Ion Chromatography Analysis of Dibutyl Phosphoric Acid

by

R. J. Ray

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

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R.J. Ray
Analytical Development Section - Savannah River Technology Center,
Westinghouse Savannah River Company, Aiken, SC

Technical Review: Thomas W White 10/5/98

T. White Date

Manager Approval: John Young 10/5/98

J. Young Date

C.C. Jenkins 10/6/98

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Abstract

Analysis of dibutyl phosphate (DBP), a degradation product of tributyl phosphate (TBP), has long been a problem analysis by Ion Chromatography at the Savannah River Site. Due to the presence of UO_2^{+2} and high NO_3^{-1} concentrations, inadequate recovery and separation of DBP on the chromatographic column had rendered the analysis undependable and very inconsistent, thus causing high uncertainties in the data.

The method presented here by the Savannah River Technology Center (SRTC)/Analytical Development Section (ADS) addresses the sample preparation problems encountered when analyzing for DBP in the presence of uranium and nitrate. The data presented reflects the improvements made to decrease data uncertainty and increase data accuracy and precision.

Introduction

The Savannah River Site has enriched uranium (EU) solutions that have been stored for the past 10 years since being purified in the Plutonium-Uranium Extraction Process (PUREX). Residual tributyl phosphate in these solutions has slowly hydrolyzed to form uranium dibutyl phosphate complexes which have limited solubility.[1] The potential to form $UO_2(DBP)_2$ precipitates raises criticality safety concerns; therefore, the concentration of DBP must be measured accurately and precisely.

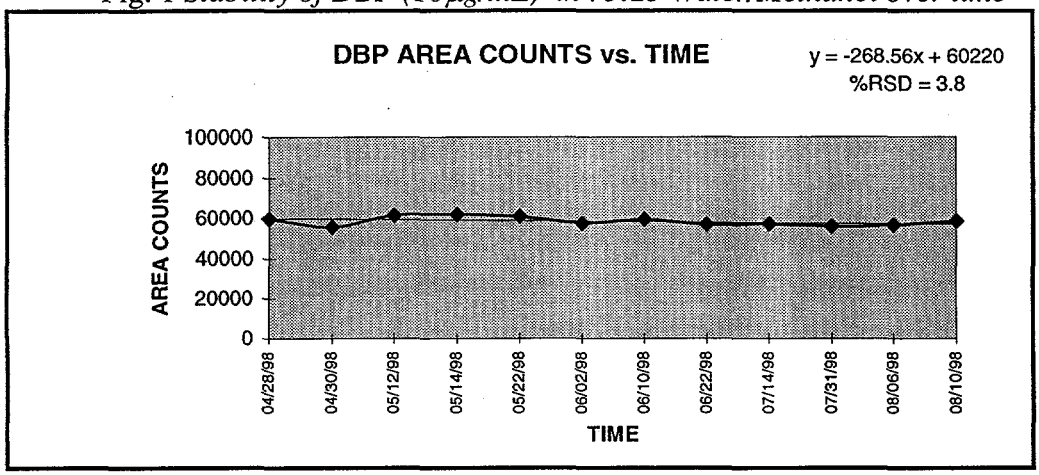
Ion Chromatography (IC) is a viable and cost-effective method of analyzing for the presence of DBP. This paper describes the calibration curve, sample matrix, and sample preparation associated with DBP analysis. In summary, DBP is extracted from an aqueous matrix containing 15g/L uranium and 0.15M nitrate into 2-ethyl hexanol, back extracted into 1M sodium hydroxide, filtered to remove sodium interferent, and analyzed by IC. The statistical data describes the method detection limit and the accuracy/precision of this method.

Experimental

Standard solutions of DBP (not containing uranium) were prepared using a 97% reagent standard from Aldrich Chemical Company. A 100mL standard stock solution was prepared at 1000µg/mL using 25mL of HPLC grade methanol to dissolve DBP into solution with water. Calibration standards were prepared from this stock solution at 10µg/mL, 50µg/mL, and 100µg/mL. The linearity of this 3-point calibration curve had a relative standard deviation (RSD) of 10%. Figure 1 shows the stability of DBP in 75% water and 25% methanol, in the presence of light. Figure 2 shows the linearity of the calibration curve.

[1] Bob Pierce, Major Thompson, Robert Ray. WSRC-TR-98-00188, Rev. 0.

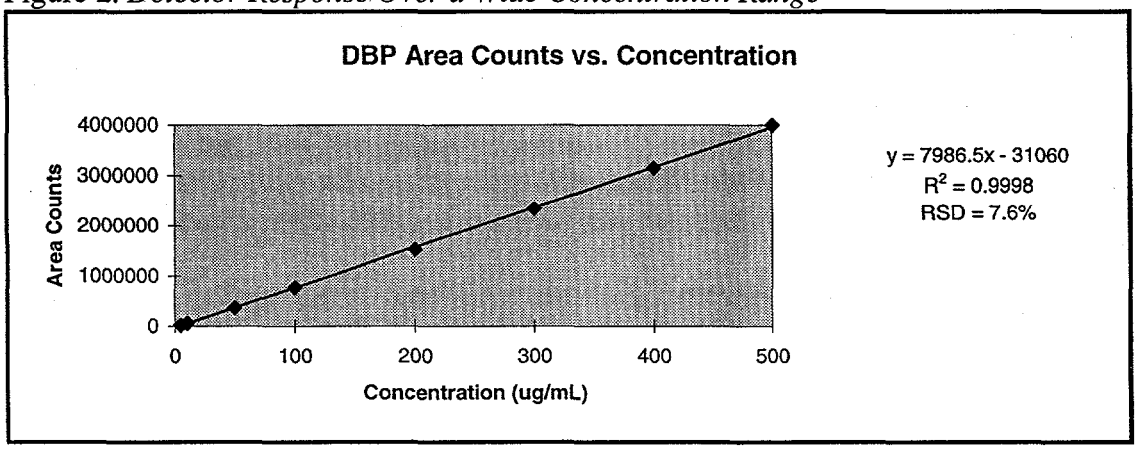
Fig. 1 *Stability of DBP (10μg/mL) in 75:25 Water/Methanol over time*



As evidenced in Figure 1, the daily calibration verification standard is very stable as a function of time. There is minimal degradation. The standard prep by the technician is very reproducible. Moreover, the analytical system has a very stable response to DBP as a function of time. This stability is the basis for reproducible measurements performed by Ion Chromatography.

The calibration curve shown in Figure 2 is a plot of detector response over concentration. Detector linearity is demonstrated by a relative standard deviation of 15% or less.[2] Figure 2 also illustrates the capacity of the conductivity detector for a wide range of linearity. A wide range of linearity is useful when analyzing samples which have wide ranges of DBP concentrations. However, most of the samples we have analyzed thus far range between 0.2μg and 1μg DBP on column, dilution factor not accounted for. Therefore, a calibration range between 0.2μg and 2μg DBP on column can serve as a practical calibration curve.

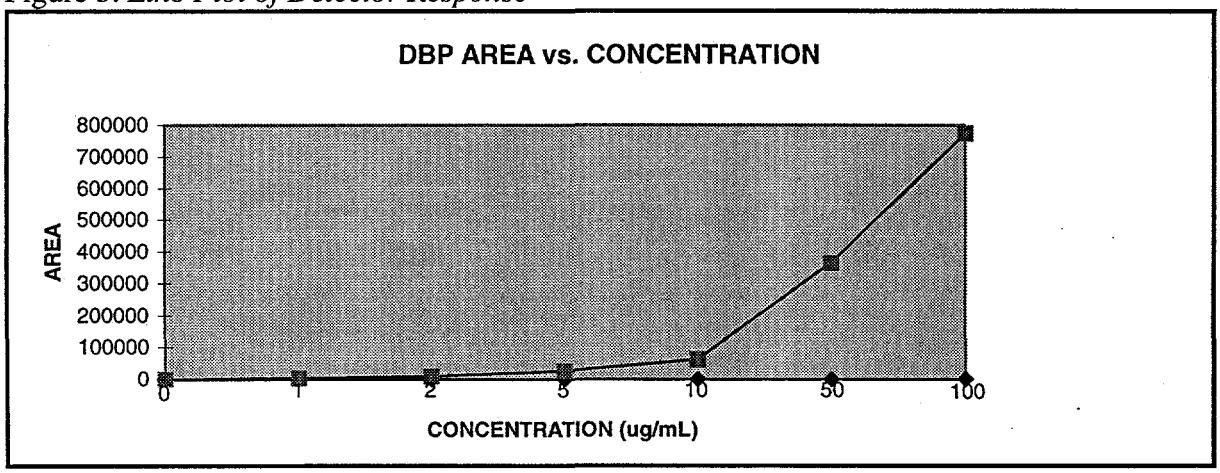
Figure 2. *Detector Response Over a Wide Concentration Range*



[2] EPA, 1990. SW-846, Method 8000.

Linearity and sensitivity decreases significantly below the 10μg/mL (0.2 μg on column). See Figure 3 for illustration. The response factor of the 10μg/mL DBP standard may be used to quantify samples that have DBP concentrations between 2μg/mL and 10μg/mL, dilution factor not included. The relative standard deviation between 0.04μg and 0.2μg DBP on column was 14%.

Figure 3. *Line Plot of Detector Response*



The IC system consists of a Dionex gradient pump (DX-300), conductivity detector (CDM-I), and an anion self-regenerating suppressor (ASRS II). The analytical columns were two AS4A columns (4mm ID) connected in series. The guard column was an AG4 (4mm ID). The eluent was a mixture of sodium carbonate/sodium bicarbonate at 0.225mM respectively. Flow rate was 1.2 mL/min. A 20μL sample loop was used for all injections.

A 1mL aliquot of the matrix material (15g/L uranium and 0.15M nitrate) was added to a 22mL glass vial containing 5mL of milli-Q water. The contents were spiked with 20μg of DBP. Two milli-liters of 2-ethylhexanol were added. The vial was then capped (teflon liner) and vortexed for 20 seconds. At an acidic pH, DBP is predominately present in the protonated form and will readily transfer to the 2-ethylhexanol organic phase as a function of solubility. The mixture was allowed to settle (about 3 minutes). No stable emulsions were formed. This is due to the anti-foaming characteristics of the 2-ethylhexanol solvent and the ionic strength of the mixture. In the event that a stable emulsion was formed, the addition of 5 drops of 1M nitric acid increases the ionic strength of the solution, thus breaking the emulsion.

The organic phase (top layer) was transferred, via disposable plastic pipette, to another vial containing 5.0mL of 1M NaOH. The vial was capped and vortexed for 20 seconds to back-extract DBP. During the back-extraction with NaOH, DBP is deprotonated to DBP- (an anion more soluble in water). After the phases separated, the organic layer was carefully separated from the NaOH layer and discarded.

Sodium is an interferent ion when analyzing for anions. The ASRS II only suppresses about 0.125 meq of sodium in the recycle mode; therefore, it is necessary to remove the excess sodium from the sample before analyzing it. Three Dionex On-Guard H+ ion exchange cartridges

were connected in series to remove the 5 meq of sodium from the NaOH back-extraction. Each On-Guard H+ ion exchange cartridge has a capacity for removing 2 - 2.5 meq of sodium, exchanging H+.[3] The first 3mL of the NaOH back-extract was pushed through the cartridges rather quickly to displace the residual water from rinsing and discarded. The final 2mL were filtered drop-wise at rate of 2mL/min and collected in a 5mL Dionex autosampler vial. Collection of the filtrate was stopped when the apparent liquid level reached the first cartridge, thus keeping the residual 2-ethylhexanol from passing through the cartridges. The resulting pH range should be between 3 and 7. If the pH is 9 or above, the Na+ has not been exchanged adequately.

Standards and recovery studies indicate that this method is quantitative and reproducible for determining the presence of DBP in H-Canyon process material. DBP is effectively extracted and analyzed in a protonated or partially protonated form. Figure 4 is a chromatogram of the 10ug/mL calibration verification standard. DBP is calibrated in the neutral pH range, above the pKa. Figure 4 displays the 10µg/mL standard analyzed using the improved DBP method.

Figure 4. *Chromatogram of 10µg/mL Standard*

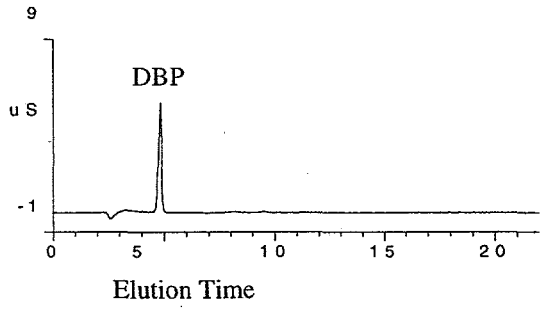
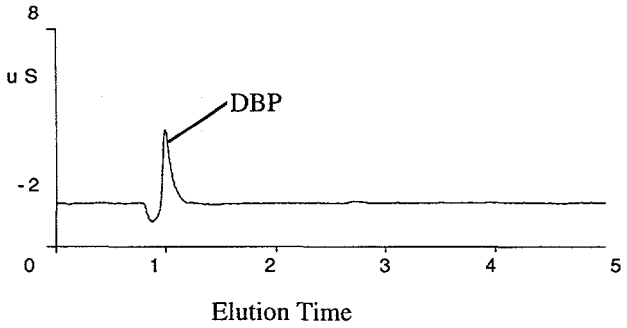


Figure 5 illustrates the 10µg/mL standard prepared in 0.225mM Carbonate/Bicarbonate eluent. DBP, as shown, has very little retention on the analytical column and is eluting very close to the water dip as part of the void volume.

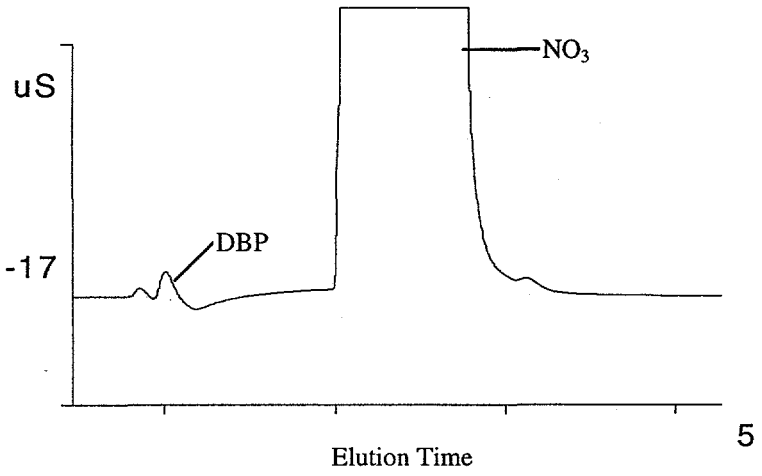
. *Old DBP Method (10µg/mL DBP STD)*



[3] Dionex Corporation. Installation Instructions and Troubleshooting Guide for Onguard™ Cartridges. Document No. 032943, Revision 08, October 17, 1995, On-Guard-H Cartridges.

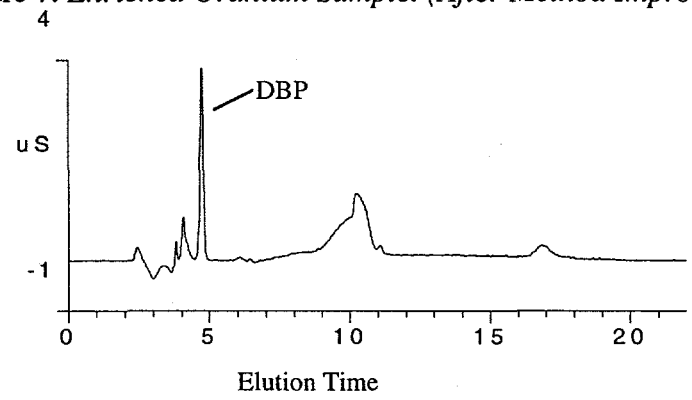
Figure 6 illustrates the chromatography of DBP from past samples before method improvements were made. A 0.5 - 1mL sample aliquot (in 2-ethyl hexanol) containing DBP in the presence of uranyl-nitrate ($UO_2(NO_3)_2$) was partitioned against 0.005M NaOH. After the solution settled, the bottom layer (slightly yellow) was diluted and injected into the IC system. Low DBP recoveries were observed. As the nitrate concentrations increase, analysis of DBP becomes more and more problematic because of column overloading, thus causing DBP to be retained even less on the analytical column.

Depleted Uranium Sample (pre-method development)



To counter low DBP recovery, DBP had to be isolated from the uranyl species in the form of HDBP and back-extracted in the form of DBP- using 1M NaOH. After the Na+ interferent was removed and the retention of DBP on the column was increased, this method proved to be accurate and reproducible. Figure 7 displays the chromatography of samples after method improvements. DBP concentration is 33ug/mL ±4.4%. The nitrate species eluted in the blank following the sample.

Figure 7. *Enriched Uranium Sample. (After Method Improvements)*



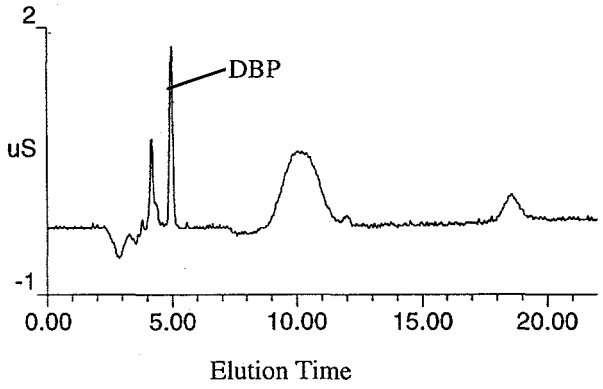
Method detection limit (MDL) studies were performed using the 15g/L uranium-0.15M nitric acid matrix material. A 1mL aliquot of the matrix material was added to a 22mL glass vial

containing 5mL of reagent water. The solution was spiked with 10μg of DBP (0.04μg on column) and carried through the rest of the extraction/back-extraction procedure. The average recovery was 108%. The MDL value for seven replicates was 1.55μg/mL using a t-statistic value of 3.14. The results for the MDL study is shown in Figure 8. Figure 9 is a chromatogram of the MDL matrix spike.

Figure 8. Method Detection Limit Study

	Trial #1	**Trial #2**	**Trial #3**	**Trial #4**	**Trial #5**	**Trial #6**	**Trial #7**
%Recovery	108	107	104	105	114	102	115
Average Recovery	108%						
Standard Deviation	0.495						
MDL Value	1.55						

Figure 9. *Chromatogram of MDL Spike*

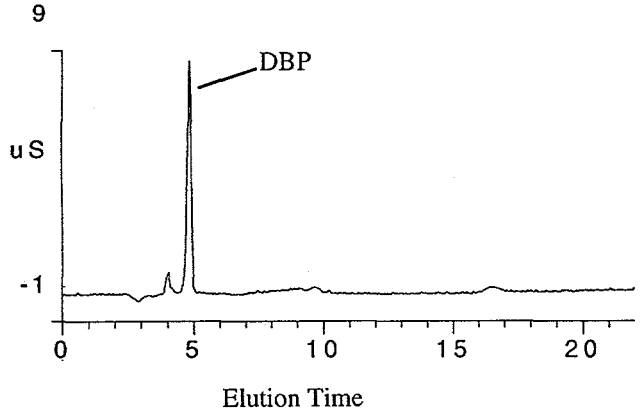


The accuracy/precision study was carried out in the same manner except the spiked amount of DBP was increased to 100μg into solution (0.4μg on column). An average recovery of 76% was observed. The results for the Accuracy/Precision study is shown in Figure 11. Figure 12 is a chromatogram of the accuracy/precision Spike. The method uncertainty value was calculated to be ±4.4%. This uncertainty value was taken from the %RSD and represents the total error for this analysis.

Figure 10. *Accuracy/Precision Study*

	Trial #1	Trial #2	Trial #3	Trial #4
%Recovery	73	73	76	80
Average Recovery	76%			
Standard Deviation	3.317			
%RSD	4.4			

Figure11. *Chromatogram of Accuracy/Precision Matrix Spike*



Conclusions

Analysis of DBP by Ion Chromatography is an accurate and precise method. Analytical problems encountered from past analyses have been addressed and corrected. Data Uncertainties have been decreased from over ±25% to ±4.4%.

Analytical results by this method have proven to be consistent and reproducible. It is advised that a matrix spike and a matrix spike duplicate be analyzed per sample batch, per matrix type to assess analte recoveries. Based upon the accuracy and precision of this method, analytical values can be adjusted to account for DBP recovery. This adjustment is closer to the true value with a ±4.4% Uncertainty.

The calibration curve should range from 0.2µg to 2µg of DBP on column. Samples with less than 0.2µg of DBP on column will be in a different response range of the conductivity detector as demonstrated in Figure 2. However, linearity does exist between 0.04µg and 0.2µg DBP on-column. Therefore, the response factor for 0.2µg may by used to quantify samples containing between 0.04µg and 0.2µg of DBP on column. Alternatively, the sample size may be increased.

References

1. R.A. Pierce, M.C. Thompson, R.J. Ray. "Solubility Limits of Dibutyl Phosphoric Acid in Uranium Solutions at SRS (U)", WSRC-TR-98-00188, Rev. 0.
2. K.E. Grant, G.M. Mong, S.A. Clauss, K.L. Wahl, J.A. Campbell. "Determination of Monobutyl Phosphate and Dibutyl Phosphate in Mixed Hazardous Wastes by Ion-Pair Chromatography", Journal of Radioanalytical and Nuclear Chemistry, Vol. 220, No. 1 (1997) 31-35.
3. EPA, 1990, "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods", SW-846, Revision 1, U.S. Environmental Protection Agency, Washington, D.C.