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Research

Computer Programs for Uncertainty Analysis of Solubility Calculations: Windows Version and Other Updates of the SENVAR and UNCCON

Program Description and Handling Instructions

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SKI

SKI perspective

Background

Solubility calculations for phases incorporating radionuclides are an essential element of estimating releases from the near-field of a final repository for spent nuclear fuel. Implementation of solubility estimates in safety assessment requires an evaluation of uncertainties associated with this category of input data. Particularly important uncertainties in the context of radionuclide solubility can be related to the choice of thermodynamic data for dissolved species and solid phases, as well as the composition of a groundwater in which a particular solid phase might precipitate. The evaluation of such uncertainties is simplified if computer programmes dedicated for this task are available. The SENVAR and UNCCON solubility and speciation programmes have been developed solely for uncertainty and sensitivity analysis.

Purpose of Project

The purpose of this project was to develop user friendly Windows-based versions of the previously developed SENVAR and UNCCON computer programmes. This should promote the spreading of the codes to potentially interested new users.

Results

The new code versions, SENVARWIN and UNCCONWIN, can be downloaded from the following link: www.nc.chalmers.se/software/program.htm Alternatively, the codes can be obtained directly from the author, Dr. Christian Ekberg at Chalmers University of Technology (email adess: che@chem.chalmers.se).

This report describes how the codes can be used for a case with a plutonium solubility calculation.

Effects on SKI work

The codes may be useful for SKI in a future evaluation of solubility calculations conducted by the Swedish Nuclear Fuel and Waste Management Company (SKB).

Project Information

Bo Strömberg has been responsible for this project.
SKI reference: 14.9-030165/03101

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Computer Programs for Uncertainty Analysis of Solubility Calculations: Windows Version and Other Updates of the SENVAR and UNCCON

Program Description and Handling Instructions

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1. Introduction

Since the construction of the first computer, simulations have become a more or less indispensable tool in research and industry. With increasing speed and cheaper computer time, computer simulations have become the major contributions to the art of foreseeing the future. However, most computer programs are deterministic, i.e. the same set of input data will give the same set of output data, and it is therefore essential for the correctness of the results that the input data are correct. Unfortunately, it is seldom possible to obtain correct data and, hence, the results from computer simulations are more or less uncertain.

An investigation is usually partitioned into a sensitivity analysis and an uncertainty analysis. In most cases, these two analyses complement each other well and are therefore often performed simultaneously. The sensitivity analysis indicates the relative importance of each input parameter, and the uncertainty analysis gives estimations of the fluctuations in the calculated results from uncertainties in the input data. Several methods exist to treat the uncertainties associated with computer simulations, either by sampling techniques or experimental designs (Helton, 1993; Iman and Helton, 1985; Kleijnen, 1997).

In studying the potential construction of an underground repository for spent nuclear fuel according to the multi barrier concept (KBS-3, 1983; PASS, 1993), investigations and predictions, e.g. rates of canister corrosion and radionuclide transport, have to be made with computer programs. In these calculations, the input data are usually not accurately determined but more often only estimated from incomplete experimental results or theoretical correlations. This results in uncertainties, which varies tremendously in magnitude and importance. For near-field radionuclide transport calculations, one important factor is the solubility of the radioelements released from the fuel within a breached canister. The solubilities can be measured as well as calculated from fundamental thermodynamic data. If they are calculated, several input data, such as stability constants, enthalpies of reaction and water composition, will affect the results. The influence of the thermodynamic data uncertainties are investigated in (Ekberg et al., 1995; Ekberg and Lundén, 1997) using the SENVAR program (Ekberg 1996:1; Ekberg and Emrén1996), and the water composition influence is discussed in, e.g. (Ekberg et al. 2000).

The variation in water composition owing to uncertainties in rock composition which is a separate but complementary issue has also been investigated and reported in, e.g. (Ekberg et al. 2000). Due to the increasing demand for these old programs they have now been rewritten to be fully Windows compatible. The user interface is now like what every ordinary computer user is accustomed to with easy-to-use menus. The names of the programs have been changed accordingly to easily differentiate from the older programs by adding a “WIN” at the end of the program name, e.g. SENVARWIN. In addition to the change in the user interface the calculation motor has been changed from the older FORTRAN PHREEQE (Parkhurst et al. 1980) to the newer PHREEQC (Parkhurst 1995) written in C. This change has enhanced the stability of the programs.

2. SENVARWIN

The older SENVAR program has been extensively described in (Ekberg 1995, Ekberg 1996, Ekberg and Emrén 1996). However, for the conveniency of the reader a short summary of this information is given below. In addition, the description given below refers to the new version called SENVARWIN.

2.1 Program description

The SENVARWIN package is a combined statistical sampling and evaluation program. The solubilities are calculated by the thermodynamic equilibrium program PHREEQC (Parkhurst 1995) .

The calculation frame, which is given by the user, is constituted by choice of solid phase, water composition and database used. It is also necessary to give some iteration criteria. The calculations are then made in steps, first a preliminary sensitivity analysis and then an uncertainty analysis, the results of which are also used for the stepwise regression, which serves as the final sensitivity analysis.

2.1.2 Sensitivity analysis (screening)

The preliminary sensitivity analysis aims at reducing the number of parameters to be entered into the uncertainty analysis and the final sensitivity analysis. It may be performed in two ways, either by using a variance analysis or by a binary search tree. The main advantage of the variance analysis is that a preliminary ranking of the parameters is made, but the calculations take a great deal of time. The binary search tree, on the other hand, is fast but does not rank the parameters. The concepts of the two approaches are explained below.

2.1.2.1 Variance analysis

The variance analysis is made by holding one of the investigated parameters at a fixed value while the others vary for a given number of iterations, e.g. 20. The variance in solubility for these iterations is then calculated, and the next parameter of interest is held at a fixed value. The species that gives the smallest variance when held constant is deemed the most important and so on.

At the beginning of the calculations, a random matrix is created. It contains random values for the different parameters, each sampled within a given uncertainty range.

There is one row for each investigated parameter. These rows combined forms a matrix with as many rows as there are investigated parameters and as many columns as the selected iteration number. In the first iteration, the first parameter is held at a fixed value and the others receive values according to the first column of the matrix. In the next iteration, the values are taken from the second column and so on for the given number of iterations. The second parameter is then held at a fixed value and the others receive values according to the columns of the random matrix. Evidently this approach will give the same variance for the unimportant parameters, thus making the selection

criterion simple. The selection criterion is usually that the difference between two successive variances must be at least one thousandth of the last one. The important parameters are then transferred to the uncertainty analysis.

2.1.2.2 Binary search tree

The theory behind the binary search tree is rather simple, and the approach is more commonly used in optimisation problems. The inputs to the model are seen as a vector containing the different parameter values. It is known, *a priori*, that only a few of these are important. Therefore, by using a binary search tree, the number of iterations needed to identify the important parameters may be less than the total number of parameters.

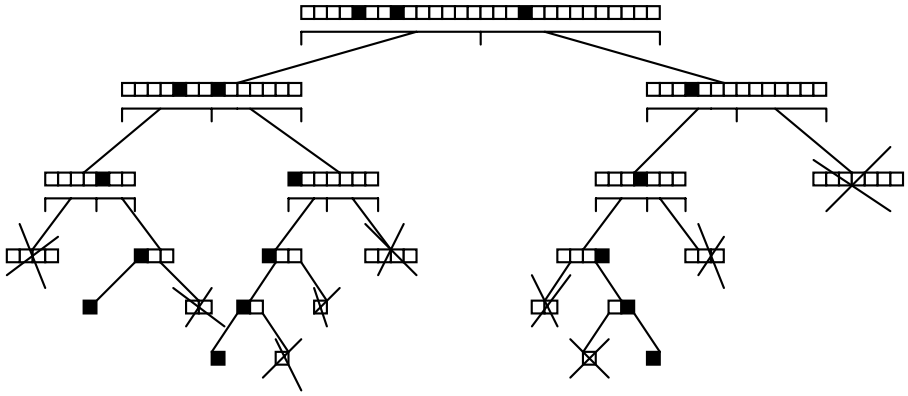

Figure 1, Binary search tree for a 28-cell input vector with three important parameters (filled boxes).

The method illustrated in Figure 1 may be described in the following way. The calculations are made two times, one with every investigated parameter at their maximum value, and one with the minimum value. The results are then compared to investigate whether or not there is a significant difference. If so, the input vector is divided into two parts, each becoming the base for further calculations. The same approach is used at the next level of the search tree, except that at this level it is the values in half of the original vector that are changed while the rest are held fixed. If there is no significant change this time, it is concluded that there are no important parameters in that part of the vector and it is not further investigated. If the change is significant, the new vector is divided into two parts and the method described above is applied to both parts.

Finally, all the important parameters are identified. Synergistic or antagonistic (positive or negative correlation) effects will not be explicitly detected in this version, however this might be added at a later stage. Consider the case in which two iterations are made at each level, i.e. high and low values for the parameters. The range of values should be selected to mirror the real uncertainty range. This implies that the sensitivity analysis is only valid given an uncertainty range of parameters, which is the normal way it is done. The number of iterations needed to investigate which parameters influence the result may then be significantly reduced if the method indicated in Figure 1 is used.

As seen for the case described above, the number of iterations was only slightly reduced compared with the "one factor at a time" approach. However, as the number of

parameters grows, the greater the profit will be of using a binary search tree. For the cases described in this section, the number of parameters is usually about two hundred and there are between one and six important ones. Thus the approach is very effective in the sense that it requires only a few iterations, usually reduced to about a third of the number of parameters.

2.1.3 Uncertainty analysis

In the uncertainty analysis, the Monte Carlo sampling is made without any restrictions, i.e. the values of the parameters are selected randomly within each interval at each iteration. This approach makes it possible to detect any synergistic effects between two or more species. The calculations are usually made with 1000 to 2000 samples, thus giving enough values to cover the parameters' space sufficiently well. Every solubility calculation is saved in a file which is later used for the final sensitivity analysis.

The results of the uncertainty calculations are a plot showing the calculated density function of the solubilities and some statistics. The calculated statistics are the mean, the variance, the skewness, a 95% confidence interval for the mean based on the solubilities being log-normally distributed and a 95% confidence interval for the solubility population based on an arbitrary distribution, see Appendix in (Ekberg and Emrén 1996). These data may then be used as input to, for example, a transport model.

The final sensitivity analysis is made from the solubility calculations in the uncertainty analysis, thus requiring no further PHREEQC runs. The program that performs these calculations is the STEPR program (Liljenzin 1995). It is assumed that the sensitivity to one parameter is described by the regression coefficients, a_0 through a_n, in a linear model, such as:

$$Y=a_0+a_1x_1+.....a_nx_n \qquad (1)$$

where x_1 through x_n represent the input parameters, e.g. the logarithm of the stability constants or the enthalpies of reaction, and Y represents the output result, i.e. solubilities. Such an approach yields very small regression errors in the cases used here and may therefore be usable.

2.2 Handling instructions and test case

The user interface of SENVARWIN is made in the Borland C++ builder and thus comprise compatibility with the common Microsoft Windows format. In addition the menus look and work like most other modern applications. In this section we will make a project based on an solubility investigation of the solid phase $Pu(OH)_4$. We do not state that this phase is necessarily the solubility limiting one in this water, but is only selected as an example. The use of the program, when investigating the effect of uncertainties in enthalpies of reaction, are made in a similar way as the stability constants and will not be further dealt with here. Another reason for excluding these calculations is the lack of reliable data on enthalpies of reaction. The water used here will be the one selected as a reference water for the Äspö site in Sweden, see Table 1.

Table 1, Composition of reference water from the Äspö site, borehole KAS 02, level 530-535m (Smellie et al. 1992, Nilson 1992). Concentrations in mM.

Ca	47.2		Cl	181		U[a]	5.45E-07
Mg	1.73		C_{tot}	0.164		Sr	0.399
Na	91.3		S_{tot}	5.83		Li	0.144
K	0.207		F	7.90E-02		N_{tot}	3.52E-03
Fe[a]	4.37E-03		Br	0.501		pH	8.1
Mn	5.28E-03		P	1.61E-04		pe[b]	-4.37
Al[a]	1.00E-03		Si	0.146		Temp (°C)	15

[a] The analysis did not contain any value for this species. The concentration was estimated on the basis of other Äspö ground water samples (Emrén 1995).

[b] The pe value was adjusted from the measured value (-5.42) with regard to additions of Al, Fe, U, and the equilibrium between SO_4^{2-}/SO_3^{2-} in the solution (Emrén 1995).

We will in this case use the uncertainties given as default by SENVARWIN, i.e. the uncertainty in the logarithm of the stability constants are two units wide for the screening and one unit wide for the uncertainty analysis. These values are default and may be changed in the program. However, for the screening it is reasonable to keep these values while in the uncertainty analysis real values may be entered if they may be obtained. These latter values will also be used in the final sensitivity analysis
The main screen comprises all the necessary information for an analysis. The layout is shown in Figure 2.

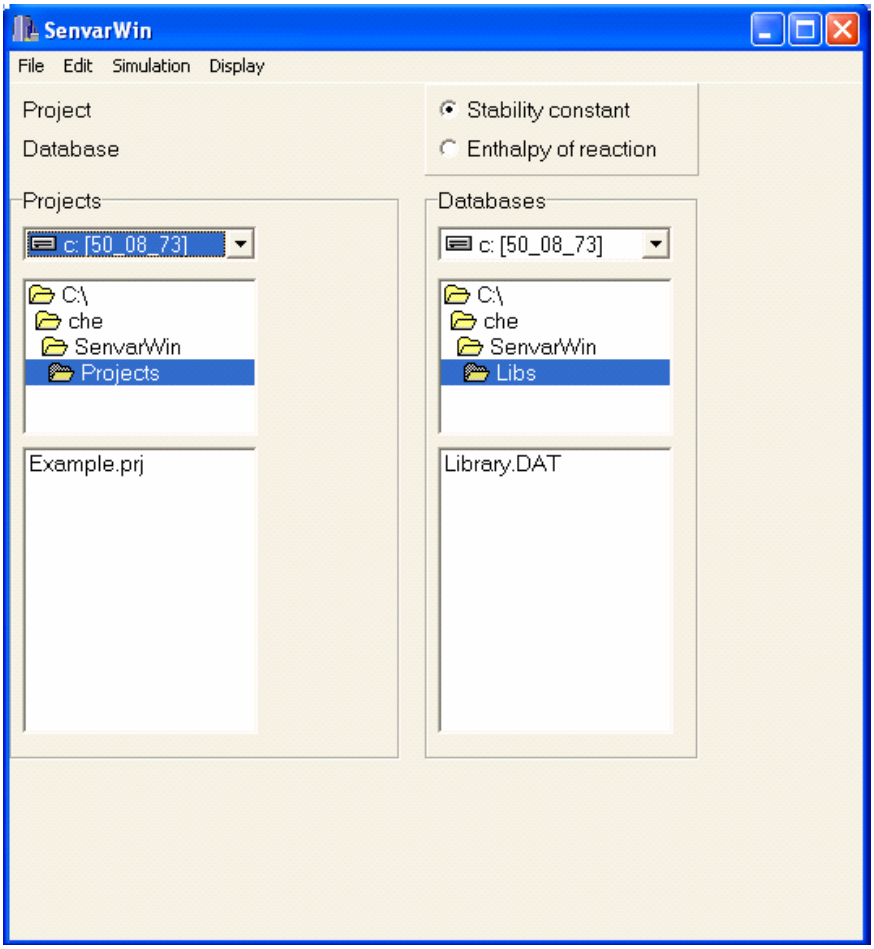

Figure 2, The main window of the SENVARWIN program.

In this screen the project is managed and the user may choose project and database. In the “Edit” menu it is possible to select which water to use and also the project parameters are given, see Figure 3. These project parameters may either be changed here or a complete set of project parameters may be imported from another project by using the “Import project parameters” option in the “File” menu.

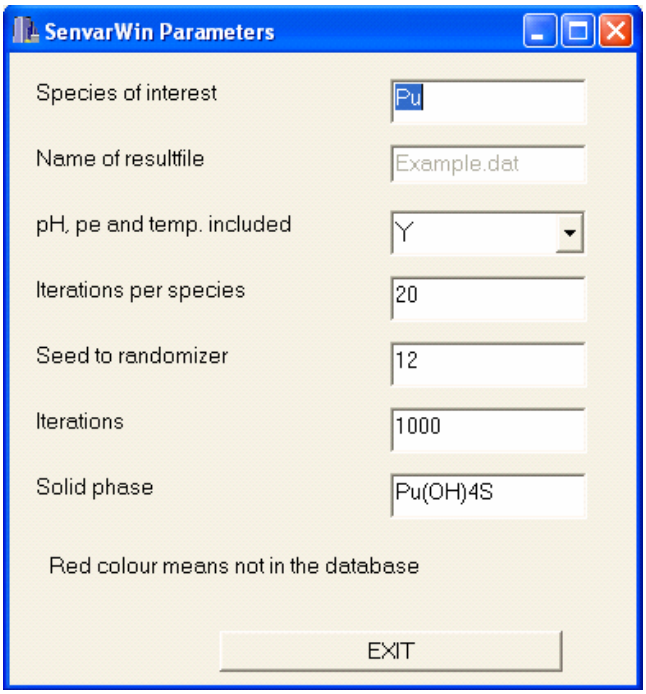

Figure 3 The project parameters window

It is worth noting that in this screen, c.f. Figure 3, the user also gives some information related to how the following sensitivity and uncertainty analysis should be made, e.g. the number of iterations per species in the variance analysis and total number of iterations in the uncertainty analysis. This last number of iterations is also the number used for the stepwise regression used in the final sensitivity analysis. It is possible to select whether the pH, pe and temperature should also be treated as uncertain parameters. This option is available for the variance and the uncertainty analysis, but not for the binary search tree. The solid phase selected must be present in the selected database and printed in the same way in this window. If not the name will become red and thus indicating that it has to be changed before a calculation can be made.

For this test case the concentration of each element is already the correct one, but if this is not the case it can easily be changed by left clicking in the element name column, se Figure 4. If a completely different water composition is to be used just use the “File” menu and select import water. There it is possible to import a complete water composition from another project.

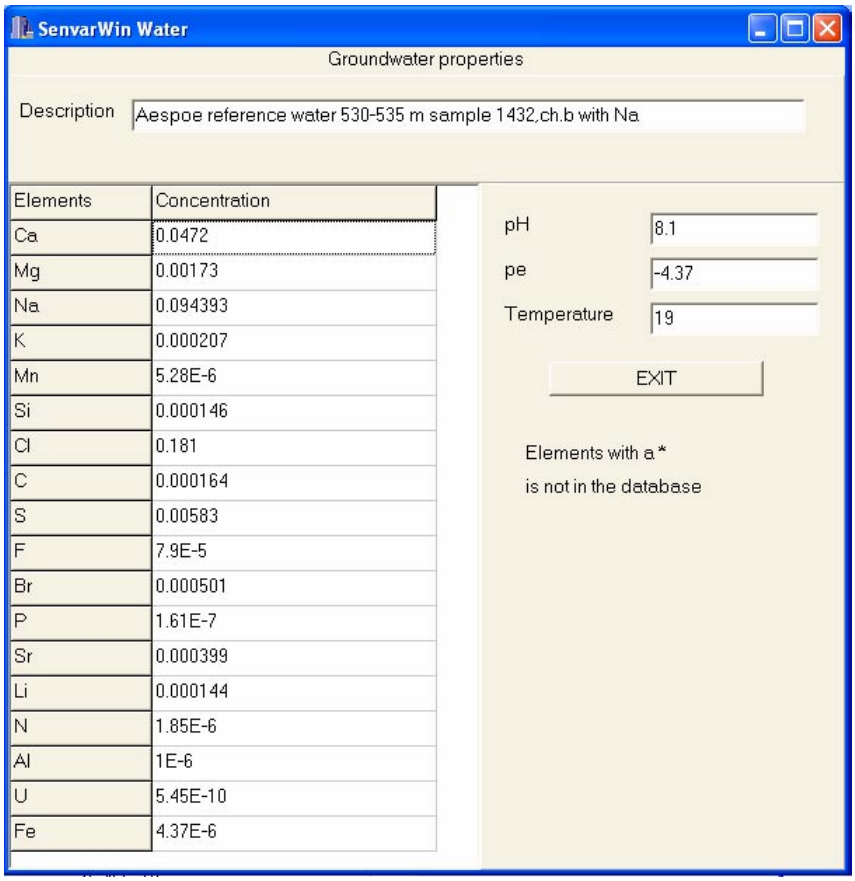

Figure 4, The water window

All the choices made in the paragraphs above are saved in the project file named "example.prj", see Appendix 1. Having this information, the ground is set for starting a new simulation by selecting whether to make the preliminary sensitivity analysis (screening) by using the variance analysis or the binary search tree approach. The variance analysis, as explained above, is slower but gives a more specific result than the binary search tree. In the case presented here we will run both simulation types starting with the variance analysis. It is started by using the menus "simulation" and select "variance analysis".

Table 2, Results from the variance analysis

Species	variance
Solid_phase	9.00E-08
pH	1.35E-07
$Pu(CO_3)_3^{2-}$	4.23E-07
Pu^{3+}	5.84E-07
OH^-	6.44E-07
temp	6.47E-07
$PuCO_3^+$	6.55E-07
$CaOH^+$	6.55E-07
$NaCO3^-$	6.59E-07
$Pu(OH)_2^+$	6.60E-07

The result displayed in Table 2 is an excerpt from the file "example.spc", which is found in the "Project" folder in the SENVARWIN directory.
To make this example as thorough as possible we will also run the binary search tree which is made in a similar manner as the variance analysis. The results are shown in Table 3 and found in the file "Example.bst".

Table 3, Results from the binary seach tree analysis

Species
$NaCO_3^-$
$NaHCO_3$
$PuCl^{2+}$
$Pu(CO_3)_3^{2-}$
$Pu(CO_3)_4^{4-}$
Pu^{3+}

It can be interesting to compare the results from the variance analysis with the binary search tree. Often the species suggested by the binary search tree will be found among the ones selected by the variance analysis. If they should display completely different sets there are large synergistic or antagonistic effects present. In any case the results from the above mentioned analyses should be compared with the results from the final sensitivity analysis shown in Table 4 below.

When the sensitivity analysis is made it is possible to simultaneously perform a uncertainty analysis. This is made by selecting "uncertainty analysis" from the "Simulation" menus.

The results from the uncertainty analysis may be displayed by selecting the "display" menus. In this window the user must select the number of iterations to display. This should, naturally, be less than or equal to the number of runs in the uncertainty analysis. Then the number of intervals should be selected. It may give the user a basis for selecting an empirical distribution function, e.g. by changing the input values and observe the changes in the appearance of the picture to the right in Figure 5.

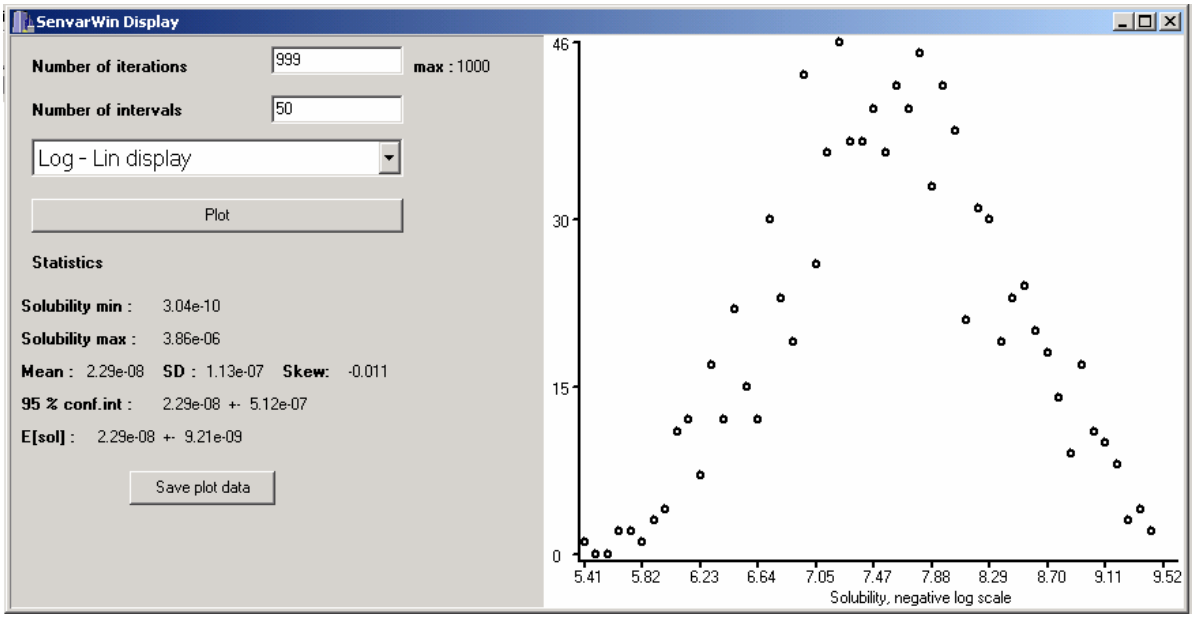

Figure 5, The SENVARWIN display window

In the left side of the Display window, some statistical estimators are shown, i.e. mean solubility, standard deviation, minimum solubility, maximum solubility, skiewness and some confidence intervals namely those representing the confidence interval for the mean and the population, respectively. It is also possible to save the displayed plot data by clicking on that button. The "x" and "y" values will be saved in a file specified by the user.

The final sensitivity analysis is made by stepwise regression of the logarithm of the solubility versus the logarithm of the stability constants. The results from this test case is shown in Table 4. They are found in the file "Example.res".

Table 4, The results from the stepwise regression

Species	Regression coefficient
pH	-1.60
Solid	0.99
$Pu(CO_3)_3^{2-}$	0.75
pe	0.16
Pu^{3+}	0.15
OH^-	0.019

Clearly the results from the variance analysis and the stepwise regression are very similar. This gives confidence in that the adopted linear model is valid. In addition there seems to be few correlations of importance which can be expected when only one species of each type is dominating, e.g. only $Pu(CO3)3^{2-}$ the for the plutonium carbonates.

3. UNCCONWIN

The UNCCON program investigates how uncertainties in water composition affect the solubility of a solid phase. Each element concentration is given as a uniformly distributed interval, indicated by the user, from which the samples are taken using simple Monte Carlo sampling. Other factors that can be selected are different iteration criteria, e.g. number of LHS intervals, and which database to use. The preliminary sensitivity analysis is made in a similar way to the SENVARWIN program, i.e. the user may select either a variance analysis approach or a binary search tree. However, in contrast to the SENVARWIN program the number of uncertain variables here is rather small. Thus, if the number of elements in the water is smaller than 19 there is no need for the screening by the preliminary sensitivity analysis. These approaches implicitly takes correlations into account, which may, when compared to the final sensitivity analysis, give an answer whether the correlations are important or not. The final sensitivity analysis is made based on the runs of the uncertainty analysis. This sensitivity analysis uses simple linear regression and thus only first order interactions are detected. If there is a distinct difference between the results of the first sensitivity analysis and the linear regression it may be due to that higher order interactions, e.g. correlations, play an important role.

The result of an UNCCONWIN uncertainty calculation consists of two parts: first, a file containing some statistical estimators such as the mean solubility, minimum and maximum solubility and a confidence interval for the mean and, secondly, a part consisting of plots of the calculated distribution function for the solubility. Depending on the sample size the plots may be somewhat jagged, but they will at least give a hint of the distribution of the solubility.

3.1 Handling instructions and test case

The handling of the UNCCONWIN is very similar to that of SENVARWIN with a specific purpose. In the future these programs will, together with a rewritten version of the MINVAR (Ekberg et al. 2000) and the LJUNGSKILE (Ekberg et al. 2003) program, be combined into one large computer package for uncertainty analysis of chemical calculations.

When the program is started the main window is displayed, see Figure 6.

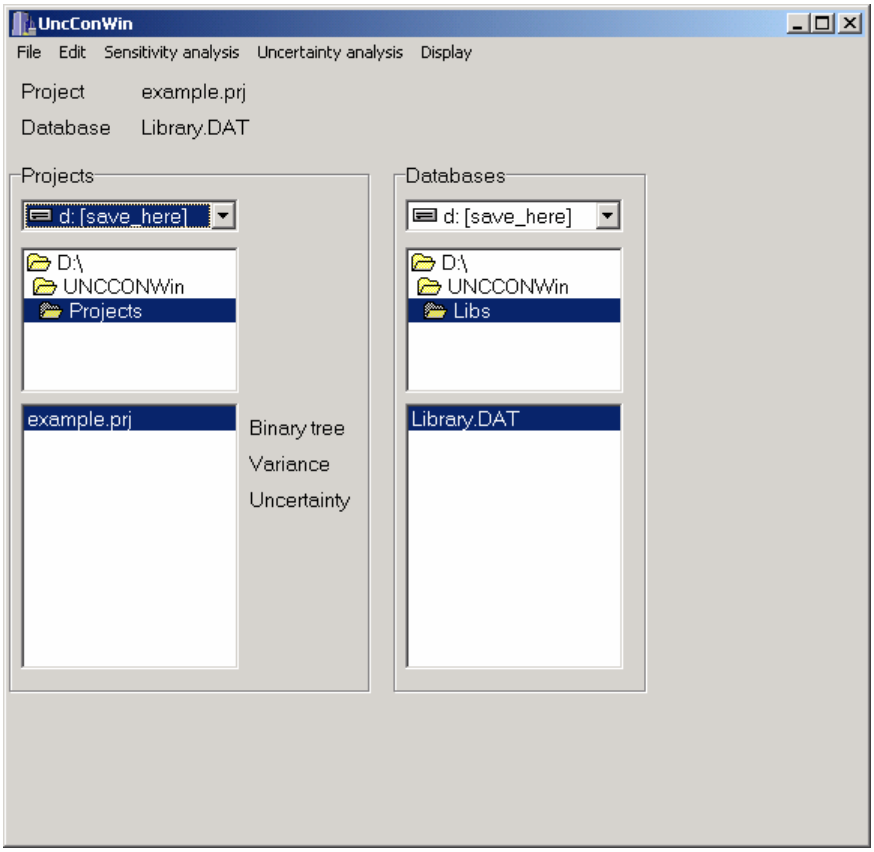

Figure 6, The main window of the UNCCONWIN program

The calculations starts by the user selecting a project from the list. There should always be at least one project in that list. The default is the "example" project. Then a database is selected. In the "Edit" menu the water and the project parameters are then edited, see Figure 6 and 7. The water used in this case is the same as for the SENVARWIN calculations presented earlier in this report. The uncertainties in the concentrations are from Nilsson (1992) and Samuelsson (1996).

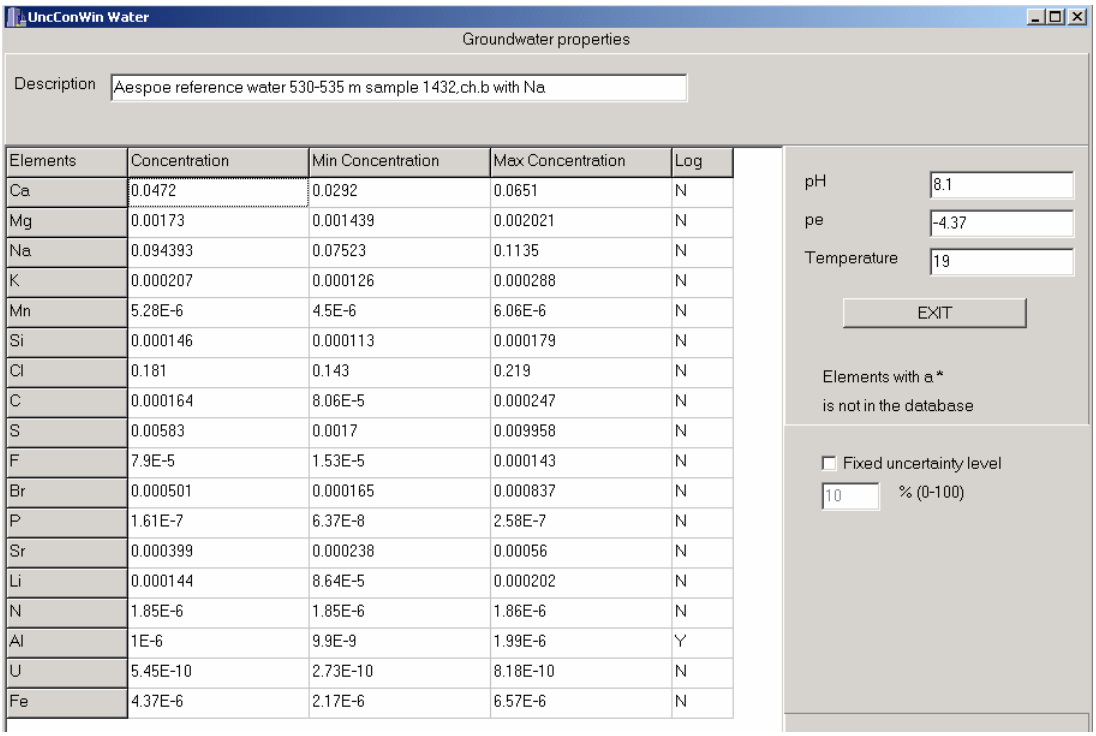

Figure 7, The water composition window.

In the "water composition window" the user need to specify the water chemistry parameters. In addition, a choice is needed whether or not a constant percentage uncertainty should be used. Generally, it may be difficult to obtain specific values for the different uncertainties and in such a case it might be a good idea to select this option. However, if uncertainty data exist or may be estimated with reasonable accuracy it is better to utilise them, as is done in this test case. The user has then to give the minimum and maximum value for the different element concentrations and also state whether the sampling should be made within a linear or logarithmic interval. Generally, a linear interval is enough but if some element has an uncertainty interval ranging over several orders of magnitude (in this case see the Al interval) this fact is better reflected with a logarithmic interval. The sampling is the made from a uniform distribution in order not to underestimate the effect of the uncertainties since in this case there are no tails in the distribution.

When the water parameters are selected the different parameters for the calculations need to be set. This is done by selecting the "Project parameters" option in the "Edit" menu, see Figure 8.

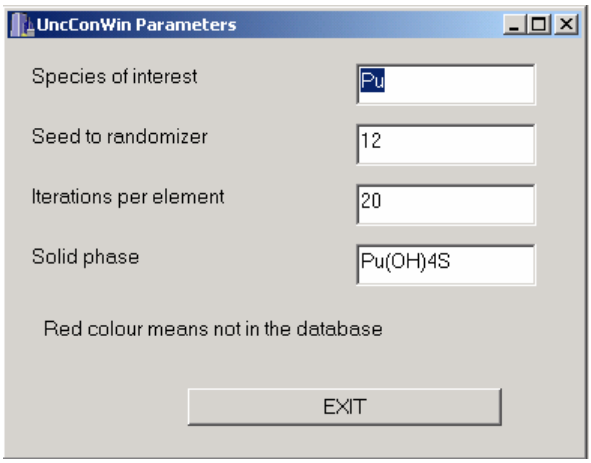

Figure 8, The Project parameter window

In this window the user selects which element to monitor and which solid phase to equilibrate with. The element name and the solid phase is case sensitive so if they appear red, i.e. not in the database, this could be due to just a mistyping of the cases. The statistical parameters "seed to randomiser" and "iterations per element" is also selected here. As for SENVARWIN the seed may be selected arbitrarily but the number of iterations per element for the variance analysis should be at least 20. Contrary to the SENVARWIN program the user does not give the number of iterations here. In UNCCONWIN this number is set to 900.

If changes were made to either the water or the project parameters it is probably a good idea to save this new project as a new project. This is done by using the "Save as" option in the "File" menu.

For tutorial purposes we will now run both the variance analysis and the binary search tree as preliminary sensitivity analyses. However, preliminary sensitivity analysis is not a prerequisite in UNCCON since the number of uncertain input variables is relatively small. Thus, if the number of elements in the water is less than 19 it is just as easy to run the uncertainty analysis from the beginning. However, if the number of elements is greater than 19 it is recommended to run a screening. The binary search tree is run by selecting it from the sensitivity analysis menu. The results from the binary search tree may be found in the "example.bst" file. However, as will be seen later, investigation of this file is not necessary. The variance analysis is selected in a similar way and the results may be found in "example.spc".

When the screening sensitivity analysis is done the uncertainty analysis is started by selecting it from the menu. The uncertainty analysis window will then appear, see Figure 9.

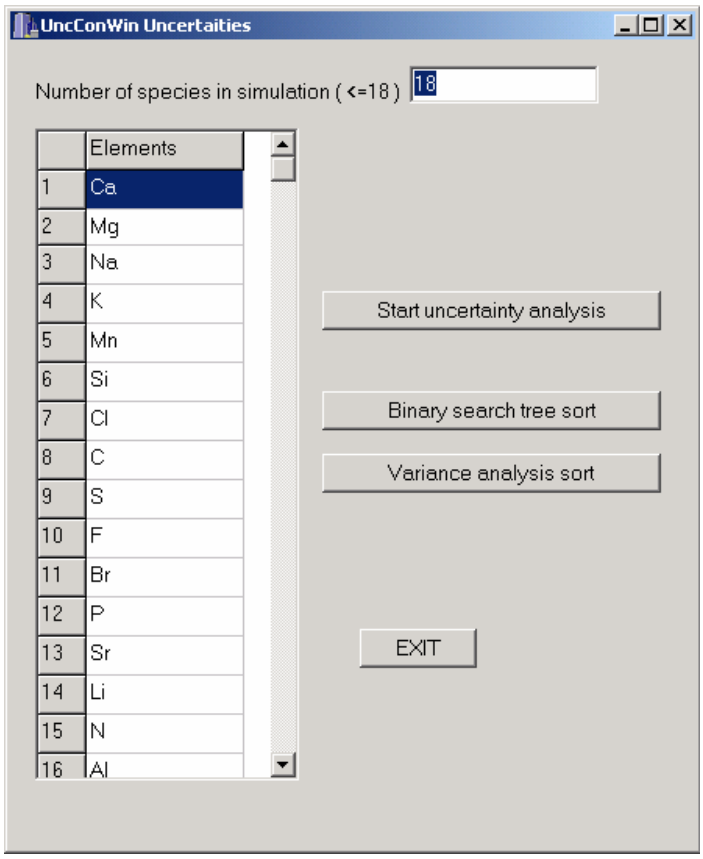

Figure 9, Uncertainty analysis window

The main function of the "Uncertainty analysis window" is to determine which elements should be included in the uncertainty analysis. The number for this analysis is limited to 19. However, this is not a big limitation since often the number of elements in a given water analysis is usually smaller than 19. If this is not the case, UNCCONWIN can make a preliminary sensitivity analysis to rank the elements with respect to their importance, as described earlier. The user may select the order of the elements in the uncertainty analysis and may also move them around arbitrarily by right clicking on the particular element that should be moved. The important thing is to remember that only the 19 first elements will be used in the uncertainty analysis. It is also possible to include fewer elements in the uncertainty analysis by adjusting the number at the top of the window.

The uncertainty analysis is started by clicking on this button, c.f. Figure 9. When the uncertainty analysis is ready the results may be displayed by selecting this option from the menus of the main window, see Figure 10.

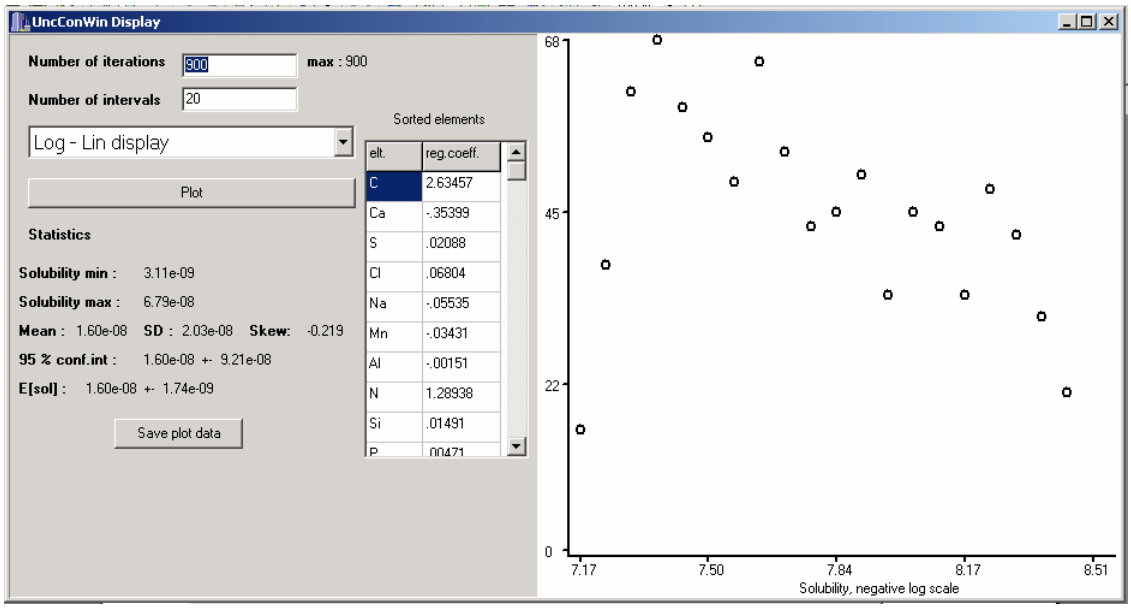

Figure 10, The Display window

In the Display window all relevant information from the uncertainty analysis and the final sensitivity analysis may be found. At the top the user may select the number of iterations that should be used for the plot of the distribution function and also how many intervals to use. There is also a possibility to select different axes such as linear or logarithmic. Then the statistical data such as mean, standard deviation, skiewness and some confidence intervals are given. These are explained in more detail in Ekberg and Emrén (1996). Proceeding to the right, the results from the final sensitivity analysis are shown together with their regression coefficient. The greater the absolute value of this coefficient, the more important the element is for the solubility of the solid phase in this water and with the uncertainty ranges given. In this case inorganic carbon is, by far, the most important element and this is due to strong plutonium carbonate complexation in the water used. The plot data may also be saved in a separate file for use by another plotting program and this is done by clicking on the “Save plot data” button.
For interpretation of these kinds of calculations we refer to the relevant papers in the reference list.

4. Conclusions

Uncertainty and sensitivity analysis is becoming more and more important for testing the reliability of computer predictions. Solubility estimations play important roles for, e.g. underground repositories for nuclear waste, other hazardous materials as well as simple dissolution problems in general or industrial chemistry applications. The calculated solubility of a solid phase is dependent on several input data, e.g. the stability constants for the complexes formed in the solution, the enthalpies of reaction for the formation of these complexes and also the content of other elements in the water used for the dissolution. These input data are determined with more or less accuracy and thus the results of the calculations are uncertain. For the purpose of investigating the effects of these uncertainties several computer programs were developed in the 1990:ies, e.g. SENVAR, MINVAR and UNCCON. Of these SENVAR and UNCCON now exist as windows programs based on a newer speciation code. In this report we have given an explanation of how the codes work and also given some test cases as handling instructions. The results are naturally similar to the previous ones but the advantages are easier handling and more stable solubility calculations. With these improvements the programs presented here will be more publically accessible.

5. Acknowlegement

We would like to thank Allan Emrén and Gunther Meinrath for their interest and help and Anders Samuelsson for writing the very first version of the UNCCON program. This work was funded by the Swedish Nuclear Power Inspectorate (SKI).

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Appendix 1: SENVARWIN example project file

SENVARWIN project file version
1.0
Begin Project
Species of interest
Pu
NAME OF RESULTFILE
PuOH4ret.dat
pH,pe and temp included (y/n)
Y
Iterations per species
20
Seed to randomizer
12
Number of iterations
1000
Solid phase
Pu(OH)4S
End Project
Begin Water
Aespoe reference water 530-535 m sample 1432,ch.b with Na
pH
8.1
pE
-4.37
Temperature (deg. C)
19
No. elements
18
Elements ('name' 'concentration')
Ca 0.0472
Mg 0.00173
Na 0.094393
K 0.000207
Mn 5.28E-6
Si 0.000146

Cl 0.181
C 0.000164
S 0.00583
F 7.9E-5
Br 0.000501
P 1.61E-7
Sr 0.000399
Li 0.000144
N 1.85E-6
Al 1E-6
U 5.45E-10
Fe 4.37E-6
End Water