Optimization of a Sequential Extraction Method for Soils and Sediments: Development of the NIST Standard Sequential Extraction Protocol

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We are developing a standard method for the sequential extraction of actinide elements from soils and sediments. The development of this protocol will provide a standard reference point for research aimed at identifying primary geochemical phases of radioactive contaminants in solid-phase matrices (Schultz et al., 1997). Currently, no such standard method exists.

A full-factorial experimental design has been implemented to determine the optimum setting for each of three variables: reagent concentration, reaction temperature, and reaction duration. This experimental design allows for the determination of the optimum settings from predetermined choices with the application of a minimum number of strategically planned experiments (Box et al., 1978). The predetermined choices incorporate a low, high and midpoint setting for each of the three variables. There are nine experiments, with replicate analyses performed for five of them. The selection of these settings establishes the eight corners, and a midpoint, of a cube constructed in space having axes of temperature, concentration and time (Fig. 1). Two blanks are also included, for a total of sixteen individual experiments.

The experiments are being performed on a new NIST Standard Reference Material, SRM-4357 Ocean Sediment. Six operationally-defined sediment fractions are being studied, each designated by the reagent used. The $MgCl_2$ fraction targets readily exchangeable ions. The NH_4Ac fraction targets carbonate bound analytes. The $NH_2OH \bullet HCl$ fraction (in 25% acetic acid) targets easily reducible oxides of iron and manganese. The H_2O_2 fraction targets organic matter. The strong acids fraction targets resistant oxides, sulfides and aluminosilicates. The final fraction is a highly refractory phase termed residual. Figure 2 depicts the arrangement and order for the sequential leachings in terms of the targeted geochemical phases. Each successive experimental suite requires pretreatment of the sediment under the optimum settings established in the previous suite.

The criteria we have applied for determination of the optimum settings is based on the maximum extraction of ^{238}U and ^{239}Pu in conjunction with a minimum dissolution of non-targeted geochemical phases, monitored by the analysis of stable elements such as Ca, Fe, Mn, Al, K and Sr. The experimental design (Fig. 1) allows for determination of the relationship between the measured response, **y**, and the independent variables, $\mathbf{x_a}$, $\mathbf{x_b}$, and $\mathbf{x_c}$ (temperature, concentration, and time, respectively); the identification of significant variables in terms of the greatest change in response due to changes in that variable; and the possibility of increased response due to coupling effects of more than one variable. This response is the percent recovery of the specified constituent from the known total amount of that constituent in the sediment (Inn et al., 1996). The inclusion of a midpoint experiment monitors any curvature in the relationship between the response and the independent variables. Equation 1 shows the mathematical relationship describing the model for the measured response, assuming all variables and interactions are significant. The grand mean of all responses is given by $\boldsymbol{\mu}$.

$$y = \frac{1}{2}(\mu + \beta_a x_a + \beta_b x_b + \beta_c x_c + \beta_{ab} x_{ab} + \beta_{ac} x_{ac} + \beta_{bc} x_{bc} + \beta_{abc} x_{abc}) \qquad \text{Equation 1}$$

$$\beta_i = \bar{y}_+ - \bar{y}_- \qquad \text{Equation 2}$$

To estimate the effect, $\boldsymbol{\beta}$, an individual variable has on the response, the slope is determined for the relationship between the average of the measured responses at low settings and the average of the measured responses at high settings (Figure 3), shown in Equation 2. This can also be determined for any interactions between the independent variables $\mathbf{x_a}$, $\mathbf{x_b}$, and $\mathbf{x_c}$,. For example, Figure 1 shows two shaded areas. These represent all possible interactions between **concentration** and **time** for the low temperature (Area 1), and for the high temperature (Area 2). Based on Equation 2, β for the **concentration/time** interaction is the difference in the average measured response for the high temperature setting ($\bar{y}_+$) and the average measured response for the low temperature setting ($\bar{y}_-$). In the determination of significance of an independent variable, and the significance of variable interactions for ^{238}U and ^{239}Pu, a lower limit for β of 1% is used. In the analyses for the stable elements, a lower limit of 5% is used due to the "informational" nature of the values listed in the SRM certificate for total concentrations of stable elements.

The β for each of the independent variables, and the interactions of the independent variables are ranked by largest value for β. Those that do not meet the lower limit are assumed insignificant, allowing for the simplification of Equation 1. The final equation models the most significant factors contributing to the largest response for a given fraction. The relevance of a large response is qualified by the stable element analyses, i.e., minimal release from non-targeted geochemical phases. By this method, the optimum settings for each fraction are established, defining the standard method for sequential extraction of actinide elements from soils and sediments.

References

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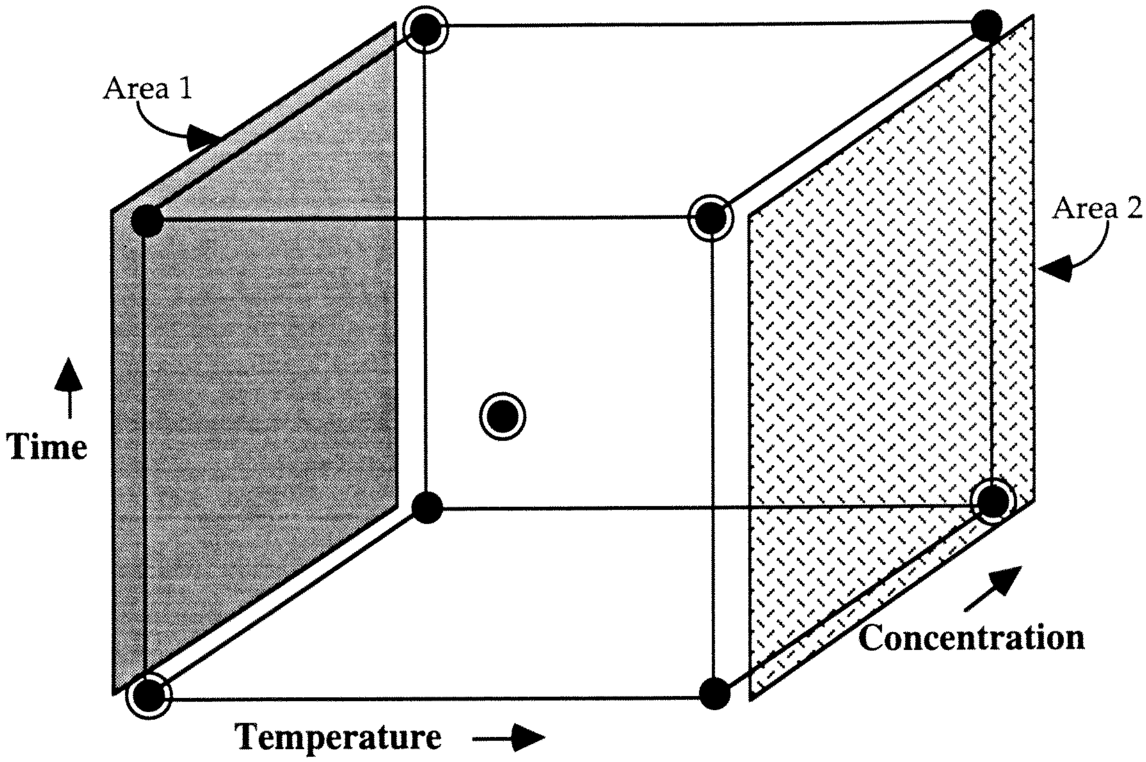

Figure 1. Cubic design for suite of experiments. The plain circles represent settings at which experiments were run. The ringed circles indicate replicate analyses. Area 1 represents all possible combinations of **time** and **concentration** at the low temperature setting. Area 2 represents all possible combinations of **time** and **concentration** at the high temperature setting.

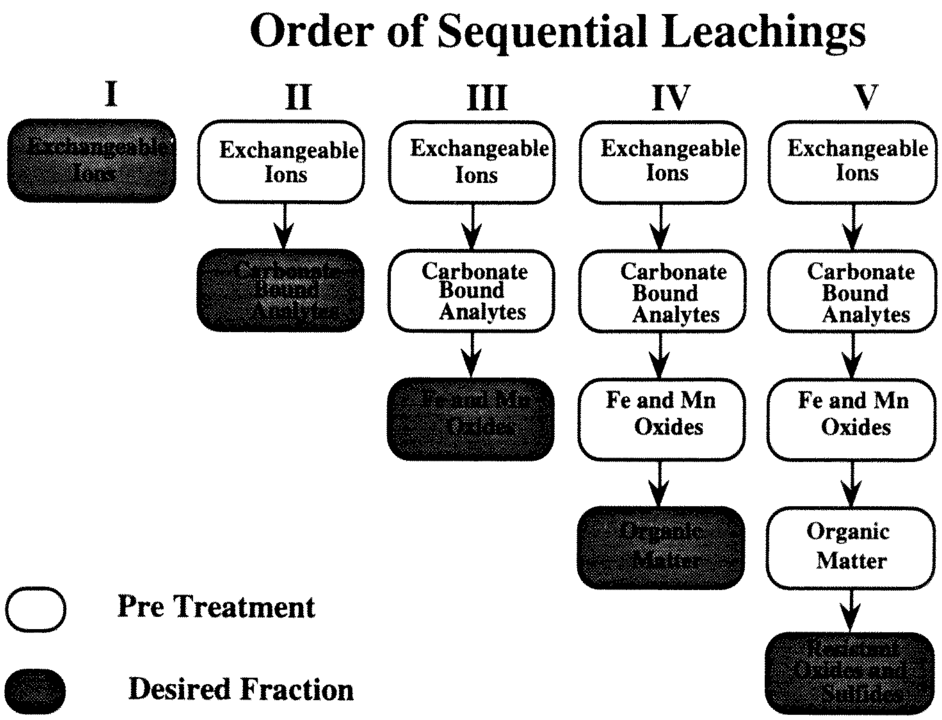

Figure 2. The shaded boxes represent the desired fraction for experiment suites I - V. Each previous leaching must be performed on the sediment at the optimal settings. By this, the sediment is ensured to be in the correct state for a particular leaching experiment suite.

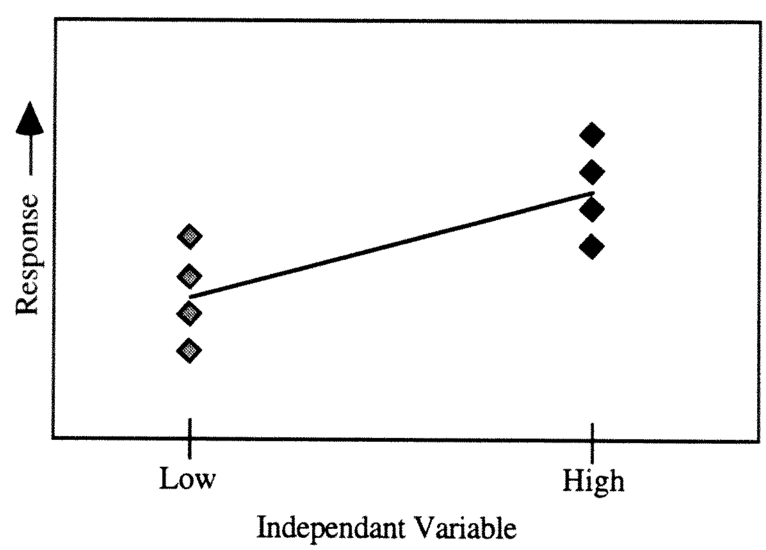

Figure 3. Example of estimation of effect, β, based on measured responses due to an independent variable at low and high settings. An average response at each setting is used to determine the slope, which indicates the effect, β. A lower limit of 1% is used in establishing the significance of the independent variable for measurements of ^{238}U and ^{239}Pu, and 5% for the stable element analyses.