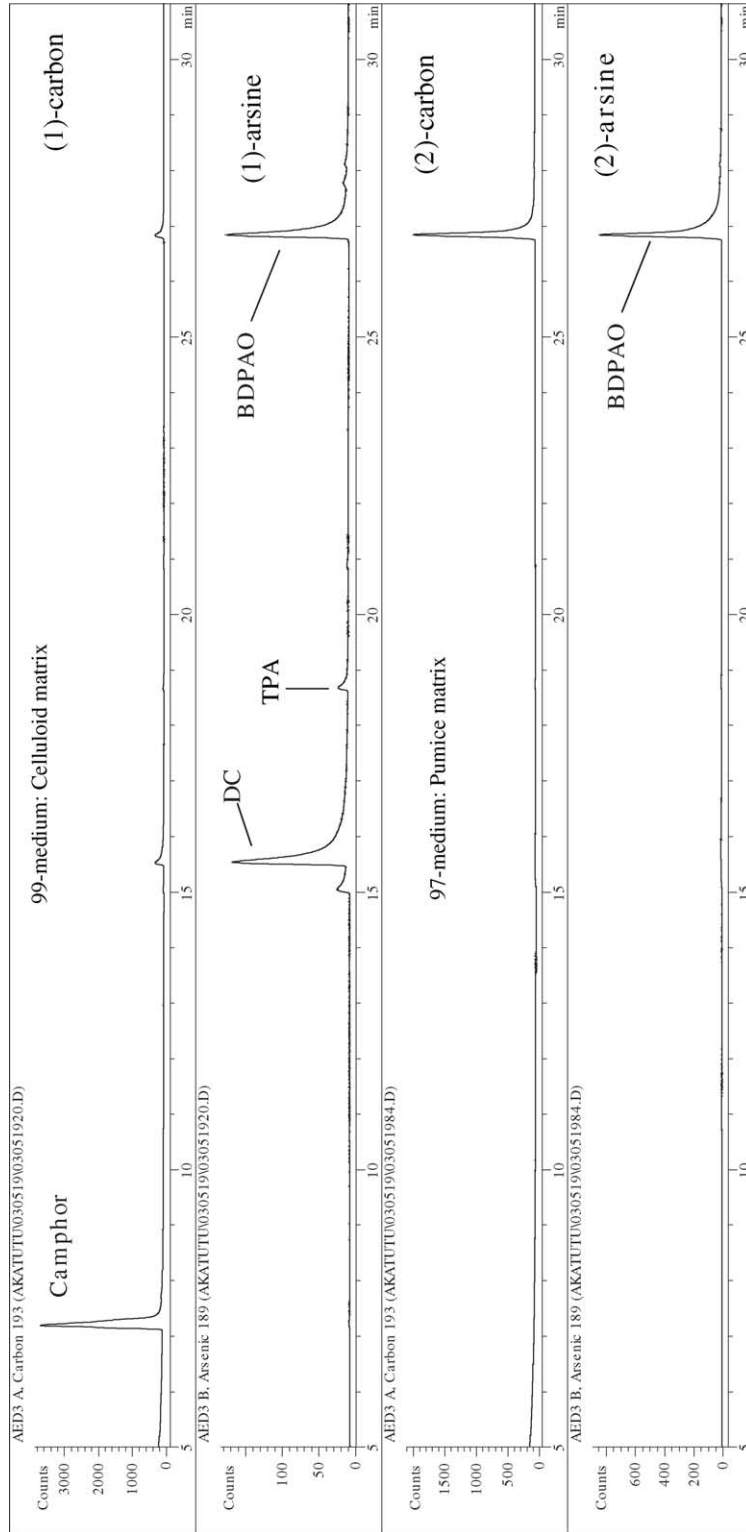
Fig. 2. (*Continued*).

Recoveries of DA, DC, BDPAO and DPAA, was as high as $100 \pm 6\%$ ($n = 2$ each), under the analytical procedure finally chosen. GC/AED elemental chromatograms of standard solution and the extracts of the celluloid and pumice matrix sample (99-medium and 97-medium Red canister) are shown in Fig. 2.

Calibration curves of DA, DC, BDPAO and TPA were determined by GC/AED (arsine-mode) using splitless injection and acetonitrile as a solvent. DPAA calibration was carried out by HPLC-UV. Linear calibration curves from 10 to 200 ng of DA ($y = 5.3896\chi - 55.471$, $\gamma^2 = 0.990$), DC ($y = 4.434\chi - 51.784$, $\gamma^2 = 0.998$), BDPAO ($y = 9.002\chi - 80.29$, $\gamma^2 = 0.998$) and DPAA ($y = 38816\chi - 97657$, $\gamma^2 = 0.998$) were successfully obtained, as well as from 1 to 40 ng of TPA ($y = 12.09\chi - 3.2965$, $\gamma^2 = 0.999$).

Small peaks due to degradation products appeared in the chromatograms (Fig. 2A) and some dispersion was observed in the analytical reproducibility, especially for DA, but they were sufficiently low as not to disturb the quantification.

All sample analyses were carried out within a few days after extraction. And solvent blank was regularly determined via GC analysis as memory effects in the injection system and/or on GC column were observed.

3.5. Chromatographic analysis of the Red canister samples

The composition of medium-size Red canisters (both pumice and celluloid matrix samples), were determined using the approved analytical procedure, and summarized in Table 4 and Fig. 3. Data on the old large-size Red canisters recovered at Okuno Island were also shown therein.

Most of the DC and DA had been degraded to BDPAO in all pumice samples. On the other hand, considerable DC was still detected in celluloid samples (A-2), even though it mostly degraded to BDPAO and further to DPAA.

The composition ratio of the compounds in celluloid samples from different origins, Nanjing and Okuno Island, were similar as shown in Fig. 3, and this tendency was true for most of the other celluloid matrix samples. Otherwise, in a case of unusual celluloid sample (D-3: 98-small) shown in Table 4, only a lower level of the related compounds was detected when comparing others. Although total arsine was present in both extract and residue in this sample, most of the arsine was detected in the residue (Table 5). Besides, the CHN results of residues show low nitrogen content. Based on this result, it is expected that considerable organic arsine-containing compounds remained in the residue as non-extractable form.

The observed differences between components of celluloid and pumice matrix sources were considered to be caused by contact with water and pH differences. In fact, the pumice matrix sample (B-2: 97-medium) was neutral (pH 7.1), otherwise the celluloid matrix sample (A-2: 99-medium) showed a lower pH value (pH 4.9), and the unusual celluloid matrix

Table 4
Concentration of the detected compounds from several Red canister samples (mg/dry g)

Type of Red canister	Sample code	Camphor	Diphenyl	DA	DC	TPA	BDPAO	PAA	DPAA	Total organoarsenic compounds[a]	Total arsine in extracts[b]
Nanjing 99-medium (celluloid)	A-2	124.9 (1.2)	ND	13.4 (5.6)	51.2 (3.3)	3.5 (8.6)	69.3 (5.3)	4.4 (2.3)	188.1 (4.6)	329.9 (4.1)	87.7 (2.0)
	A-3	129 (1.9)	ND	12.6 (2.0)	1.2 (16.7)	2.6 (13.5)	24 (5.8)	5.9 (0.8)	271.7 (0.5)	317.9 (0.3)	84.0 (1.6)
Nanjing 98-small (celluloid)	D-3	81.6 (0.7)	ND	0.3 (33.3)	0.2 (50)	1.75 (8.6)	ND	0.2 (0)	11.85 (2.1)	14.3 (0.7)	8.9 (7.9)
	D-4	135.95 (0.8)	ND	5.8 (17.2)	8.05 (3.1)	11 (3.6)	8.3 (4.8)	0.75 (6.7)	226.8 (3.8)	260.65 (3.8)	79.2 (3.3)
Nanjing 97-medium (pumice)	B-2	ND	ND	2.4 (20.3)	1.4 (16.7)	0.66 (13.2)	326.45 (1.5)	0.30 (4.6)	10.3 (4.5)	341.5 (1.9)	114.4 (0.3)
	B-4	ND	ND	2.5 (1.6)	1.3 (2.7)	0.67 (1.8)	302.5 (1.4)	0.20 (7.0)	9.8 (10.3)	316.9 (1.1)	103.2 (0.4)
Okuno Island 1-Large (celluloid)	O-1	93.6 (23.2)	0.35 (52)	35.4 (25.8)	2.3 (18.4)	5.5 (47.1)	26.5 (14.4)	5.4 (29.4)	289.5 (0.4)	458.4 (5.3)	104.0 (1.4)
	O-2	120.9 (2.6)	0.24 (4.0)	15.1 (14.8)	2.6 (11.8)	2.5 (1.2)	26.5 (2.4)	8.3 (9.7)	335.0 (2.8)	511.2 (0.9)	118.1 (1.8)

[a] Total concentration of DA, DC, TPA, BDPAO, PAA and DPAA.
[b] Total arsine in extracts; extracts were treated acidic degradation and measured by ICP-AES Relative standard deviation (RSD) (%) ($n = 2$) were shown in parentheses, ND: not detected.

Table 5
Total arsine mass balances of the Red canister samples

Type of sample canisters		Concentration of total arsine (mg/dry g)			
		Extracts	Residue	Total	As DC[a]
99-Medium (A-2)	Nanjing (celluloid)	88 (2.0)	33 (3.5)	120 (0.5)	410
98-Small (D-3)	Nanjing (celluloid)	8.9 (7.9)	105 (0.6)	114 (1.1)	390
97-Medium (B-2)	Nanjing (pumice)	114 (0.3)	5.8 (0.9)	120 (0.3)	410
1-Large (O-1, 2)	Okuno Island (celluloid)	–	–	111 (6.6)[b]	380

Concentration of total arsine detected from extracts and their residues of Red canister samples measured by ICP-AES. The yield values were an average of two samples data and Relative standard deviation (RSD) % were shown in parentheses.

[a] Concentration of total arsine × 255/75 (MW: DC = 255, As = 75).

[b] Four samples data.

sample (D-3: 98-small), in which the same level of related compounds was not detected, indicated a still lower pH 3.6. We suspect that under acidic conditions the degradation of Red agents to DPAA was accelerated.
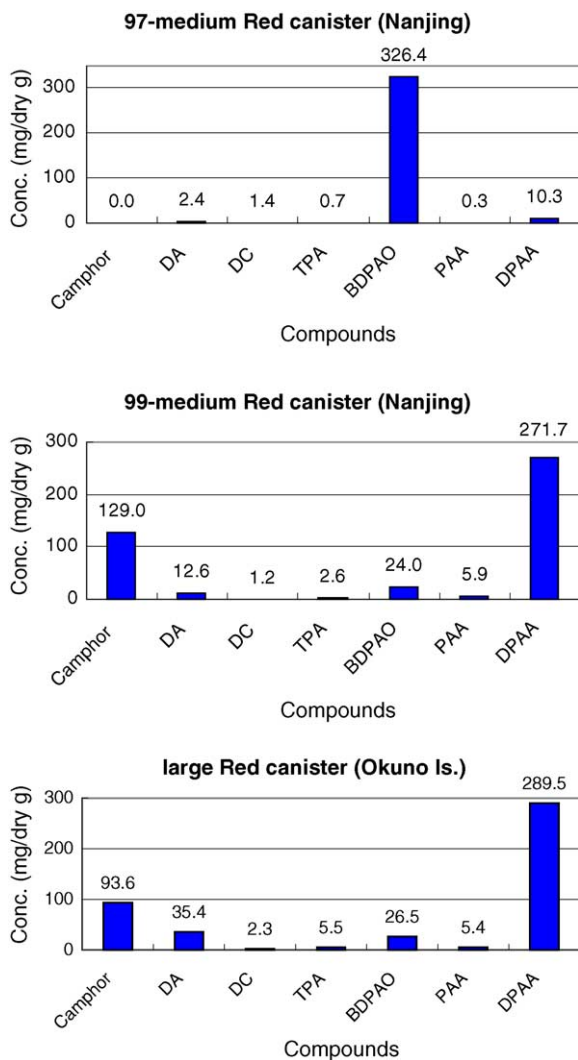

Fig. 3. Components of the Red agent related compounds in different type of Red canisters. Above: 97-medium (B-2: pumice), middle: 99-medium (A-3: celluloid), below: large (O-1: celluloid)

3.6. Mass balance of the Red canister samples

Comparing the total arsine amounts in original samples, the mass balances of an extract and an extracted residue from each sample were checked.

Total arsine contents in both original samples (pumice and celluloid matrices) were approximately 12%. Hence, we could estimate that ca. 40% DC was present in the contents of Red canisters when assuming all arsines originate from this source (Table 5). This result showed close agreement with the natures of Red canisters showed in Table 1.

And arsine mass balance of the extracts and residues provides a practically complete mass balance.

As the analytical data for individual diphenylarsenic compounds scatter within approximately ±5%, they can be used for the purpose to ascertain the nature of Red agent in advance of the initiation of their destruction.

In conclusion, although DA and DC from the original sternutator were hardly present in the Red canister, their degradation products, DPAA and BDPAO were still present in high concentrations. As the case in of Kamisu shows, these munitions must be disarmed and destroyed safely to prevent human and environmental safety hazards.

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