

# Recovery of Ammonium and Cesium Ions from Aqueous Waste Streams by Sodium Tetrphenylborate

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Sodium tetrphenylborate (NaTPB) can be used to recover trace amounts of ammonium and cesium ions from aqueous waste stream simulants. The cesium or ammonium salts precipitated by mixing aqueous NaTPB with the waste stream are dissolved in acetone. In the case of ammonia, the pH is increased by addition of NaOH<sub>(aq)</sub>. The resulting solution, containing a much higher concentration of ammonia than the original waste stream, is then distilled to recover both ammonia and acetone. In the case of cesium, the TPB anion is precipitated by addition of tripropylamine and HCl, and the Cs cation is isolated as CsCl. Subsequent treatment with base liberates tripropylamine and leaves an aqueous solution of NaTPB. In either case, the regenerated NaTPB can then be recycled back into the waste stream. Recovery of cations was quantitative for ammonium and 90% for cesium. Recovery of TPB was quantitative within experimental error. Process designs based on the iterative batch methods are proposed to allow continuous-flow recovery of the products from aqueous waste streams. The conversion of CsTPB to CsCl, with recovery of the TPB anion, may help to avoid problems associated with radiolysis of TPB by radioactive Cs cations.

## Introduction

The recovery of the final traces of a product from an industrial waste stream not only reduces loss, but is also desirable for the minimization of negative environmental impact. However, the recovery of trace amounts (<5000 ppm) of ammonium or cesium ions from an aqueous stream is not practical with traditional methods. Increasing the pH of the entire waste stream, followed by evaporation/distillation, is not economically feasible for low concentrations of ammonia. Similar problems attend Cs<sup>+</sup> recovery. The tetrphenylborate anion (TPB) is capable of precipitating, and thereby removing these compounds from dilute streams as insoluble solids. However, the TPB anion is easily decomposed, and is significantly more expensive than the cations it precipitates. Thus, an economically viable recovery system that uses TPB must not only recover the target molecule or ion, but the TPB as well. We describe here processes by which traces of ammonia or cesium ions may be recovered from bulk aqueous streams, while also recovering the TPB and recycling it back into the waste stream.

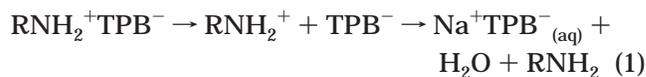
Sodium tetrphenylborate has long been known to quantitatively precipitate amines, ammonium, and large alkali metal ions such as Cs<sup>+</sup> or Rb<sup>+</sup> by forming a water-insoluble salt. The efficacy of TPB as a precipitating anion is attested to by the fact that TPB is used as a reagent for gravimetric analysis.<sup>1–3</sup> There are few interferences to this reaction, and pretreatments for these interferences, such as the addition of ethylenediamine-tetraacetic acid or Na<sub>2</sub>CO<sub>3</sub>, are readily available.<sup>4</sup> The low solubility of the TPB salt compounds in water (2.88 × 10<sup>-4</sup> M for NH<sub>4</sub>TPB)<sup>5</sup> means that very little TPB is lost to the waste stream in the precipitation step.

The loss of trace amounts of ammonia to a waste stream is not usually an environmental issue, but it still

represents a loss of potential product. Cesium is not typically an industrial product, but is a matter of high concern in military aqueous wastes because of the high radioactivity of <sup>137</sup>Cs.<sup>6</sup> The recovery of <sup>137</sup>Cs is not only necessary for final waste disposal, but also because its radioactivity can interfere with downstream processing. Its removal is therefore needed before any further treatment steps.

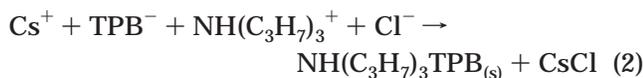
The precipitation of ammonium or cesium ions by TPB is nearly quantitative for even very low concentrations of the target cations. However, TPB is expensive, and therefore it must be separated and recycled. Additionally, the TPB anion is subject to hydrolysis in basic solutions. This reaction adds organic contaminants, such as benzene, to the waste stream. Recent work has shown that sodium tetrphenylborate (NaTPB) is relatively stable in mildly basic solutions.<sup>7</sup> Thus, by maintaining a mildly alkaline pH in the process solutions, TPB can be stabilized and its decomposition to borate and benzene greatly slowed. This allows TPB to be used in a regenerative process by 1) precipitating the target ion from the bulk stream, 2) redissolving the precipitate in a nonaqueous solvent (acetone) to make a solution of much higher concentration than the original waste stream, and 3) regenerating aqueous TPB for reintroduction into the bulk solution.

Once the initial precipitate has been recovered from the waste stream and dissolved in acetone, a dilute aqueous NaOH solution is added to the mixture and the aqueous Na<sup>+</sup> TPB<sup>-</sup> is regenerated by the metathesis reaction:



where RNH<sub>2</sub> is ammonia or an organic amine. In the case of Cs, an additional preliminary step is required wherein the cesium is substituted with an organic ammonium cation such as tripropylammonium (NH<sub>3</sub>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub><sup>+</sup>):

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The solid TPB salt recovered in reaction 2 can be separated by filtration and treated as in reaction 1. The products in reaction 1 are distilled to recover the ammonia (amine) and acetone from the aqueous NaTPB solution.

### Experimental Section

This study was conducted in batch mode for proof-of-concept purposes. A continuous-flow system would be used in actual waste recovery applications. Typically, a waste stream simulant containing 1000–5000 ppm of the target ion in water, at pH 5–6, was chilled to 15 °C and a stoichiometric amount of NaTPB was added. A white solid precipitated immediately and was filtered with a 0.2- $\mu\text{m}$  nylon filter. This solid was then dissolved in acetone, and aqueous NaOH was added to the solution. The mixture was heated, and the vapors containing the product and the acetone were collected by a water-cooled condenser. The remaining aqueous solution of NaTPB was then placed into a new batch of waste stream simulant to repeat the process.

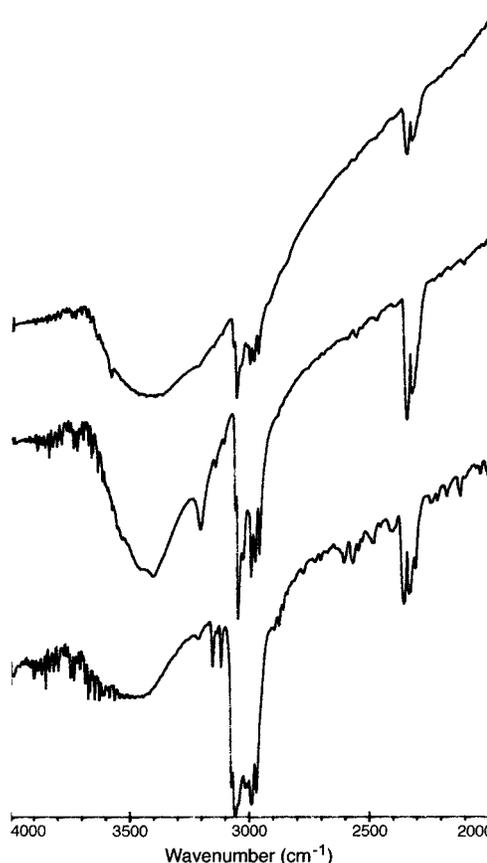
Infrared spectroscopy was performed on a Nicolet 730 FTIR spectrometer. Powder X-ray diffraction (XRD) patterns were obtained on a Phillips X'Pert MPD diffractometer.

**Ammonia.** To bring the pH of the mixture to 5.4, 300 mL of 0.07 M  $\text{NH}_{3(aq)}$  was mixed with about 40 mL of glacial acetic acid. 1.0751 g (3 mmol) NaTPB (Aldrich) was added to about 50 mL of the simulant (about 3.5 mmol  $\text{NH}_3$ ). The resulting solid was filtered and the composition was verified by Fourier transform infrared spectroscopy (FTIR). This recovered solid was then dissolved in 30 mL of acetone. Twenty milliliters of 0.0623 M NaOH (1.25 mmol) was stirred into the flask, the mixture was heated to 50 °C, and the initial vapors were recovered by bubbling into 100 mL of 0.10 M HCl. Total ammonia recovery was tracked by the change in pH of the HCl solution. The mixture was then heated to 85 °C, and the resultant vapors (acetone) were recovered by condensation. To verify the presence of TPB in the remaining solution, a stoichiometric amount of NaOH (an additional 2.75 mmol) was added, the solution was evaporated to dryness, and the resulting crystals were analyzed by FTIR.

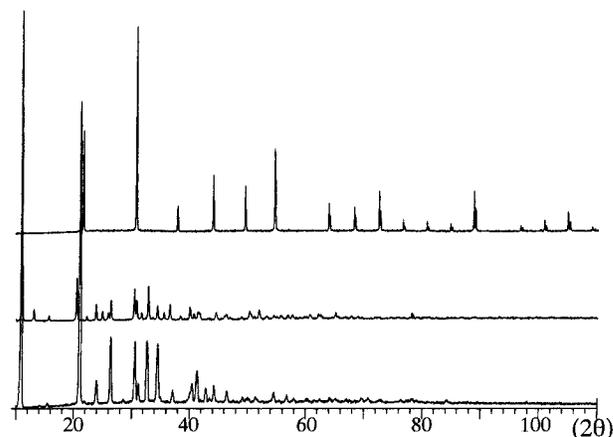
**Cesium.** To form CsTPB, 1.4602 g of  $\text{Cs}_2\text{CO}_3$  (9.0 mmol Cs, Aldrich) was dissolved in water and mixed with 3.0589 g of NaTPB (8.9 mmol). The resultant solid was filtered and air-dried. X-ray diffraction (XRD) was performed on the solid to verify the presence of CsTPB. 2.0032 g CsTPB (4.4 mmol) was dissolved in 100 mL of acetone; 1.000 mL of tripropylamine (5.3 mmol, Aldrich) was added; then 0.400 mL of 12 M HCl (4.8 mmol) was added, and the precipitate was filtered. This solid was treated as described for  $\text{NH}_4\text{TPB}$  above. The filtrate was evaporated to dryness, forming crystals which were identified by XRD as CsCl.

### Results and Discussion

The extent of recovery of ammonia from  $\text{NH}_4\text{TPB}$ , as measured by pH change of the HCl solution, was 102%  $\pm$  10%. The exchange of ammonium and sodium in the solid, as tracked by FTIR, can be seen in the progression



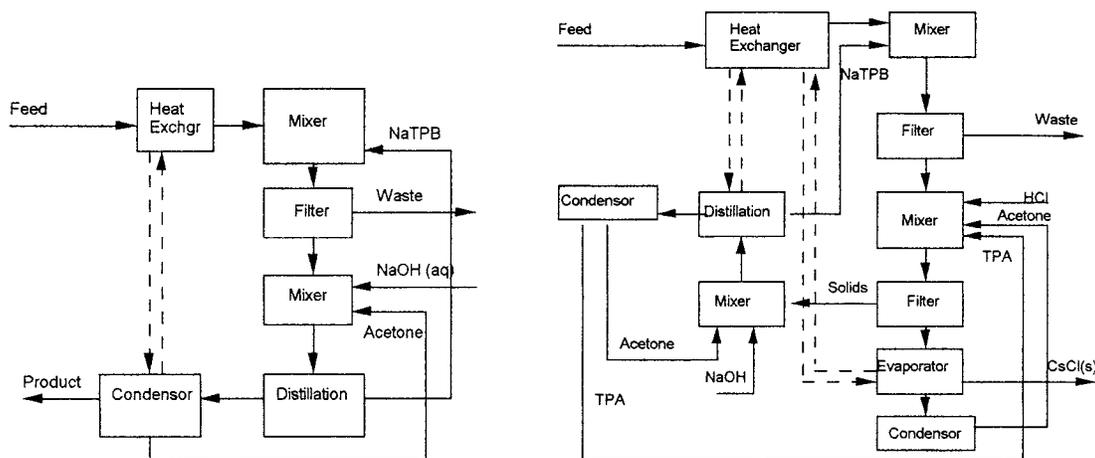
**Figure 1.** FTIR spectra tracking the regeneration of NaTPB. Bottom: NaTPB as received. Middle: After exposure to  $\text{NH}_4\text{OH}$  solution, the TPB solids exhibit the characteristic broad N–H absorbance of  $\text{NH}_4\text{TPB}$  with sharp peaks at 3218 and 3413  $\text{cm}^{-1}$ . Top: Regenerated NaTPB after  $\text{NH}_3$  recovery. Some water is still present in the solids.



**Figure 2.** XRD patterns of solids from the cesium recovery process: Bottom: NaTPB. Middle: CsTPB. Top: CsCl.

of IR spectra shown in Figure 1. The recovered NaTPB does not show the characteristic N–H stretching vibrations of  $\text{NH}_4\text{TPB}$  at 3218 and 3413  $\text{cm}^{-1}$ . Recovery of Cs, as CsCl, from CsTPB was 88.9%  $\pm$  0.5%. The product was identified as CsCl by powder XRD (See Figure 2.) Typical loss of TPB from batch to batch amounted to 1.4%  $\pm$  0.5, which is thought to arise primarily from transfer losses.

Ammonia, which has a much lower boiling point than water, was easily recovered from the redissolved solid. Collection of ammonia began immediately once the pH of the dissolved  $\text{NH}_4\text{TPB}$  was raised to 10 by addition



**Figure 3.** Proposed steady-state recovery processes. Left: Ammonia recovery process. Right: Cesium recovery process.

of the NaOH, and increased as the temperature increased to a maximum of about 30 °C. The temperature was subsequently increased to 85 °C, and acetone was then recovered using a condenser.

When the recovered TPB ion was isolated and identified in solid form as NaTPB, extra NaOH was needed to precipitate the salt quantitatively. In contrast, less than half the stoichiometric amount of sodium (as NaOH), relative to TPB, was needed to increase the pH of the  $\text{NH}_4\text{TPB}$ /acetone solution so that  $\text{NH}_3$  and acetone could be recovered. The form of the TPB ion which was then recycled to the bulk waste stream thus was thought to be a mixture of the acid form (HTPB) and NaTPB.

To recover Cs as CsCl, CsTPB was dissolved in acetone and treated with tripropylamine. Tripropylammonium tetraphenylborate began to precipitate immediately when HCl was added to the solution. The pH of the mixture equilibrated at 8.2. The reason for the less than quantitative yield of Cs is currently unknown. However, because the missing Cs totals about 0.3 mmol at this scale, there is probably significant transfer loss.

A further cautionary point with recovery of  $^{137}\text{Cs}$  is that the radiation emitted by this isotope can both decompose the TPB and raise the process stream temperature. The result of these effects is to create bubbles of volatile organics that periodically burst at the surface, creating a serious safety hazard.<sup>8</sup> With the recovery process described here, the total exposure time of TPB to Cs is minimized. Because the precipitates form as quickly as the reagents are added, the limiting factor in time of exposure is the time required to isolate the solids by settling, filtration, or centrifugation.

The recovery methods used in this study follow very simple process steps which could be used on bulk streams of low concentration. The high latent heat of vaporization of water makes the recovery of trace amounts of these analytes by distillation very unfavorable economically. By removing the ammonium and cesium from the bulk stream through the use of TPB, treatment and distillation can be performed at high concentrations with minimal energy expenditures. Additionally, much of the heat needed for the distillation can be recovered through heat exchange while cooling the bulk waste stream. By controlling the pH of the NaTPB mixture, the TPB anion can be stabilized long enough to recycle it back into the product waste stream, thereby closing the process loop without loss of expensive reagents.

### Proposed Process Designs

The successful recovery of ammonia or cesium by repeated batch methods allows the proposal of steady-state continuous processes. A continuous process is particularly important for bulk stream conditions wherein the TPB is unstable.

Recent events at the Department of Energy's Savannah River Site exemplify this problem.  $^{137}\text{Cs}$  was to be recovered by precipitation with TPB in a batch process performed in million-gallon tanks. During the period required to mix and then collect the precipitate in such large vessels, an unacceptable amount of hydrophobic organics (primarily benzene) was generated, which would phase separate from the aqueous solution, then rise rapidly to the surface and burst as they vaporized from the heated aqueous solution.<sup>8</sup> This safety hazard caused the shutdown of the entire waste-processing line.

Of the methods proposed to solve this problem, by far the least expensive is the use of the same process with 15 000-gallon tanks. However, it seems likely that generation of organics will still be a problem, even in this size tank, because of the time needed to mix and separate the TPB. At the same time, the lack of a recovery step for the TPB adds to the expense of the process and allows the continued formation of benzene even after separation of CsTPB from the bulk waste stream.

Minimal exposure of TPB to the bulk stream is the simplest means to avoid decomposition of the anion in the aqueous phase and in the  $^{137}\text{Cs}$  salt, wherein it is unstable. To this end, a continuous-flow, steady-state process could allow maximum Cs and TPB recovery while minimizing exposure time to the bulk stream. Proposed process designs for recovering  $\text{NH}_3$  and  $\text{Cs}^+$  are shown in Figure 3.

### Conclusions

The quantitative precipitation of ammonium ion, amines, and some alkali metal salts from aqueous solution is a well-known use of NaTPB. However, for this separation process to be economically viable in an industrial setting, TPB must be recycled into the waste stream without loss of the reagent. The reactivity of the TPB ion in strongly basic or acidic solutions increases the difficulty of process design.

The processes described above allow for the recovery and recycling of TPB by redissolving the product-TPB

solids, separating the cationic species by exchange and filtration, and distilling the resulting solution. Energy loss can be minimized using a heat exchanger, and the nonaqueous solvent (in this case, acetone) can be recovered as part of the distillation process. These processes are performed at a mildly alkaline pH, where the TPB ion is stable and can be recovered without decomposition. Thus, the only reagents used in these processes are small amounts of NaOH (or NaOH and HCl in Cs recovery), which are lost when the NaTPB is regenerated and recycled back into the waste stream.

The recovery of ammonium ions was shown to be quantitative, whereas recovery of cesium ions was about 90%. Because rubidium(I), mercury(II), and protonated amines also precipitate in water with TPB, it is expected that these ions also could be recovered by the same process.

### Acknowledgment

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