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COMPUTERIZED PORCEDURE FOR PREPARATION OF SECONDARY STANDARDS (U)

by

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Abstract:

Laboratory quality control programs depend on the analysis of known standards to judge the accuracy and reliability of the results they generate. The standards used for routine checks are generally made by diluting and mixing well characterized and traceable primary standards because the primary standards are too expensive and difficult to certify to use in large quantities.

We have developed a computer program to help automate the production of secondary standards and to help assure their accuracy and reliability. The program preforms four major functions: input and tracking of information about primary stock standards; input and editing of procedures to make secondary standards from available stock standards; calculation of secondary standard concentrations and uncertainties based on weights and densities; and inventory of components in stock standards, secondary standards, and waste.

The reliability of the secondary standards is verified by testing measured secondary standard density against its calculated density. Secondary standard uncertainties are calculated by propagating the uncertainties of the stock standard concentrations and weight and density measurements. Weight and density measurements can be automatically transmitted from instruments with RS-232 interfaces or manually entered.

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INTRODUCTION:

Accurate and well characterized standards are an essential part of any laboratory quality assurance program. Results from the analysis of standards are the basis for estimating the accuracy and reliability of analysis methods. The character-ization process to measure the accuracy of standards is often time consuming, tedious and expensive. To minimize the trouble and expense, stock standards are prepared in large quantities at fairly high concentrations for extensive analysis. These well characterized stock standards are rarely used directly but are diluted or mixed with other stock solutions to prepare secondary standards which better match the concentration and matrix of unknown samples to be analyzed. The concentrations and uncer-tainties of components in secondary standards can be calculated from concentrations and uncertainties in the stock standards and the uncertainties in the quantity of the stocks used to make the secondary standard.

The secondary standard (SSTD) program is a computerized procedure to help laboratory technicians make liquid secondary standards from well characterized stock standards. Given target concentrations for secondary standards and stock standard concentrations, SSTD calculates the weights of stock standards necessary to achieve the target concentrations. When an operator enters the weights of stock standards actually used and the density of the resulting secondary standard, SSTD calculates actual concentrations and uncertainties of each component in the secondary standard. Uncertainties are computed by propagating stock standard concentration uncertainties and measurement uncertainties through the concentration calculations. Measure-ments used in SSTD are stock standard weights and densities, and secondary standard density. Standards made by weight and density are typically more accurate and reliable than standards made by volume.

In addition to concentration calculations the SSTD program includes the following functions:

INVENTORY - to keep track of the amounts of components in stock solutions, disposed to waste, transferred to other locations, removed as samples, or used in secondary standards.

ENTER - to allow easy entry of new stock solution

information or new secondary standard procedures.

UPDATE - to allow modification of existing stock solution information or secondary standard procedures. Old information is saved and labeled as inactive.

CONVERT - to convert concentration values between any of these six units; Mole/Liter, Gram/Liter, Microgram/Gram, Weight%, Curies/Milliliter, Disintegrations/Minute/-Milliliter

BACKUP - to archive all data files used or created by the SSTD program. Files include; stocks, procedures, component list, instrument parameters, secondary standards, waste, transfers, samples, and any inactive files.

INSTRUMENT - to allow entry of balance and densitometer bias and precision data.

These functions are especially useful in managing a radio-chemical standards laboratory where large quantities of special nuclear materials are handled and stored.

DESCRIPTION:

The SSTD program is written in MicroSoft QuickBasic ver 4.0, and compiled for use on IBM-PC and compatible computers using MS-DOS 3.0 and later operating systems. Minimum recommended computer hardware is 512K memory, two double density floppy disk drives and a printer configured as LPT1. Separate serial port interfaces are required for the balance and densitometer if they are connected directly to the computer. The operator starts the program by typing SSTD. The main objective of the program is to computerize procedures used to make secondary standards from stock standards. Figure 1 is a block diagram of the program.

Stock Standards

Stock standards are relatively concentrated and well characterized materials which will be diluted or mixed to make less concentrated secondary standards. Information about stock standards must be entered before procedures which use the stock can be built. Necessary stock standard data are:

(1). Number of Components - Components are the different chemical, elemental or isotopic species found in the standard in which the operator is interested. For instance a uranyl nitrate - nitric acid standard might have three components (uranium, nitrate and acid) if all

the operator is interested in is total uranium concentration. If the operator is interested in the uranium isotopics the standard may have eight components (total uranium, U^{238}, U^{236}, U^{235}, U^{234}, U^{232}, acid, and nitrate).

(2). Component Name - The program maintains a list of all components. The list includes the component name, its molecular weight, and its half-life. If a new component name is entered the operator is given the option of entering the new component (and supplying the molecular weight and half-life) or searching the component list to look for the correct spelling of the component.

(3). Concentration - A concentration must be supplied for each component. Liquid concentration may be entered in any one of six units; Mole/Liter, Gram/Liter, Weight%, Microgram/Gram, Curie/Liter, Disintegrations/Minute/Milliliter. Liquid concentrations are converted to Mole/Liter before data is stored on disk. If the stock is a solid, it is assumed to be a stoichiometric compound and concentration is entered as moles of component per mole of compound.

(4). Concentration Uncertainty - The uncertainty in the concentration of each component should be entered if known. Uncertainty is entered in the same units as the concentration (NOT AS A PERCENT).

(5). Stock Density - If the stock solution is a liquid, its density in Grams/Milliliter must be entered. If the stock is a solid, its formula weight is entered. Formula weight should include any water associated with the crystalline structure. The program also asks for the number of moles of water associated with each mole of solid compound.

(6). Number of Aliquots - For convince the same stock standard is often stored small lots or aliquots.

(7). Aliquot Weight - The weight of stock standard in each aliquot must be entered. The program keeps track of the amount of stock used from each aliquot.

Stock standard information is entered using the ENTERSTOCK command which prompts the operator for the necessary inputs. Input data is organized in disk files with the DOS extension ".STK".

Procedures

Procedures tell operators how to make secondary standards from

stock solutions. Information needed to make a procedure is:

(1). Volume of secondary standard - This is the amount of secondary standard that the operator wants to have at the end of the procedure.

(2). Number of Stock Standards - The number of stock standards which will be used to make this batch of secondary standards. The operator must have one stock solution for each component that he wishes to specify. For instance, if the operator wishes to make plutonium secondary standards, and he wants to independently vary both the plutonium concentration and the acid concentration he needs two stock solutions, one for plutonium, and one for acid. The plutonium stock may contain acid and the acid stock may contain plutonium, but their ratios may not be equal.

(3). Stock Standard Name - The disk file name of each stock standard that will be used.

(4). Stock Principal Component - Each stock solution was chosen to provide a particular component. This is the principal component of that stock. The same stock can have different principal components in different procedures.

(5). Reporting units - The program searches the chosen stocks and catalogs all components. It allows the operator a choice of six different concentration units for entering principal component target concentrations and reporting result concentrations.

(6). Number of Secondary Standards - The number of different secondary standards to make from the selected stock standards.

(7). Secondary Standard Name - Each secondary Standard is refereed to by a name provided by the operator.

(8). Principal Component Target Concentration - For each secondary standard the operator enters the desired concentration of each principal component. These desired concentrations are called the target concentrations for that secondary standard. The program tests target concentrations to make sure that they can be achieved using the given stock standards. If the target concentrations cannot be made, the operator is alerted and given the option to reenter targets, or accept the closest achievable concentration.

Procedure information entered using the ENTERPRO command which

prompt the operator for necessary inputs. Data is stored in disk files with the DOS extension ".PRO". Figure 1 is a block diagram of the program.

Secondary Standard Preparation

When an operator wishes to make secondary standards from a procedure, he enters its filename. A summary of the procedure is listed indicating the number of secondary standards to be made, their volume and the necessary stock standards. He is asked to measure the density of each liquid stock solution to verify that the correct stock was obtained. The measured density must agree with the density on file to within 2 times the sum of the uncertainty in each density measurement. If densities of stock standards check, the program computes the estimated weight and volume of stocks necessary to make-up each secondary standard and then lists the estimates. The equations used to compute the estimates are:

$$T(I) = \text{SUM-S} \{ [C(I,S)] * W(S) / D(S) / V \} \quad \text{eq.1}$$

where T(I) is the target or desired concentration of component I in the secondary standard; C(I,S) is the matrix of stock solution concentrations describing the concentration of component I in stock standard S; D(S) is the density of the Sth stock; V is the total volume of secondary standard; and W(S) is the weight of stock S necessary to achieve the target concentration. W(S) is the unknown in equation 1 and can be found by inverting the stock concentration matrix.

$$W(S) = V * D(S) * \text{Sum-I} \{ [\text{InvC}(I,S)] * T(I) \} \quad \text{eq.2}$$

Where InvC(I,S) is the inverse concentration matrix. The concentration matrix must be square and non-singular if the inverse exists. This means that a separate stock solution must be chosen for each component specified in the secondary standards (one stock for every specified component), and that the concentrations of components in the stocks must be independent (stocks cannot be dilutions or mixtures of other stocks used in the procedure). As mentioned above the selected component in each stock is called the principal component. For practical purposes the principal component should be one of the major components in the stock, and should be higher in concentration than it is in the other stocks used in the procedure.

The weights computed in equation #2 are not exactly the weights the operator would read from a real balance. To correspond to balance readings the computed weight must be 'uncorrected' for instrument bias and buoyancy before they are displayed. The corrections are:

$$W'(S) = (W(S) - W(air)) / Bias \qquad \text{eq.3a}$$

$$W(air) = D(air) / D(S) * W(S) \qquad \text{eq.3b}$$

$$W'(S) = W(S) / Bias * (1 - D(air)/D(S)) \qquad \text{eq.3c}$$

Here W(S) is the actual weight of stock S, W'(S) is the weight as read on a balance, W(air) is the weight of air displaced by the stock, Bias is the balance bias, D(S) is the density of stock solution S, and D(air) is the density of the air. Air density is computed from room temperature and barometric pressure using the equation:

$$D(air) = .001293/(1+.00367*T) * (P/760) \qquad \text{eq.4}$$

where T is temperature in degrees celsius and P is pressure in mm of Hg. The equation is from the 48th edition of the CRC handbook of chemistry and physics, page F-10. D(air) is in grams/ml of dry air.

Calculation of Actual Concentrations

The calculated weights and volumes are approximate because the program cannot correct for volume non-additivity of concentrated solutions or salts. It may not matter though because we can never measure exactly the weight called for anyway. So to correct for volume non-additivity and our inability to meter exact weights, the program computes concentrations from the actual weights of stocks used and the measured density of secondary standard.

Weights and density may be automatically input from the instruments as samples are prepared or keyed in afterward. Stock weights entered from the balance are corrected for buoyancy in dry air and for balance bias according to the equation:

$$W(S) = W'(S) * Bias / (1 - D(air)/D(S)) \qquad \text{eq.5a}$$

The uncertainty in the weight is:

$$UnW(S) = W(S) * (UnBal/W'(S) + UnCorr/Corr) \qquad \text{eq.5b}$$

where UnW(S) is the uncertainty in the weight of stock solution S, UnBal is the uncertainty in the balance reading, and UnCorr is the uncertainty in the corrections. The uncertainty in the balance reading is taken to be the balance precision as stored in the instrument data file SSTD.SET. If the bias is assumed to have negligible uncertainty compared to the precision, UnCorr is the uncertainty of the buoyancy correction. Using conservative

uncertainty estimates of 5% in the density of air and 0.1% in the density of the stock UnCorr is less than 0.00006 if the correction, Corr, is close to 1.

When final component concentrations are expressed in terms of weight ratios (Wt% or ug/gram), their concentrations and uncertainties are calculated according to the equations:

$$A(I) = \text{SUM-S} \{ C(I,S) * W(S)/W(tot) \} \quad \text{eq.6a}$$

$$UnA(I) = \text{SUM-S} \{ UnW(tot)/W(tot) + UnW(S)/W(S) + UnC(I,S)/C(I,S) \} \quad \text{eq.6b}$$

where A(I) and UnA(I) are the actual concentration and uncertainty of component I in the secondary standard, W(tot) and UnW(tot) are the total weight and uncertainty of the secondary standard, and UnC(I,S) is the uncertainty in the concentration of component I in stock S. The sum of the first two terms in equation 6b represent the precision to which the operator can make up the secondary standard and is reported as well as the total uncertainty.

When final component concentrations are expressed in terms of volume ratios (mole/L or gram/L), their concentrations and uncertainties are calculated according to these equations:

$$A(I) = \text{SUM-S} \{ C(I,S) * W(S)/W(tot) * D(S)/D(tot) \} \quad \text{eq.7a}$$

$$UnA(I) = \text{SUM-S} \{ UnW(tot)/W(tot) + UnW(S)/W(S) + UnD(tot)/D(tot) + UnD(S)/D(S) + UnC(I,S)/C(I,S) \} \quad \text{eq.7b}$$

where D(tot) and UnD(tot) are the density and uncertainty of the secondary standard. The sum of the first four terms in equation 7b represent the precision.

It is apparent that standards made to concentrations based on weight ratios are inherently more precise than those based on volume ratios because of the added uncertainty of the density measurement. But the choice between making standards to weight or volume ratios depends on the end use of the standard more than their ultimate precision. For some measurement methods, such as X-ray fluorescence or gamma ray emission, the analytical signal is more linear to weight fraction. But for other methods, such as absorption spectrophotometry, the signal is more linear to volume fraction. It is important then to make standards for a particular analytical method in the natural concentration unit for that method.

The actual volume of the secondary standard is calculated from its total weight and density. Actual volume is compared to the sum of the volumes of the stock standards for validation of the secondary standard. Typically the actual volume is slightly less

than the volume estimated from the sum. Warnings are printed if the actual volume is greater than the estimated volume by more than 2 times the sum of the uncertainties in the volumes. Also the user is warned if the actual volume is less than 95% of the estimated volume minus the combined volume uncertainties or if the actual volume is more than 10% different than the desired volume. These warnings typically indicate that a weight or density input was incorrectly entered and the user is given the opportunity to reenter the values.

If the volume of the secondary standard is within limits, data about the secondary standard is written to two disk files. One file has the same file name as the procedure but an extension of .SSD (FILENAME.SSD). The other file also has the extension .SSD but uses the date as the file name (DATE.SSD). The weight used from each of the stock solutions is subtracted from the total weight of the stock and the new weight, date and time are appended to the stock data file. The date secondary standard file is used in inventory functions.

CONCLUSION

The Savannah River Laboratory Secondary Standard program (SSTD) effectively combines the functions necessary for operating a radio-chemical standards laboratory. Included are functions to generate procedures to make secondary standards from stock standards; to calculate concentrations, uncertainties, and precisions from weights and density; to document laboratory operations; and to inventory all components found in the stock standards.

Many features are included to assure that results are accurate and reliable. Densities are used to verify the consistency of stock and secondary standard solutions. Weight and density measurements are bias corrected and can be automatically entered from instruments with RS-232 communication ports. The concentrations of radioactive components are corrected for decay. Weight measurements are corrected for buoyancy in air.

The program is currently being tested in the quality control laboratory at Savannah River Site.

SSTD Program Overview

Enter Stock → **Enter Procedure** → **Make Standards**

Stock Name
# of Components
Component # 1
Concentration
Uncertainity
Mol. Wt.
Half-life
Units
Component # 2
etc.
Density
# of Aliquots
Weight Ali. #1
Weight Ali. #2
etc.

Procedure Name
Secondary STD Vol.
# of Stock STDs
Stock STD # 1
Principal Comp.
Units
Stock STD # 2
etc.
 # Secondary STDs
Sec. STD # 1
Conc P. Comp 1
Conc P. Comp 2
etc.
Sec. STD # 2
etc.

Enter Procedure
- Print Review -
Secondary STD #1
Enter STK #1 Wt
Enter STK #2 Wt
etc.
Enter density
Secondary STD #2
etc.

Figure # 1.