

RECEIVED

PNNL-12085

FEB 16 1999

OSTI

Pacific Northwest National Laboratory

Operated by Battelle for the
U.S. Department of Energy

The SX Solver: A New Computer Program for Analyzing Solvent- Extraction Equilibria

G. J. Lumetta
B. K. McNamara
B. M. Rapko

January 1999

Prepared for the U.S. Department of Energy
under Contract DE-AC06-78RLO 1830

PNNL-12085

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161



This document was printed on recycled paper.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

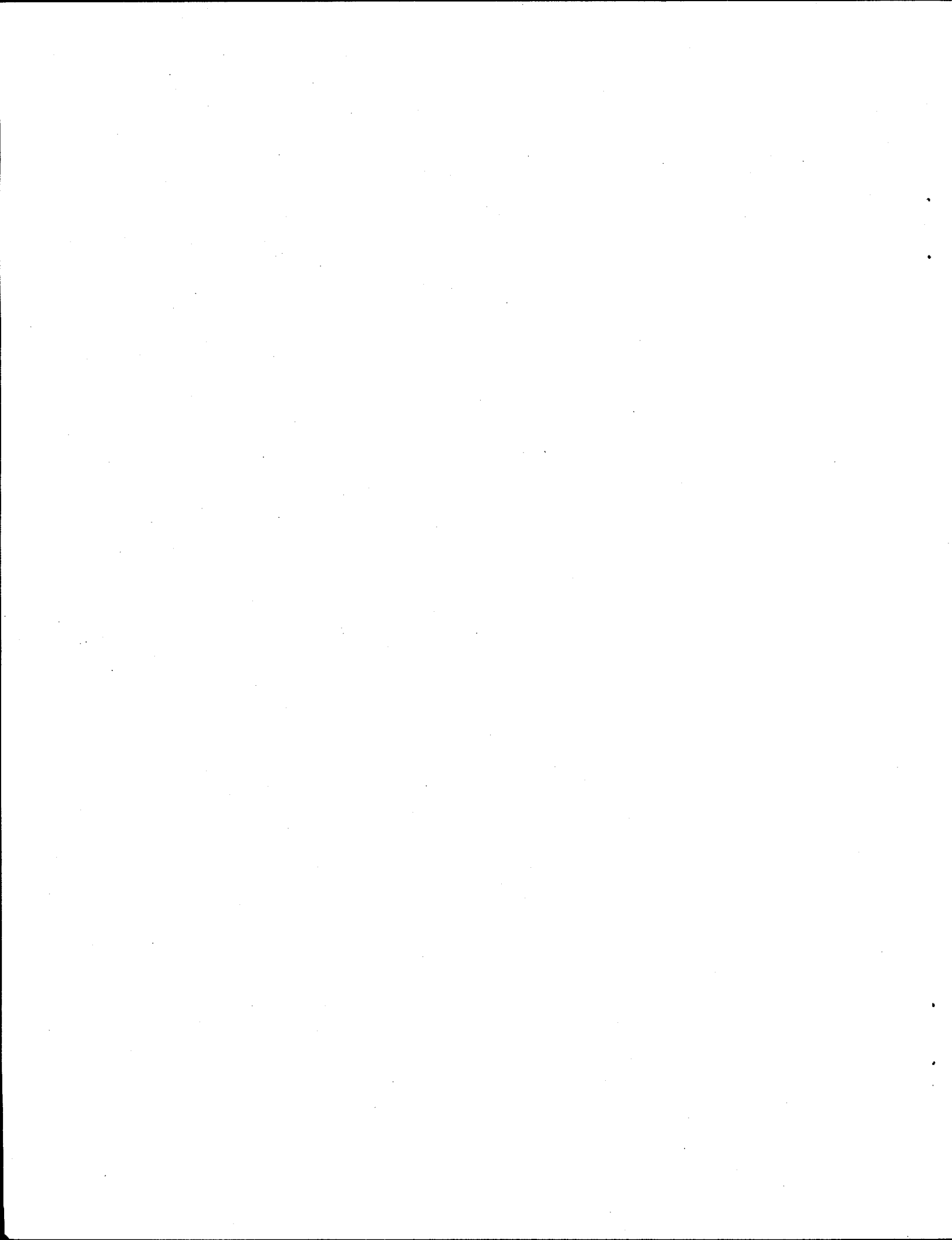
The SX Solver: A New Computer Program for Analyzing Solvent- Extraction Equilibria

G. J. Lumetta
B. K. McNamara
B. M. Rapko

January 1999

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76 RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

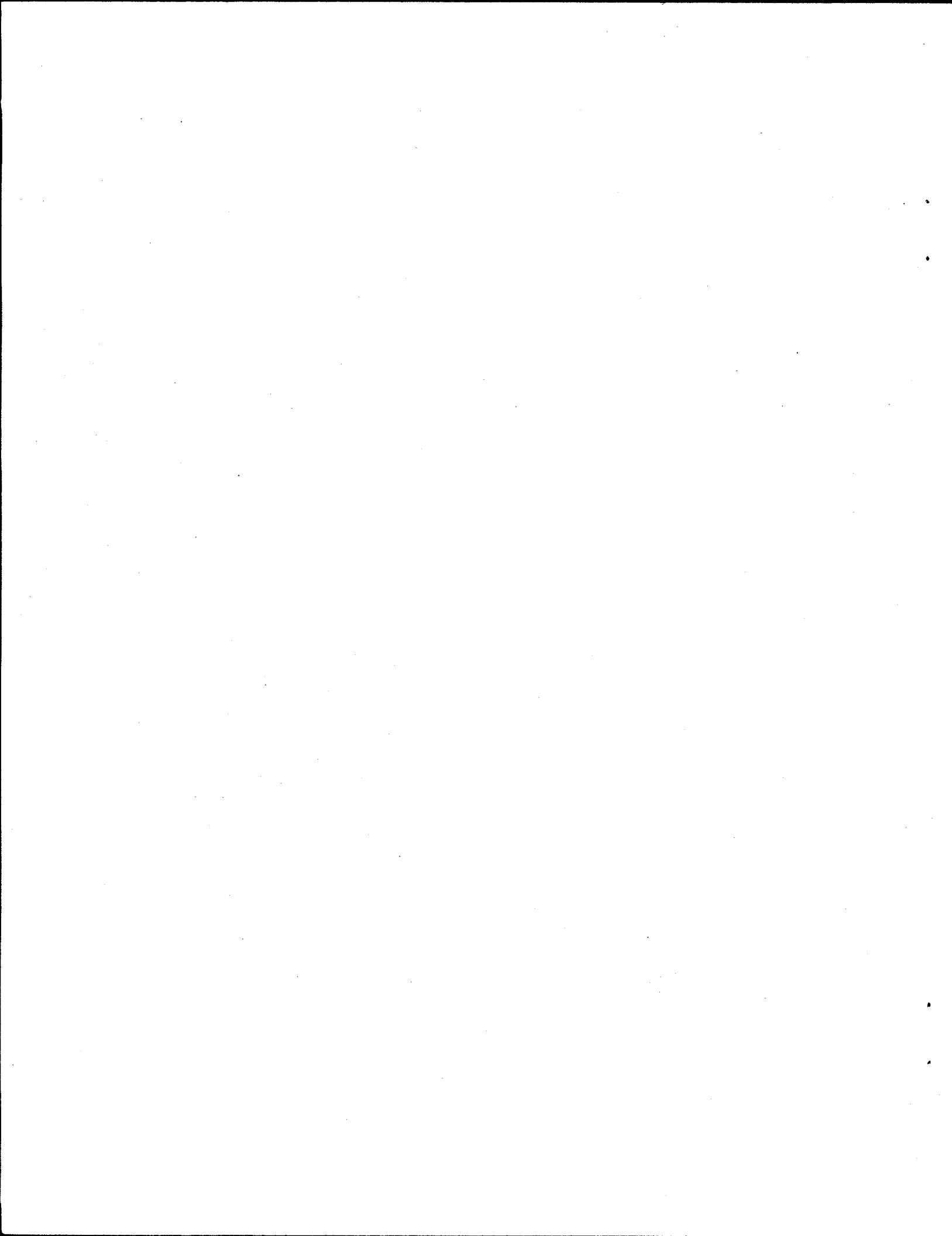


Summary

A new computer program, the SX Solver, has been developed to analyze solvent-extraction equilibria. The program operates out of Microsoft Excel® and uses the built-in "Solver" function to minimize the sum of the square of the residuals between measured and calculated distribution coefficients. The extraction of nitric acid by tributyl phosphate has been modeled to illustrate the program's use.

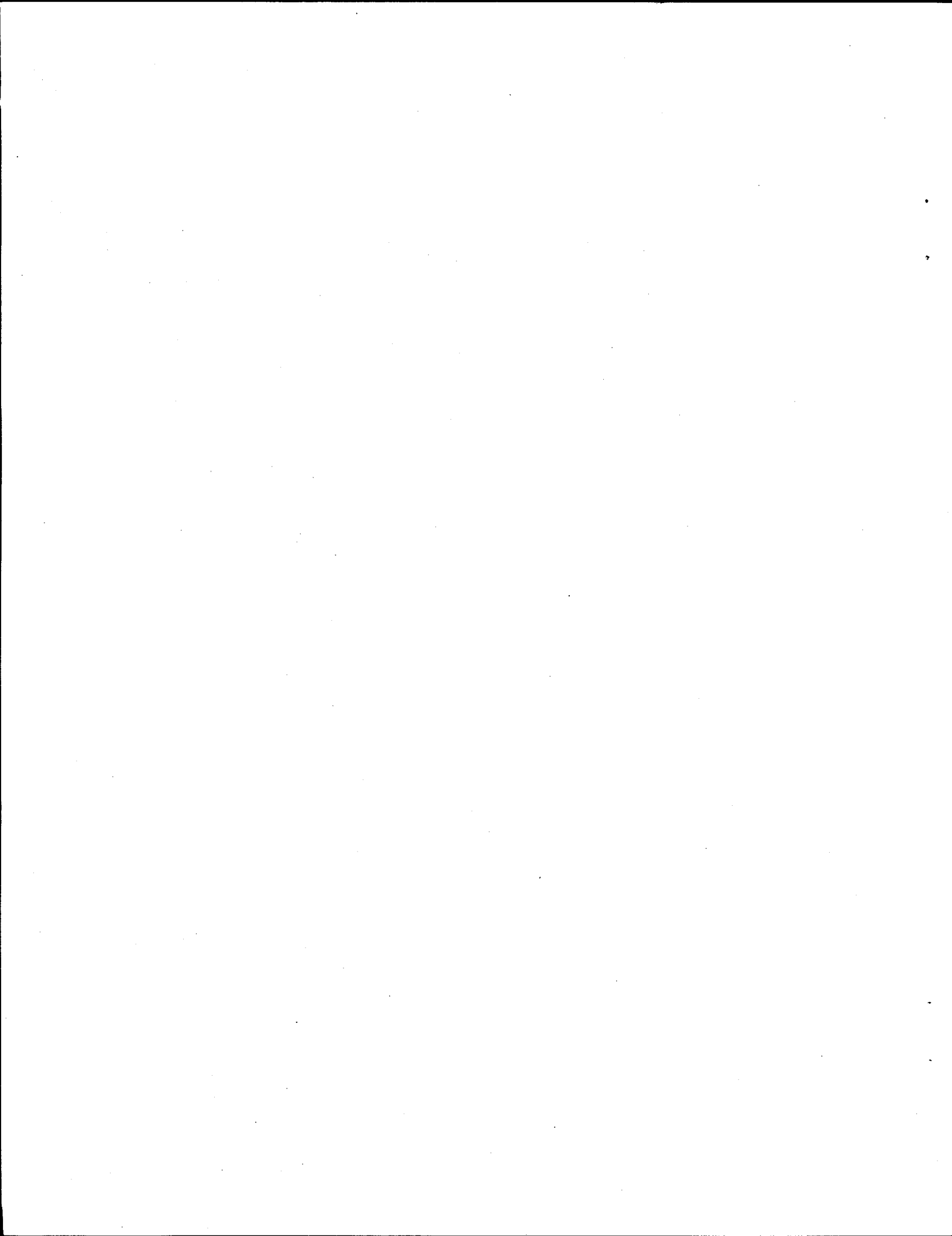
Acknowledgements

This work was funded by the U.S. Department of Energy through the Environmental Management Science Program. Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.



Contents

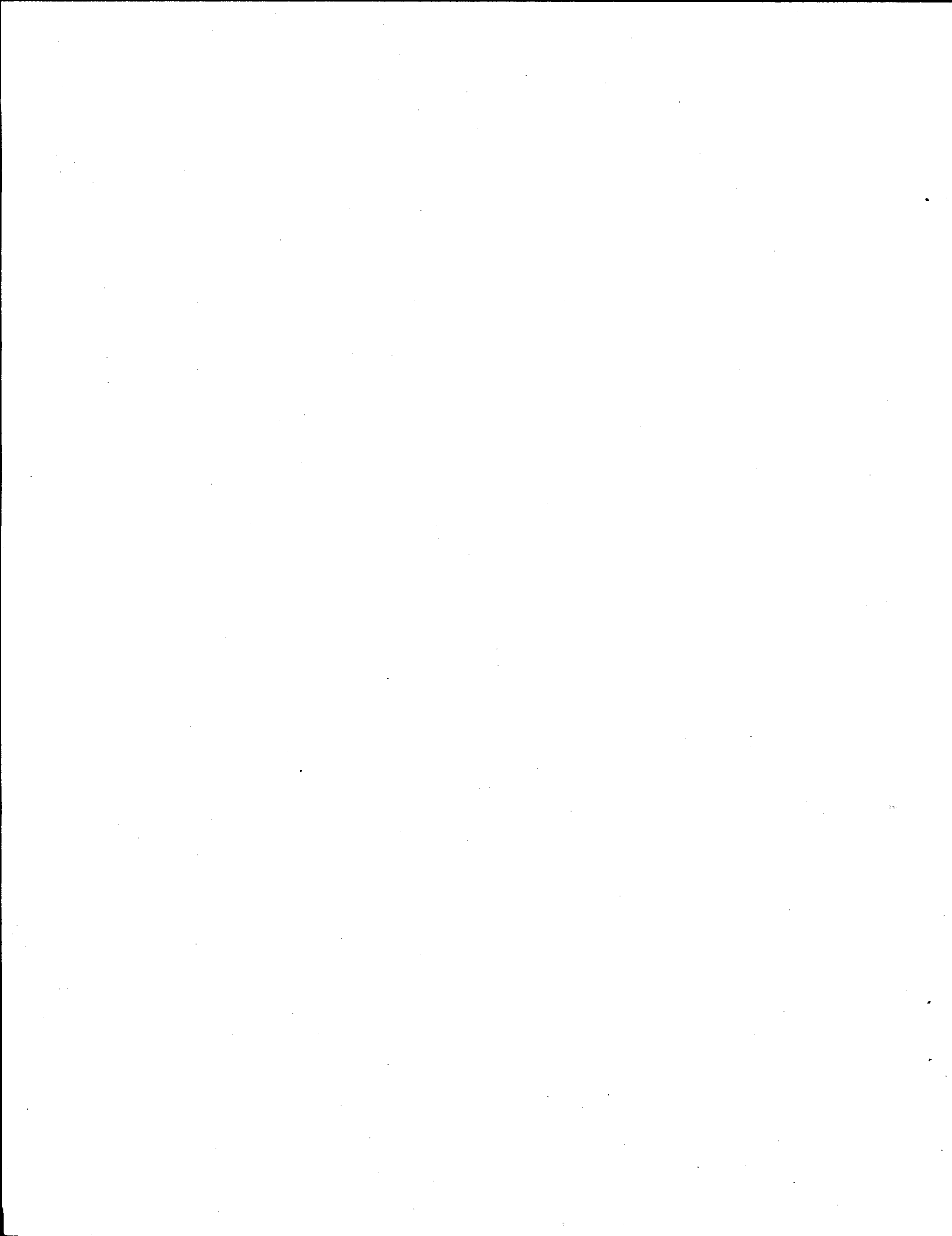
Summary	iii
Acknowledgements	iii
Introduction	1
Model Description.....	3
Program Description.....	5
Example: Extraction Of Nitric Acid By Tributyl Phosphate.....	6
Future Developments	9
References	11



Introduction

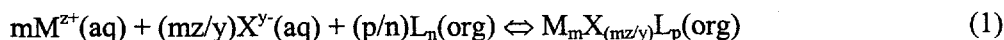
Equilibria phenomena are of central importance to solvent-extraction science (Rydberg et al. 1992). Such phenomena have been investigated for many decades. Two primary methods are employed in studying solvent-extraction equilibria—graphical methods (slope analysis) and numerical methods (computer modeling). Despite the widespread availability of computers, graphical methods are still extensively used. A review of the journal *Solvent Extraction and Ion Exchange* for 1997 revealed a fairly even split between papers in which numerical methods were used versus papers in which slope analysis was used—13 papers using numerical methods versus 12 using slope analysis. For many of the papers that used numerical methods, unspecified curve-fitting routines were used to model specific equilibrium expressions. The following computer programs have been designed specifically for analyzing solvent-extraction equilibria: LETAGROP-DISTR (Liem 1971), MODEX (Noirot and Wozniak 1985), and SXLSQA (Baes et al. 1990).

We have been developing a program using the “Solver” function in Microsoft Excel® to analyze solvent-extraction equilibria. Because the program revolves around the Solver function, we have named the program the “SX Solver.” The Solver function has previously been successfully employed in solvent-extraction technology, namely in the Generic TRUEX Model (GTM) (Vandegrift et al. 1990). The GTM has a considerable level of sophistication, but it is primarily a tool for process and flowsheet design. The program we are developing is designed to model solvent-extraction equilibria at a fundamental level. The SX Solver program takes advantage of the graphical user-interface of Excel®, so it is designed to be user-friendly. This paper describes the basis for this program and an example of its use.



Model Description

The SX Solver model is based on the following general equation for the extraction of a metal cation (M^{z+}) by a neutral ligand (L).



The equilibrium constant for this reaction is defined as

$$K = \frac{y_c [M_m X_{(mz/y)} L_p]_o}{(y_M [M^{z+}]_a)^m (y_X [X^{y-}]_a)^x (y_L [L_n]_o)^{(p/n)}} \quad (2)$$

where y_c , y_M , y_X , and y_L are the molar-scale activity coefficients for $M_m X_{(mz/y)} L_p$, M^{z+} , X^{y-} , and L_n , respectively; and $x = mz/y$. Quantities in brackets refer to the molar concentration of the individual species. The subscripts "a" and "o" refer to species in the aqueous and organic phases, respectively. The distribution coefficient is defined as the total concentration of the metal in the organic phase divided by the total concentration in the aqueous phase, and is given by the following equation:

$$D = \frac{[M]_o}{[M]_a} = \frac{m [M_m X_{(mz/y)} L_p]_o}{[M^{z+}]_a} \quad (3)$$

It should be noted that $[M^{z+}]_a$ represents the total metal concentration in aqueous phase. This is a simplification because aqueous phase complexation of the metal ion (e.g., by nitrate ion) is not taken into account. The result of this simplification is that the binding constants for metal complexation in the aqueous phase are incorporated into the calculated extraction constants. Combining Equations 2 and 3 gives

$$K = \frac{y_c}{y_M^m y_X^x y_L^{(p/n)}} \cdot \frac{D}{m [M^{z+}]_a^{m-1} [X^{y-}]_a^x [L_n]_o^{(p/n)}} \quad (4)$$

Rearranging Equation 4 gives

$$D = \frac{y_M^m y_X^x y_L^{(p/n)}}{y_c} \cdot m K [M^{z+}]_a^{m-1} [X^{y-}]_a^x [L_n]_o^{(p/n)} \quad (5)$$

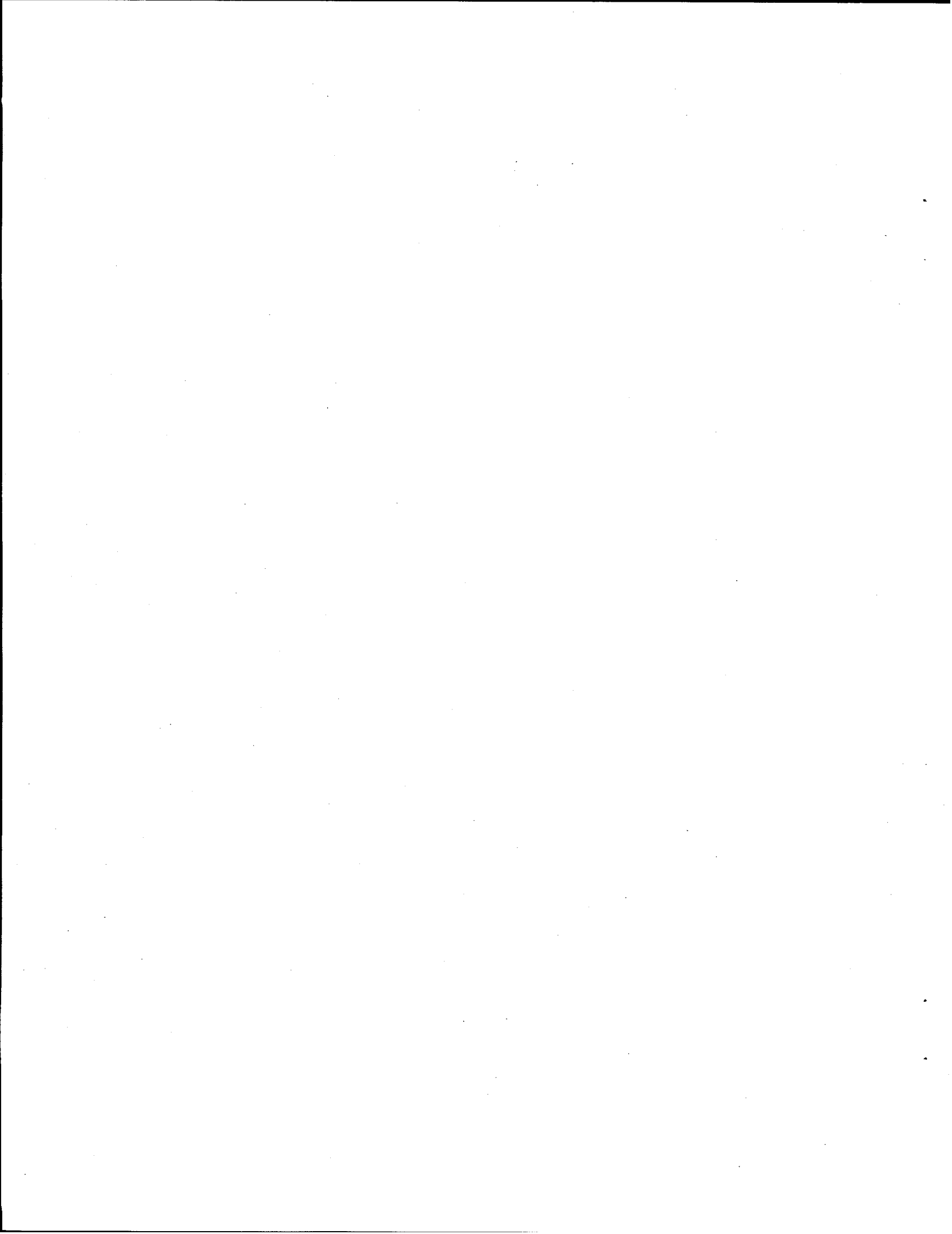
If more than one extraction equilibrium (of the type shown in Eq. 1) is involved, Equation 3 becomes

$$D = \frac{\sum_i m_i [M_{m_i} X_{x_i} L_{p_i}]_o}{[M^{z+}]_a} \quad (6)$$

and Equation 5 becomes

$$D = \frac{\sum_i \frac{y_M^{m_i} y_X^{x_i} y_L^{(p_i/n)}}{y_{c_i}} \cdot m_i K_i [M^{z+}]_a^{m_i-1} [X^{y-}]_a^{x_i} [L_n]_o^{(p_i/n)}}{[M^{z+}]_a} \quad (7)$$

where K_i is the extraction constant for species i .



Program Description

Equation (7) is general for extraction of metal ions by a neutral extractant, provided the extracted species are not ionic in nature (as might occur in highly polar solvents). Distribution data can be fit to this equation using nonlinear regression techniques. The SX Solver is a spreadsheet application that uses the Microsoft Excel® "Solver" function to minimize the function:

$$SSR = \sum w(D - D_{\text{calcd}})^2 \quad (8)$$

where D and D_{calcd} are the measured and calculated distribution coefficients, respectively, for a given measurement; and w is a weighting factor defined by the user. D_{calcd} is determined through Equation 7.

In the current version of the SX Solver program, it is generally assumed that the concentration of the extracted cation, M^{z+} , is much lower than the concentration of the counter anion, X^{y-} . That is, a supporting electrolyte is used to buffer the system. Preferably, experiments should be designed so that changes in the aqueous phase X^{y-} concentration, due to coextraction with the metal ion, are less than 5%. It is also assumed that the cation of the supporting electrolyte is not extracted to any extent. Under these conditions, the aqueous phase can be treated as a solution of a single electrolyte. The activity coefficient for the anion, γ_X , is then primarily defined by the activity of the supporting electrolyte. The aqueous-phase activity coefficients are determined using the method established by Bromley (1973). For this calculation, molar concentrations are converted to molal concentration using a second-order polynomial fit to plots of molality versus molarity. The Bromley method yields the molal-scale activity coefficient, which is converted to the molar-scale activity coefficient by applying the formula (Robinson and Stokes 1959): $\gamma_{\pm} = \gamma_{\pm} m d_0 / c$, where γ_{\pm} is the molal-scale activity coefficient, m is the molal concentration, c is the molar concentration, and d_0 is the density of water (0.9971 g/mL at 25°C). Currently, the program only supports activity calculations for NaNO_3 , LiNO_3 , HNO_3 , and NaCl as the supporting electrolytes, but subsequent versions of the program will incorporate activity calculations for other electrolytes. The activity coefficient for M^{z+} is assumed to be unity under these conditions; in the extraction experiments, the concentration of M^{z+} should be kept low enough that this assumption is valid.

The activity coefficient for the extractant L in the organic phase is estimated by the Hildebrand-Scott model (Hildebrand and Scott 1950), which has been successfully employed in the SXLSQA program (Baes et al. 1990). Reference 4 provides a description of the procedure used to calculate the ligand-activity coefficients. It should be noted that the SX Solver program allows the user to assume ideality in either the organic or aqueous phases, in which case, the activity coefficients are set to unity. The activity coefficients for the extracted species (γ_C) are assumed to be one.

It is assumed that all of the extractant remains in the organic phase. That is, the extractant is assumed to have no appreciable solubility in the aqueous phase. The extractant concentration indicated in Equation 7, $[L_n]_o$, refers to the organic-phase concentration of the aggregated (if applicable) extractant. This is related to the concentration of the free extractant, $[L]_o$, by the following equation:

$$[L_n]_o = K_{agg}[L]_o^n \quad (9)$$

where K_{agg} is the equilibrium constant for the aggregation reaction.^(a) The following mass balance expression applies to the extractant concentration:

$$\sum_i \frac{y_M^{m_i} y_X^{x_i} y_L^{(p_i/n)}}{y_{C_i}} \cdot p_i K_i [M^{z+}]_a^{m_i} [X^{y-}]_a^{x_i} (K_{agg})^{(p_i/n)} [L]_o^{p_i} + [L]_o - [L]_{tot} = \quad (10)$$

where $[L]_{tot}$ is the total analytical concentration of the extractant in the organic phase. The SX Solver program uses Newton's method of approximation to solve Equation 10 for the value of $[L]_o$. This is achieved by applying Equation 11. A reasonable initial value is:

$$[L]_o = [L]_o^* - \frac{f([L]_o^*)}{f'([L]_o^*)} \quad (11)$$

chosen for $[L]_o$ (in this case $[L]_{tot}$ is used as the initial value). The function, $f([L]_o)$, is then calculated according to Equation 10; the function $f'([L]_o)$ is the derivative of Equation 10 with respect to $[L]_o$. A new value for $[L]_o$ is obtained by Equation 11. This new value is assigned as $[L]_o$, and the process is repeated until there is no significant change between $[L]_o$ and $[L]_o$. The resulting value of $[L]_o$ is then applied to Equations 7 and 9.

In running the program, the user supplies the following information:

- the components initially present in the aqueous phases and their concentrations (in moles/L)
- the component of interest; that is, the metal ion that is being extracted
- the values for $z+$, $y-$, and n (the extractant aggregation number)
- the number of extracted species—up to five species are currently supported
- m_i and p_i values for each extracted species
- initial values for the K_i .

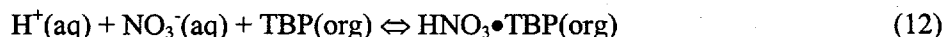
The user is prompted in a logical manner for these inputs. If the user chooses, default values as specified from previous calculations can be used for certain inputs. This feature is advantageous because it allows for rapid screening of a number of possible models on a given data set. The Excel® Solver is applied to vary the K_i values until the function in Equation 8 is minimized. The user can save the results in an Excel® spreadsheet for future reference or use.

Example: Extraction Of Nitric Acid By Tributyl Phosphate

To demonstrate the SX Solver program, we will consider an example from the chemical literature—extraction of nitric acid by hydrocarbon solutions of tributyl phosphate (TBP). This system is of industrial importance with respect to reprocessing nuclear fuel (Büchner et al. 1989).

^(a) For the current version of SX Solver, prior knowledge of the value of K_{agg} is preferable. Otherwise, the user must manually adjust K_{agg} to determine the effects of aggregation.

For aqueous HNO₃ concentrations of less than 9 M, the extraction of HNO₃ by TBP can be described by two extraction equilibria (Chaiko and Vandegrift 1988):



It is assumed that the solubility of TBP in the aqueous phase is zero, and, likewise, the solubility of HNO₃ in the hydrocarbon diluent is zero.

The data for the TBP extraction of HNO₃ were taken from Davis (1962). These data were modeled according to Equations 12 and 13 using the SX Solver program. It should be noted that in this example, there is no supporting electrolyte. The program allows for the calculation of the aqueous phase nitric acid activities at each data point. The organic-phase activity coefficients were assigned the values of 1. This, of course, is not true, but for a given total TBP concentration, it can be assumed that the term $y_L^{(p/n)}/y_C$ is constant. The data were divided into five sets for the modeling calculation—one set for each total TBP concentration. The program calculated the values of $K_{1,1}$ and $K_{1,2}$ for each data set; $K_{1,1}$ is the equilibrium constant for Equation 12, and $K_{1,2}$ is the equilibrium constant for Equation 13. Table 1 presents the calculated extraction constants for Reactions 12 and 13; analogous values from the literature (Chaiko and Vandegrift 1988) are also reported in Table 1. Figure 1 compares the experimental and calculated HNO₃ extraction isotherms. Clearly, good agreement exists between the experimental and calculated values as indicated by correlation coefficients ≥ 0.995 . The extraction constants determined in this manner are similar to those reported in the literature, but there are some discrepancies. The discrepancies may be due to differences in the manner in which the aqueous-phase HNO₃ activities were determined. Also, the molar TBP concentrations used in Chaiko and Vandegrift (1988) were slightly different than those used here. This is because Chaiko and Vandegrift adjusted the concentrations originally listed by Davis (1962) to avoid potential problems associated with extracted water. We used the concentrations given by Davis, without adjustment. Presumably, nonideality effects in the organic phase are responsible for the changes in the $K_{1,1}$ and $K_{1,2}$ values for different TBP concentrations.

Table 1. Extraction of Nitric Acid by Tributyl Phosphate^(a)

[TBP(org)] _{tot}		This Work		Chaiko and Vandegrift (1988)		$r^{(b)}$
vol %	mole/L	$K_{1,1}$	$K_{1,2}$	$K_{1,1}$	$K_{1,2}$	
5	0.17	0.20	0.59	0.13	0.77	0.999
10	0.35	0.25	0.43	0.18	0.46	0.999
15	0.52	0.25	0.52	0.17	0.53	0.995
30	1.09	0.24	0.48	0.19	0.43	0.996
65	2.33	0.19	0.40	0.15	0.33	0.999

(a) Experimental data taken from Davis (1962); TBP dissolved in Amsco 125-82.

(b) The correlation coefficient for the calculations done here.

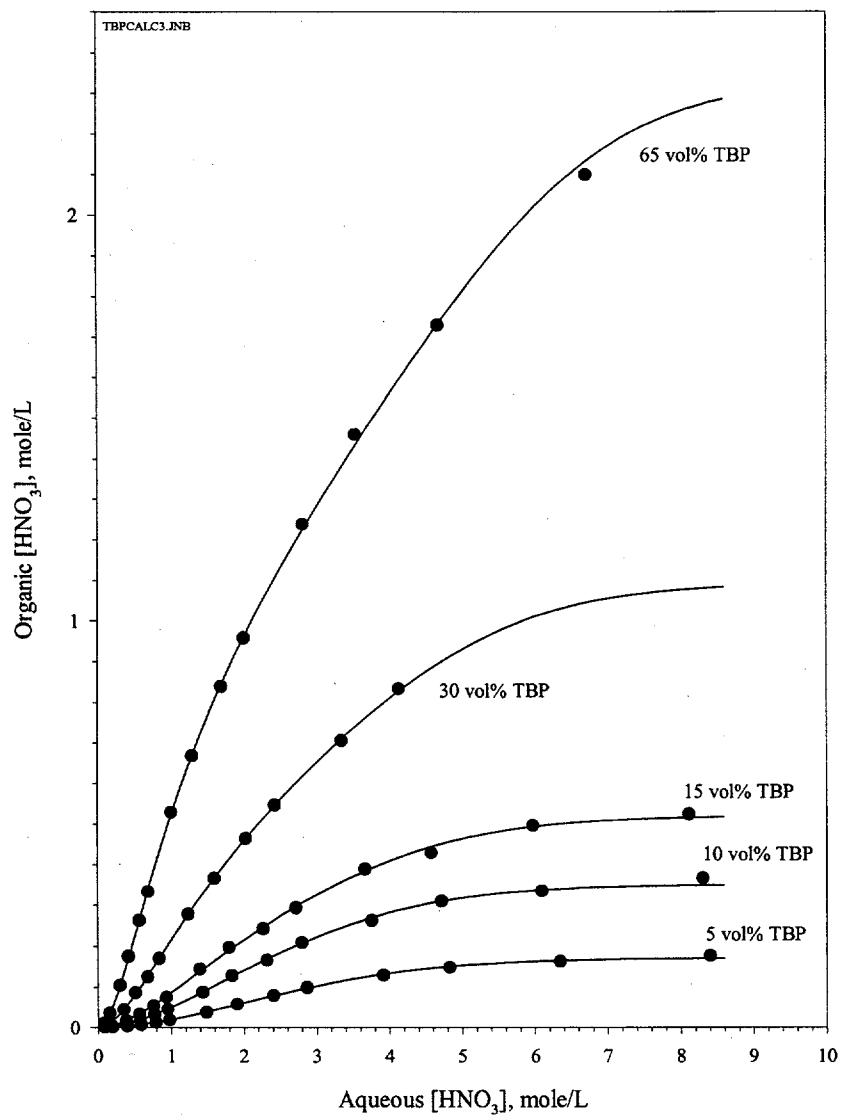


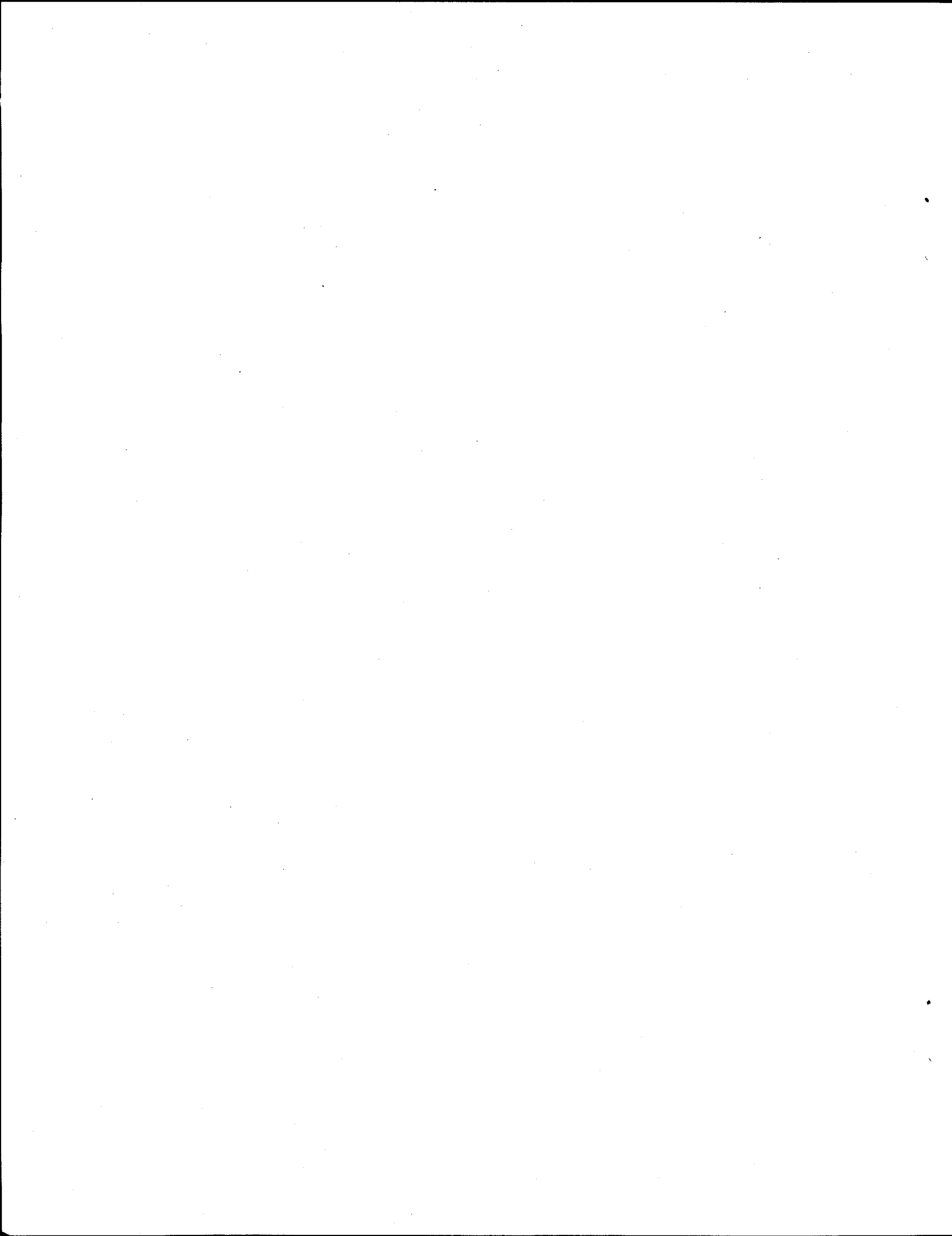
Figure 1. Extraction of HNO₃ With TBP: Comparison of Experimental and Calculated Values

Future Developments

The current version of the SX Solver program has the following limitations:

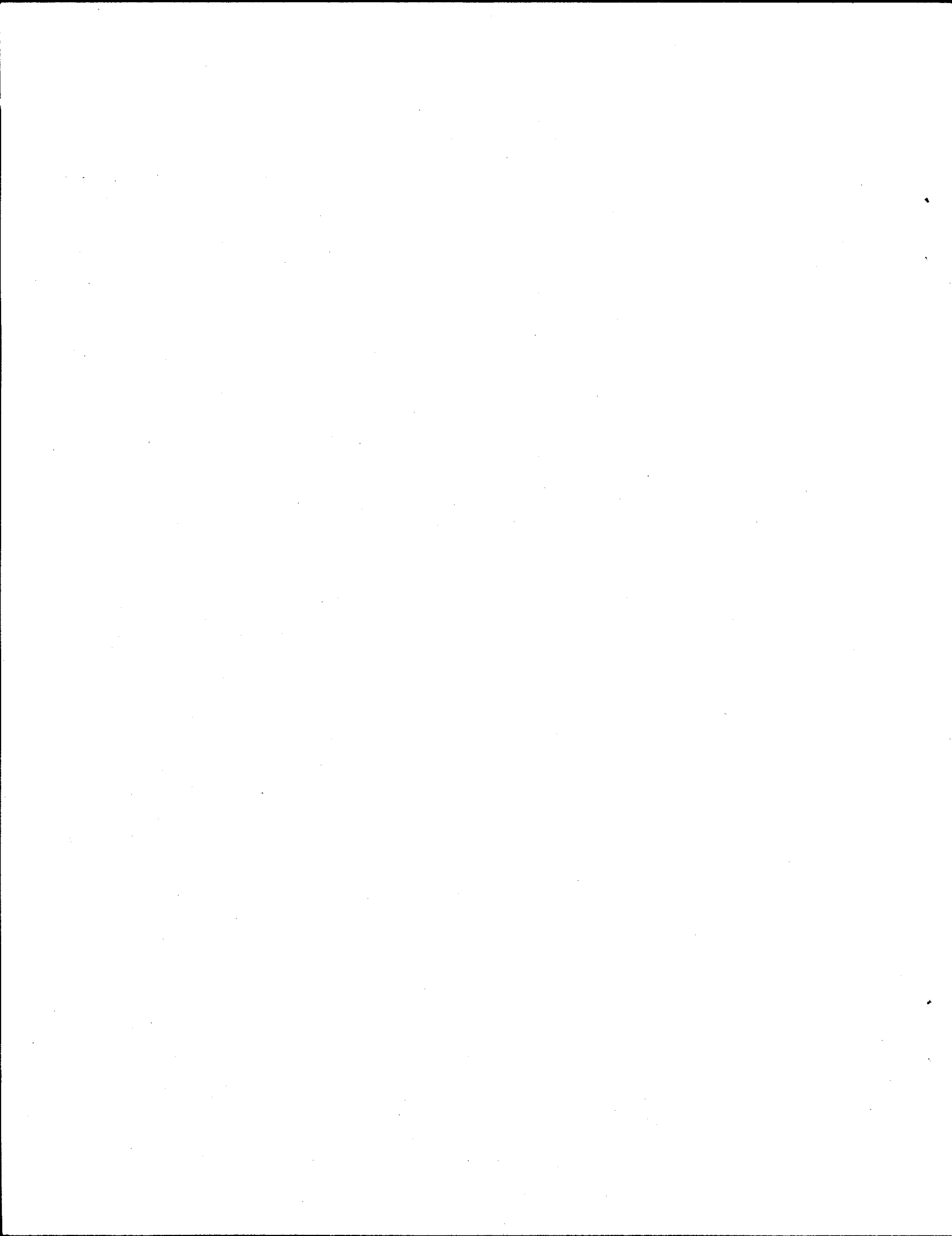
- only a limited number of supporting electrolytes is included
- activity coefficients for mixed electrolyte systems cannot be calculated
- only the extraction of one cation can be considered
- mixed extractants cannot be considered, e.g., synergistic solvent mixtures
- explicit corrections cannot be made for aqueous-phase metal complexation
- if the extractant is aggregated, prior knowledge of the aggregation constant is needed; otherwise manual adjustment of the extraction constant is required
- improved output capabilities are needed.

Future versions of the program will include enhancements to address these limitations.



References

- Baes CF, Jr., BA Moyer, GN Case, and FI Case. 1990. *Sep. Sci. and Technol.*, 25, 1675.
- Bromley LA. 1973. *AIChE Journal*, 19, 313.
- Büchner W, R Schliebs, G Winter, and KH Büchel. 1989. *Industrial Inorganic Chemistry*: VCH: New York, New York.
- Chaiko DJ and GF Vandegrift. 1988. *Nuclear Technol.*, 82, 52.
- Davis, Jr. W. 1962. *Nucl. Sci. Eng.*, 14, 159.
- Hildebrand JH and RL Scott. 1950. *The Solubility of Nonelectrolytes*, 3rd Ed., Reinhold Publishing Corp., New York.
- Liem DH. 1971. *Acta Chem. Scand.*, 25, 1521.
- Noirot PA and M Wozniak. 1985. *Hydrometallurgy*, 13, 229.
- Robinson RA and R.H. Stokes, *Electrolyte Solutions*, Butterworths Scientific Publications, London (1959).
- Rydberg J, C Musikas, and GR Choppin, eds. 1992. *Principles and Practices of Solvent Extraction*, Marcel Dekker, New York.
- Vandegrift GF, DJ Chaiko, DB Chamberlain, L Chow, JM Copple, DR Fredrickson, RJ Jaskot, JD Kwok, RA Leonard, JB Rajan, L Reichley-Yinger, J Sedlet, IR Tasker, and P-K Tse. 1990. *The Generic TRUEX Model, Volume Two—Description of the Chemistry and Engineering Principles Used in the Model*, Report ANL89/18, Argonne National Laboratory, Argonne, Illinois.



Distribution

<u>No. of Copies</u>		<u>No. of Copies</u>	
	<u>OFFSITE</u>		<u>ONSITE</u>
2	DOE/Office of Scientific and Technical Information	7	<u>DOE Richland Operations Office</u>
	Mark Gilbertson		D. E. Trader (7) K8-50
	Office of Science and Risk Policy	23	<u>Pacific Northwest National Laboratory</u>
	Office of Science and Technology		W. C. Cosby K7-62
	Office of Environmental Management		G. J. Lumetta (15) P7-25
	1000 Independence Avenue, SW		B. K. McNamara P7-25
	Washington, D.C. 20585		B. M. Rapko P7-25
	Dr. Roland Hirsch, SC-73		Technical Report Files (5)
	Mail Stop F 237		
	Medical Sciences Division		
	Office of Biological and Environmental Research		
	U.S. Department of Energy		
	19901 Germantown Road		
	Germantown, MD 20874-1290		