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Development of high-performance liquid chromatographic methods for measuring tetraphenylborate decomposition products in radioactive alkaline solutions

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Abstract

Sodium tetraphenylborate (NaTPB) is used at the Savannah River Site to precipitate and remove the gamma-emitting radionuclide Cs-137 from alkaline high-level waste. The concentrations of NaTPB degradation products such as triphenylborane, diphenylborinic acid, phenylboronic acid, and phenol indicate the rate of decomposition of TPB in storage tanks prior to processing. A simple and speedy sample preparation protocol and two reverse-phase HPLC methods were developed to monitor the concentrations of TPB and all the decomposition products in a complex matrix mainly consisting of 5 *M* sodium salts and 0.5 *M* aluminate. Approximately 4000 radioactive and nonradioactive samples per year have been analyzed since the methods were implemented.

Keywords: Radioactive waste; Sodium tetraphenylborate; Triphenylborane; Diphenylborinic acid; Phenylboronic acid

1. Introduction

The in-tank precipitation (ITP) process at the Savannah River Site removes Cs-137 and Sr-90 from alkaline radioactive waste salt solutions by using sodium tetraphenylborate (NaTPB) and monosodium titanate as precipitants [1–3]. The insoluble species are concentrated and washed prior to storage and further processing in the Defense Waste Processing Facility. ITP began radioactive operation by adding NaTPB solution to radioactive waste salt solutions in October 1995. The stability [4] of the NaTPB in the radioactive waste salt solutions is critical to achieving separation and isolation of Cs-137. Thus, reverse-phase high-performance liquid chromatography (HPLC) is used to monitor the concentrations of NaTPB and its degradation products, triphenylborane (3PB), diphenylborinic acid (2PB), phenylboronic acid (1PB) and phenol in alkaline salt solution.

The organoborane compounds and phenol are in a highly alkaline salt solution with approximately 5 *M* Na^+ and 0.5 *M* aluminate [1]. To avoid column degradation and plugging, the compounds are isolated from the matrix by a single extraction followed by reverse-phase HPLC analysis. Two methods are needed; one measures NaTPB, 3PB, and 2PB concentrations and the second method measures 1PB and phenol concentrations. The convenience of the sample preparation under conditions that NaTPB is known to be stable [5] as well as the automation of the HPLC instrument resulted in the analysis of over

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4000 radioactive and nonradioactive samples per year.

2. Experimental

2.1. Chemicals and materials

NaTPB (99.5%), phenol (99%) and 1PB (97%) were purchased from Aldrich. 3PB is an unstable, flammable solid. A safer and more stable alternative was to synthesize the 3PB–ammonia adduct from the 3PB–sodium hydroxide adduct (nominal 9 weight% solution in water) purchased from Aldrich. 2PB was purchased from Aldrich in a stable form as the ethanolamine ester (98%). All standard solutions were prepared in HPLC grade acetonitrile from Fisher. The purity of the compound and, in the case of 3PB and 2PB, the weight% were accounted for in calculating the standards concentration.

The NH_4OH (30%), *n*-hexane, and NaOH were purchased from Aldrich and used in the preparation of the 3PB–ammonia adduct as follows:

A nominal 9% solution of 3PB–sodium hydroxide adduct (11.91 g) was filtered through a Nalgene 0.2 porosity micron cup filter. Both the filter and flask were washed with 12 ml of 20% NaOH. The filtrate was chilled in an ice bath and 7.2 ml of 30% NH_4OH was slowly added. The mixture was chilled in the refrigerator overnight and filtered the next day. Approximately 60 ml of 1.5% NH_4OH was used to wash the precipitate followed by washing with 10 ml of *n*-hexane. The white solid was vacuum dried overnight to yield 0.6077 g. The sample contains 3.9% ammonium TPB as determined by HPLC.

The HPLC grade solvents used were methanol (Spectrum), acetonitrile (Fisher), a premix mobile phase of 33% acetonitrile, 40% water, 27% methanol, and 0.1% diammonium hydrogen phosphate (La-Mar-Ka), and ultrapure water obtained from a Waters Milli-Q system. A Whatman Partisil 10 ODS-2 column and a Dychrom Chemco 5 ODS-UH column were used.

2.2. Instruments

Five HPLC instruments were used for both development and routine sample analyses. Three Hewlett Packard 1090 HPLCs (A, L, Series II-C) were equipped with autosamplers and photo diode array UV/VS detectors. The instrument and data acquisition were controlled by a Digital Celebris 560 Pentium computer with Hewlett Packard 3-D ChemStation software. One of the Hewlett Packard instruments was dedicated to radioactive samples and was located in a fume hood rated for radioactivity. Two Thermo Separation HPLCs were equipped with autosamplers and photo diode array UV/VS detectors. One of the Thermo Separation instruments was used for radioactive sample analysis and was located in a fume hood rated for radioactivity. The instruments and data acquisition were controlled by an IBM PC 350-P100 computer with PC1000 software.

2.3. Procedure

2.3.1. Shielding for radioactive samples

To avoid personnel exposure, the radioactive precipitate slurry from the Savannah River Site high-level waste tanks were filtered in a shielded cell to remove the highly radioactive CsTPB. The low activity alkaline filtrate contains the organic compounds of interest. Sample preparation and HPLC analyses were carried out in a fume hood rated for radioactivity.

2.3.2. General sample preparation

Nonradioactive samples were filtered with a 0.5 μm porosity syringe filter to remove the insoluble matter. The filtrate samples were adjusted to a pH of 6–7 by the addition of potassium phosphate monobasic ($KH_2PO_{4)}$ to remove aluminate and excessive salt content that could clog the HPLC column. One milliliter of the filtrate is placed into a 10 ml volumetric flask by pipette followed by the addition of 2.5 ml of saturated KH_2PO_4 solution. The compounds of interest were then extracted using acetonitrile in a single step with approximately 80% recovery. The volumetric flask is filled to the mark with acetonitrile, tightly stoppered, inverted several times and finally mixed on a Vortex mixer. Using a 5 ml transfer pipet, the top acetonitrile layer was removed and put into a syringe with a 0.2 μm

porosity filter attached. The solution was filtered into an autosample vial.

2.3.3. HPLC conditions

A gradient method using a mixture of acetonitrile and ultrapure water separates 1PB and phenol on a Dychrom Chemco-5 ODS-UH column. The compounds were identified by comparing the UV spectra generated on a photo diode array detector to a library of UV spectra generated under the same conditions. TPB, 3PB, and 2PB were separated using an isocratic method on a Whatman Partisil 10 ODS-2 column with acetonitrile, methanol, and 0.1% diammonium hydrogen phosphate aqueous buffer as the eluent. The diammonium hydrogen phosphate not only buffers the eluent but also stabilizes 3PB. A photo diode array detector was used to identify the compounds. Both methods are summarized in Table 1.

3. Results and discussion

3.1. Calculations

The extraction of ITP filtrate yields about an 80% recovery for the organoborane compounds and phenol. The filtrate was prepared for HPLC analyses by extracting once with 6.5 ml of acetonitrile after the solution is brought to a pH of 6–7 by the addition of 2.5 ml saturated KH_2PO_4 solution to 1.0 ml of filtrate. Since the extraction recovery of the analytes was not 100%, recovery efficiencies are needed to calculate the correct concentration for each analyte. The major components of the ITP aqueous filtrate are 2.70 *M* sodium hydroxide, 0.8 *M* sodium nitrite, 0.6 *M* sodium nitrate, and 0.26 *M* sodium carbonate [1]. Research samples simulating ITP filtrate can vary in sodium ion concentration from 0.5–5.0 *M*. To determine recovery efficiencies, the

Table 1
Summary of the reverse-phase HPLC methods

Method	Conditions
Isocratic for NaTPB[a], 3PB[a], and 2PB[a]	
Solvent system	Acetonitrile–ammonium phosphate buffer–methanol (36:36:28)
Column	Whatman Partisil 10 ODS-2, 4.6 mm×250 mm, 10 μm pore size
Oven temperature	Off
Flow-rate	1 ml/min
Stop time	22
UV	219 nm, 240 nm (NaTPB, 2PB at 240 nm, 3PB at 219 nm)
Injection volume	10 or 20 μl
Retention time for NaTPB	7.1 min
Retention time for 3PB	14.5 min
Retention time for 2PB	9.9 min
Gradient for 1PB[b] and phenol	
Solvent system	Acetonitrile–water
t_0 to t_1=11 min	30:70
t_2=12 min	40:60
t_3=15 min	100
t_4=24 min	100
Column	Chemcosorb 5 ODS-UH, 4.6 mm×250 mm, 5 μm pore size
Oven temperature	45.0°C
Stop time	24 min
UV	217 nm
Injection volume	10 μl
Retention time for 1PB	6.0 min
Retention time for phenol	8.9 min

[a] NaTPB=sodium tetraphenylborate; 3PB=triphenylborane; 2PB=diphenylborinic acid.
[b] 1PB=phenylboronic acid.

HPLC instrument was calibrated and samples of NaTPB (108 mg/l), 2PB (105 mg/l), 1PB (105 mg/l) and phenol (111 mg/l) were prepared in acetonitrile and analyzed by HPLC (NaTPB 102 mg/l, 2PB 105 mg/l, 1PB 98 mg/l and Phenol 110 mg/l). The data were compared to data generated from 5 *M*, 2.5 *M*, and 0.5 *M* salt solutions spiked with known amounts of NaTPB, 2PB, 1PB, and phenol. The salt solutions were prepared for analyses using the general sample preparation described in Section 2.3.2 (Table 2). Recovery of 100% would yield a concentration of approximately 100 mg/l. Using Eq. (1), the recovery efficiencies were determined for the filtrate samples with sodium concentrations of 5 *M*, 2.5 *M*, and 0.5 *M* and averaged to yield an average recovery efficiency value for each compound. Concentrations determined from the HPLC analyses of the salt solutions are divided by the recovery efficiency number for each compound to determine the corrected concentrations. The results are shown in Table 3.

Table 3
Average recovery efficiencies of compounds by a single extraction from 5.0 *M*, 2.5 *M* and 0.5 *M* sodium salt solution

Sample	Recovery efficiency[a]				
	NaTPB	3PB	2PB	1PB	Phenol
5.0 *M* Na^+	0.76	0.87	0.77	0.77	0.76
2.5 *M* Na^+	0.77	0.76	0.76	0.78	0.77
0.5 *M* Na^+	0.88	0.86	0.85	0.85	0.82
Average	0.80	0.83	0.79	0.80	0.78

[a] Each recovery efficiency was determined three times and averaged.

$$\text{Recovery efficiency} = \frac{\text{Measured conc. of compound in extract of spiked salt solution}}{\text{Measured conc. of compound in acetonitrile standard}} \times \frac{\text{Conc. of compound in acetonitrile standard}}{\text{Conc. of compound in spiked salt solution}} \quad (1)$$

The recovery efficiencies for 3PB were determined in a slightly different manner because the stable form

Table 2
Concentrations of recovered compounds from spiked salt solution samples

Run	Sample	NaTPB[a] (mg/l)	2PB[a] (mg/l)	1PB[a] (mg/l)	Phenol[a] (mg/l)
MSSA-1	5 *M* Na^+	73	77	70	81
MSSA-2	5 *M* Na^+	72	78	71	81
MSSA-3	5 *M* Na^+	75	78	72	83
	Average	73	78	71	82
	%R.S.D.	2	1	1	1
	Target conc.	102 mg/l	101 mg/l	99 mg/l	108 mg/l
MSSB-1	2.5 *M* Na^+	74	77	72	83
MSSB-2	2.5 *M* Na^+	76	78	72	83
MSSB-3	2.5 *M* Na^+	68	77	72	83
	Average	73	77	72	83
	%R.S.D.	6	1	0	0
	Target conc.	102 mg/l	101 mg/l	99 mg/l	108 mg/l
MSSC-1	0.5 *M* Na^+	84	85	78	90
MSSC-2	0.5 *M* Na^+	84	85	78	85
MSSC-3	0.5 *M* Na^+	85	87	78	88
	Average	84	86	78	88
	%R.S.D.	1	1	0	3
	Target conc.	102 mg/l	101 mg/l	99 mg/l	108 mg/l

MSSA = master salt solution 5 *M*; MSSB = master salt solution 2.5 *M*; MSSC = master salt solution 0.5 *M*.
[a] Each sample was spiked, prepared for analysis using the procedure described in Section 2.3.2 and analyzed by HPLC using the conditions in Table 1. Recovery of 100% is approximately 100 mg/l.

of 3PB in acetonitrile, the ammonia adduct, was not appreciably soluble in the salt solution. Nine percent 3PB in sodium hydroxide solution was diluted with 0.5 *M* sodium hydroxide and analyzed by HPLC. A similar concentration of 3PB was spiked into 5 *M*, 2.5 *M*, and 0.5 *M* sodium salt solutions, extracted, and analyzed by HPLC. The recovery of the compound was determined using Eq. (1) and the results are shown in Table 3.

3.2. HPLC method

A mixture of acetonitrile and ultrapure water readily separates phenol and 1PB on an ODS column using a gradient method (Table 1). Attempts to separate all five components in a single run were unsuccessful. The peaks were identified by matching the UV spectra to a library containing UV spectra of phenol and 1PB generated under the same instrument conditions. The chromatogram is shown in Fig. 1.

An isocratic method using acetonitrile, methanol and water containing 0.1% diammonium hydrogen phosphate was developed on a Whatman Partisil 10 ODS-2 column to separate NaTPB, 3PB, and 2PB (Table 1). Without the presence of diammonium hydrogen phosphate, 3PB decomposes during HPLC analysis. Fig. 2 is a typical chromatogram.

3.3. Application

The recovery efficiencies were tested with customer submitted blind standards by examining all five compounds in 3.5 *M* sodium salt solution (3.5 *M* Na^+, 2.0 *M* OH^-, 0.52 *M* NO_2^-, 0.51 *M* NO_3^-, 0.13 *M* AlO_2^-, 0.14 *M* CO_3^{2-} and 0.01 *M* Cl^-). Each compound was dissolved in 0.5 *M* sodium hydroxide solution at a concentration of about 6000 mg/l. These solutions were then spiked into 3.5 *M* salt solution to make standards with concentrations at 150 mg/l and 600 mg/l. These salt solutions were analyzed by HPLC after the general sample preparation. The results are shown on Table 4. Blind standards were also submitted for each compound at a concentration of 1500 mg/l in 2.6 *M* sodium salt solution (Table 4). At all three concentration levels of the compounds in the standards, there is good agreement between the theoretical concentration of the standards and the analysis concentration of the standards.

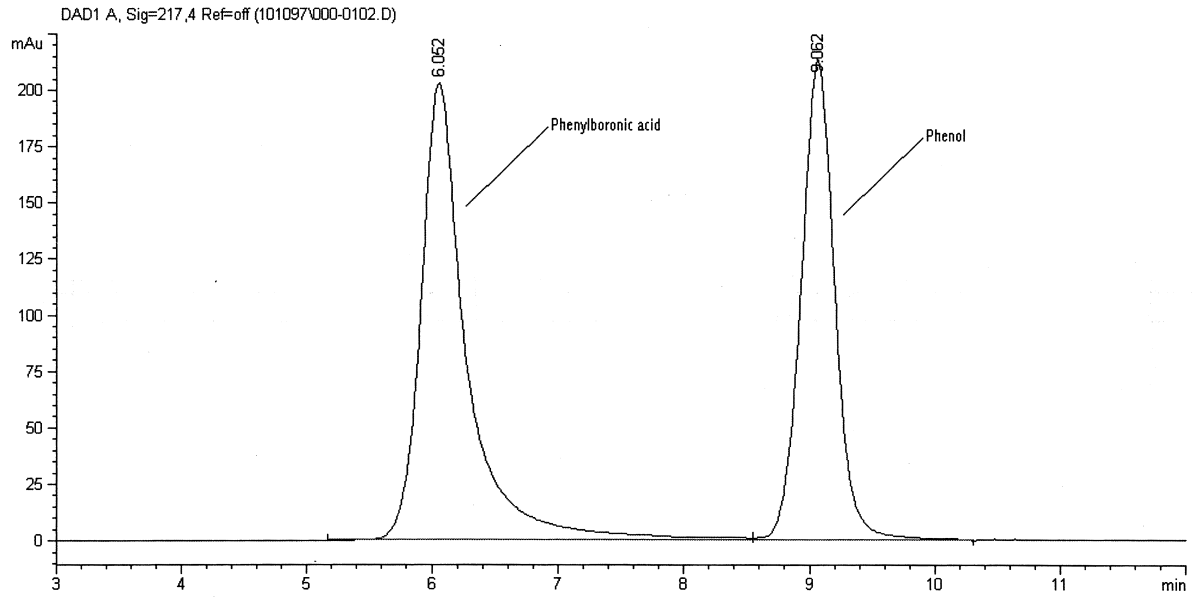

Fig. 1. A chromatogram of 1PB and phenol at 100 mg/l generated under the conditions described in Table 1.

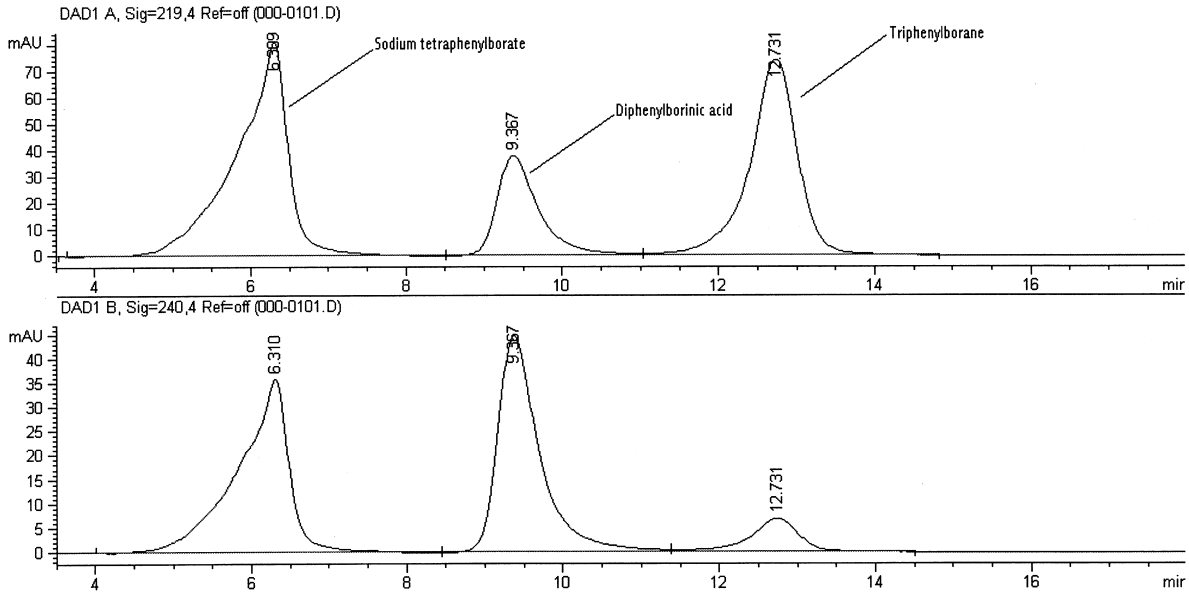

Fig. 2. A chromatogram of NaTPB, 3PB, and 2PB at 50 mg/l generated under the conditions described in Table 1.

The required precision of the analysis is 10% relative standard deviation (R.S.D.). All of the analytes shown on Table 2 are well below the set %R.S.D. limit. Generally, the %R.S.D. for 2PB varies the most. Sample concentrations are reported down to 10 mg/l. On the high end, samples above 5000 mg/l are diluted 10 to 1 with 0.5 *M* NaOH to bring them below 5000 mg/l before they undergo sample preparation and analysis. The calibration curves of the five compounds from 5 mg/l to 500 mg/l are linear.

Table 4
Organoborane compounds and phenol in Na^+ salt solution

Compound	Target concentration (mg/l)	Analysis concentration (mg/l)
At 150 mg/l level[a]		
NaTPB	148	142
3PB	144	144
2PB	148	144
1PB	146	140
Phenol	148	157
At 600 mg/l level[a]		
NaTPB	593	594
3PB	576	580
2PB	592	607
1PB	584	590
Phenol	590	618
At 1500 mg/l level[b]		
NaTPB	1483	1449
3PB	1480	1468
2PB	1439	1438
1PB	1461	1469
Phenol	1476	1521

[a] In 3.5 *M* Na^+ salt solution.
[b] In 2.6 *M* Na^+ salt solution.

4. Conclusion

The method discussed in this paper readily fulfils the requirements of our customers. Direct injection of the highly alkaline salt solution samples would lead to column degradation and plugging. A simple and reliable sample preparation was developed that separates the analytes from the high salt matrix. HPLC methods were developed where all analytes are stable and yielded good separation of the analytes, in a timely manner, over a large concentration range. This allowed for a large number of samples to be analyzed quickly that meet the criteria of our customers.

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