QUALITY ASSURANCE PRACTICES OF THE U.S. GEOLOGICAL SURVEY LABORATORY IN SACRAMENTO, CALIFORNIA

By Suzanne N. Makita *and* Roger Fujii

U.S. GEOLOGICAL SURVEY

Open-File Report 91-522

REGIONAL AQUIFER-SYSTEM ANALYSIS

Prepared in cooperation with the

SAN JOAQUIN VALLEY DRAINAGE PROGRAM

8006-49

Sacramento, California
1992

U.S. DEPARTMENT OF THE INTERIOR
MANUEL LUJAN, JR., *Secretary*

U.S. GEOLOGICAL SURVEY
Dallas L. Peck, *Director*

For sale by the Books and
Open-File Reports Section
U.S. Geological Survey
Federal Center, Box 25425
Denver, CO 80225

For additional information write to:
District Chief
U.S. Geological Survey
Federal Building, Room W-2233
2800 Cottage Way
Sacramento, CA 94825

CONTENTS

APPENDIXES

FIGURES

TABLES

Conversion Factors and Abbreviations

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
gram (g)	0.03527	ounce, avoirdupois
liter (L)	0.2642	gallon
pound per square inch (lb/in^2)	6.895	kilopascal

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

Temp °F=1.8 temp °C+32.

Abbreviations:

µg/L	microgram per liter
µL	microliter
µm	micrometer
mg/L	milligram per liter
mL	milliliter
mL/min	milliliter per minute
mmol/L	millimole per liter
mV	millivolt
mol/L	mole per liter
N	normal, equivalent per liter
Eh	redox potential, in millivolts, with respect to the standard hydrogen electrode

QUALITY ASSURANCE PRACTICES OF THE U.S. GEOLOGICAL SURVEY LABORATORY IN SACRAMENTO, CALIFORNIA

By Suzanne N. Makita *and* Roger Fujii

ABSTRACT

This report documents the quality assurance plan for the U.S. Geological Survey research laboratory in Sacramento, California. The main emphasis of the laboratory is the determination of selenium and selenium species in soil extracts and ground water; major ions and other water-quality properties also are determined by the laboratory. Included in this report are the analytical methods used by the laboratory, as well as other general laboratory procedures.

INTRODUCTION

High concentrations of selenium (Se) in agricultural drain water in the western San Joaquin Valley (Presser and Barnes, 1984) resulted in mortality and deformity of waterfowl hatchlings at Kesterson National Wildlife Refuge near Gustine, California (Ohlendorf and others, 1986). These occurrences prompted studies by Federal and State agencies to understand the geochemistry and biogeochemistry of selenium. As part of this effort, a research laboratory was established at the U.S. Geological Survey (USGS) office in Sacramento, California, to provide specialized analytical services for projects studying the distribution and mobility of Se in soils and ground water. These specialized services include obtaining lower detection limits for analysis of Se in water with complex matrices, analyzing small-volume samples for Se and major ions, and achieving quick turnaround times for analytical results. A unique service the laboratory provides is the determination of Se species: selenite (SeO_3^{2-}), selenate (SeO_4^{2-}), and organic Se. This report describes the practices followed in the laboratory to assure that the data are valid and can be used with confidence.

The two basic elements of a quality-assurance program are quality control and quality assessment (Taylor, 1985). The quality-control process assures the quality of the data by monitoring the analytical process and all laboratory operations. This is achieved by implementing methods to identify and correct problems. Quality assessment is the evaluation of the quality-control process by measuring precision and accuracy of data analysis.

SAMPLE HANDLING

WATER SAMPLES

All water samples submitted to the laboratory are accompanied by a sample log-in form (fig. 1). The log-in form asks for specific information such as date and time of collection, determinations requested, field specific conductivity, and any special treatment of the sample, including the need for refrigeration. With this information, a unique, traceable identification number is assigned to each sample. Samples generally are analyzed in the order received. When the analyses are complete, the date is recorded on the log-in form, and samples are stored in the laboratory until the data are reviewed and approved. Samples are then returned to the submitter.

EXPERIMENTAL SAMPLES

Samples generated in the laboratory from specific research experiments are recorded in a bound laboratory notebook and are labeled with a unique identification number. The coding scheme is documented in the laboratory notebook. The experimental work is done according to a written plan developed by the researcher(s), and all analyses follow the general quality-assurance practices of the laboratory.

Project Leader _____ Submitted By _____ Date Submitted _____
Sample Location _____ Sample Description _____
Special Instructions _____

Lab ID	Field ID	Date Collected	Time	Field Conditions	ANALYSES REQUESTED											Number of Bottles	Remarks
					Selenium				Anions				Cations				
					Total Se	Date	SeO_3	Date	Cl	HO_3	SO_4	Date	Ca/Mg	Na/K	Date		

Figure 1. Laboratory log-in form.

SELENIUM SPECIATION

The determination of SeO_3^{2-}, SeO_4^{2-}, and organic Se is a special service the laboratory provides. Each sample is first passed through a column packed with XAD-8 resin (acrylic ester polymer resin of intermediate polarity) and analyzed for Se species by hydride-generation atomic absorption spectrometry (HGAAS). The XAD-8 resin removes hydrophobic organics from solution (Leenheer and Huffman, 1976). Hydrophobic organics have been shown to interfere in the determination of Se by HGAAS (Roden and Tallman, 1982). HGAAS is sensitive only to the SeO_3^{2-} species; therefore, SeO_3^{2-} is measured directly in the effluent from the XAD-8 resin. A subsample of the effluent is analyzed for SeO_4^{2-} plus SeO_3^{2-}, using the procedure for total Se determination (see appendix A). The XAD-8 column is eluted with sodium hydroxide (NaOH) and the effluent is analyzed for total Se, which represents a minimum estimate of organic Se. This method of identifying Se species using column chromatography is described in detail by Fio and Fujii (1990); the complete procedure is given in appendix B.

The chromatography columns are rinsed with deionized water, tightly packed with the XAD-8 resin, and plugged at the ends with glass wool. The column is rinsed three times alternately with 0.1 mol/L NaOH and 0.1 mol/L hydrochloric acid (HCl) before samples are passed through. When the columns are not in use, they are stored moist to prevent the resin from shrinking and are refrigerated to prevent microbial growth. Columns are repacked if channeling occurs or resin becomes discolored.

SOIL AND SEDIMENT SAMPLES

A list of soil and sediment samples is submitted to laboratory personnel and should include instructions for the type of processing desired, such as dried, ground, or saturated soil paste. All soils are stored and processed in a room separate from the analytical laboratory. No dried soil or sediment is allowed in the analytical laboratory under normal operation, to decrease potential contamination of samples being analyzed. For experiments requiring extraction or digestion of soil or sediment, the solid material is weighed, and the solutions are added in the soil laboratory. At the beginning of each experiment, the laboratory is thoroughly cleaned to minimize contamination from airborne dust.

SAMPLE PRESERVATION AND STORAGE

Ground water, surface water, and soil extracts to be analyzed for total Se and Se species are filtered (0.45-μm filters), acidified with HCl to pH less than 2, and refrigerated to minimize precipitation of solutes and changes in Se species due to chemical or biological reduction-oxidation (redox) reactions (Cutter, 1986; Friedman and Erdmann, 1982). Samples submitted for major ion determinations are filtered and refrigerated to retard growth of microorganisms (American Public Health Association and others, 1985); acidification interferes with the technique used for these analyses. Sample-preservation methods, maximum storage times, and methods of analysis for each chemical property are given in table 1.

After the samples have been analyzed, they are stored in the laboratory until the data are reviewed and approved. The samples are returned to the project leader unless arrangements have been made to store them in the laboratory. Samples generally are stored for one year, if space is available, or until the project leader approves disposal of the samples.

Unanalyzed soil samples are stored in the soil laboratory and inventoried quarterly. Soil samples that have been analyzed are stored at the USGS warehouse in well-marked boxes, on assigned shelves. The project leader is informed of the location of the soil sample(s). The list of samples stored at the warehouse is updated periodically.

REAGENTS AND LABWARE

REAGENTS

All reagents are American Chemical Society (ACS) reagent-grade or better. Chemicals of less purity are used only if ACS reagent-grade chemicals are not available. The bottles are clearly marked with the date opened. Reagents are inventoried once a year, and the inventory list is kept in the laboratory.

For prepared reagent solutions, the contents, concentration, date of preparation, and preparer's initials are clearly marked on all bottles. The date of preparation is especially important for unstable reagents; these are discarded after the lifetime indicated in the appropriate appendix. Reagents are tested for possible contamination or interference problems by analyzing a sample of the prepared reagent.

Table 1. Sample preservation methods, maximum storage times, and methods of analysis for chemical properties analyzed in the laboratory

[Maximum storage times are from American Public Health Association and others (1985). do., ditto; HGAAS, hydride-generation atomic absorption spectrometry; XAD-8 resin, acrylic ester polymer resin of intermediate polarity; <, less than]

Chemical properties	Sample preservation method	Maximum storage time (from sampling to analysis)	Method of analysis
Alkalinity	Refrigeration	2 weeks	Incremental titration
Calcium	do.	2 weeks	Ion chromatography
Chloride	do.	4 weeks	Do.
Magnesium	do.	2 weeks	Do.
Nitrate	do.	2 days	Do.
pH	do.	4 hours	Electrometry
Potassium	do.	2 weeks	Ion chromatography
Selenium, total	HNO_3, pH<2	6 months	HGAAS
Selenium, species	HCl, pH<2, refrigeration	4 weeks	XAD-8 resin, HGAAS
Sodium	Refrigeration	2 weeks	Ion chromatography
Specific conductance	do.	4 weeks	Electrometry
Sulfate	do.	4 weeks	Ion chromatography

GLASSWARE

Class A volumetric glassware is used. Before use, all glassware is scrubbed with a phosphate-free, laboratory detergent and water. For major ion analyses, glassware is rinsed three times with deionized water and air dried in drying racks. For Se and trace-metal analyses, glassware is rinsed, leaving no soap residue; the final rinse is with deionized water. The glassware is then submerged in a covered acid bath and soaked for at least 2 hours. The acid bath contains a 20-percent solution of HCl in deionized water and is changed after 2 months (sooner if sediment is present or contamination is suspected). After the acid bath, the glassware is rinsed three times with deionized water and air dried. Glassware is stored upside down in closed cabinets or in drawers or plastic bags to minimize contamination.

PLASTICWARE

Plasticware is cleaned and stored in the same manner as the glassware; care is taken not to scratch the inside surface when scrubbing.

INSTRUMENT CALIBRATION

ANALYTICAL BALANCES

Analytical balances are calibrated monthly using class S weights. The balances are calibrated by pressing the "calibrate" button with the appropriate weight. Each time the balance is calibrated, the readings are recorded in a log book and initialed. Balances are professionally serviced when the calibrating weight varies by more than 0.1 percent from its established weight, or annually, whichever comes first.

ATOMIC ABSORPTION SPECTROMETER

The Perkin-Elmer atomic absorption spectrometer (AAS), coupled with the Varian vapor generator accessory (VGA-76), is used primarily to determine Se concentrations. The AAS is calibrated with a blank and four standards ranging from 2 to 15 µg/L Se before every set of samples is analyzed. The blank and four standards are used to establish the calibration curve. The correlation coefficient is used to

determine the acceptability of a calibration curve. A correlation coefficient value of 0.9987 is considered acceptable.

The general procedure is to warm up the electrodeless discharge lamp (EDL) and AAS while aspirating the rinse solution, for a minimum of 30 minutes. The lamp energy is monitored while the instrument is warming up. The energy level must be 76±4 units. If it does not meet this criterion, the EDL has not warmed up or needs to be replaced. Aspiration continues until a stable signal is established. The digested blank then is aspirated and the AAS is autozeroed. When the blank signal is stable, a standard with absorbance value between 0.2 and 0.6 is analyzed. The absorbance reading of the standard is monitored, and any change from previous results must not exceed 10 percent. A reading that varies by more than 10 percent indicates incorrect operational settings, decreased performance of the AAS, or inaccurate standard solutions. If this criterion is exceeded, the problem is identified and corrected before the analysis is continued.

ION CHROMATOGRAPH

The Dionex model 2010i ion chromatograph, which is equipped with a chemically suppressed conductivity detector, is used to determine calcium (Ca), chloride (Cl), magnesium (Mg), nitrate (NO_3), potassium (K), sodium (Na), and sulfate (SO_4) (appendixes C, D, and E). For anion analysis, the Dionex AS4A separator column, AG4A guard column (to protect the analytical column), and the NG-1 guard column (to remove large hydrophobic organic contaminants) are used with a carbonate/bicarbonate eluent and an anion membrane suppressor that uses sulfuric acid (H_2SO_4) as the regenerant.

Divalent cation separation utilizes a hydrochloric acid-hydroxylamine hydrochloride eluent with a Dionex CS-1 analytical column, the CS-1 guard column, and the NG-1 guard column; this separation also utilizes a tetramethylammonium hydroxide pentahydrate (TMAOH) solution through a cation-membrane suppressor. For monovalent cation analysis, a different set of the same columns used for the divalent cations is used with an HCl eluent and is suppressed with the same solution as the divalent cations (Dionex Corporation, 1985a).

The ion chromatograph is calibrated before every run. At least four standards are used for calibration of each constituent, and a correlation coefficient greater than or equal to 0.990 is acceptable. Table 2 lists calibration ranges and detection limits of each constituent. The detection limits listed are the working levels used with the complex sample matrices in high saline waters. These limits will vary in proportion to the dilution factor. Calibration procedures are performed after the instrument has stabilized, indicated by a steady conductivity reading. If the conductivity drifts more than 3 percent, the regenerant flow rate (3-5 mL/min) is adjusted and fittings are checked for liquid leaks. A leak from the suppressor or a high conductivity reading indicates that the suppressor is contaminated and needs to be cleaned (Dionex Corporation, 1986; 1987). When the instrument readings have stabilized, a set of standards is analyzed, and the peak heights of each constituent are recorded in a notebook. Control charts are constructed to determine that peak heights of the standards are within 10 percent of each other. If peak heights are too low, the columns may be contaminated and need to be cleaned (Dionex Corporation, 1985b). After cleaning the columns, the peaks are checked again. If cleaning does not remedy the problem, the column is replaced.

Table 2. Calibration and detection limits for major ions

[mg/L, milligram per liter]

Major ion	Calibration range (mg/L)	Approximate detection limit (mg/L)
Calcium	10-75	5
Chloride	10-75	2
Magnesium	5-30	2
Nitrate (as N)	1-10	.2
Potassium	1-7.5	.5
Sodium	10-75	5
Sulfate	25-100	10

pH/MILLIVOLT METER

The Radiometer pH/millivolt meter is used as a pH and millivolt meter. Prior to each pH measurement, the meter is calibrated with quality-assured buffers from the USGS Water-Quality Service Unit in Ocala, Florida. Two buffers that bracket the pH values of the samples are chosen for calibration (U.S. Environmental Protection Agency, 1979). The slope of the instrument calibration should be at least 98.0 percent. If it is less, the meter is recalibrated using newer buffers. If the slope of the calibration remains below 98.0 percent, the electrode is replaced with a new electrode and the meter is recalibrated. If the problem still persists, service personnel are contacted to repair the pH meter, and another meter is used.

The instrument calibration is checked with buffer solution at least every 3 hours during use (see appendix F). All calibration readings are recorded in a notebook and initialed by the operator. The tip of the electrode must be immersed in 2 mol/L potassium chloride (KCl) solution during the periods of nonuse.

The Radiometer pH/millivolt meter is also used to measure the redox potential of aqueous or soil extract samples. The meter is first calibrated with a pH probe and pH buffers, as described above. An excess of Quinhydrone is added to the pH 4 and the pH 7 buffers and equilibrated; the pH of each solution then is measured. The pH probe is replaced with a commercially available platinum electrode, and the meter is switched over to display millivolts. The redox potential values of the Quinhydrone solutions are measured, and calibration calculations are done, as described in appendix G. The electrode is cleaned with deionized water after each use. Between sample readings, the electrode is kept in a 2 mol/L KCl solution. Calibration readings and calculations are recorded in a notebook and initialed by the operator.

CONDUCTIVITY METER

Before specific conductivity measurements are made, the Radiometer conductivity meter is calibrated with quality assured standards from the USGS Water Quality Service Unit in Ocala, Florida. Specific conductivity of the standards should be as close as possible to that of the sample. The standard is checked and the instrument is recalibrated after every five sample readings. If the standard deviates more than 2 percent from the actual value after calibration, the electrode is replaced and the instrument is recalibrated. Service personnel are contacted to repair the meter if the problem continues. All calibrations are recorded in a notebook and initialed. The operating procedure for the conductivity meter is described in appendix H.

INSTRUMENT STANDARDIZATION PROCEDURES

STANDARD SOLUTIONS

Standard solutions are prepared according to the methods described in the appendixes or are purchased through a reliable commercial supplier. Newly prepared standards are compared against those previously prepared before discarding the old standards. When preparing a standard stock solution, the preparation date and preparer's initials are marked on the standard bottle. For commercially supplied standards, the dates when the standard was received and opened are indicated on the bottle. The commercial standard solutions are discarded when they have reached the manufacturer's recommended expiration date.

TEST OF INSTRUMENT STABILITY

At the beginning and end of each analytical run, standards are analyzed as samples to test instrument stability. If standards vary more than 10 percent from the initial reading, the instrument is recalibrated and analyses are repeated. For analysis of Se on the AAS, the third standard is used as the reslope to recalibrate the initial standard curve.

STANDARD OPERATING PROCEDURES

Analytical procedures have been adapted specifically for the determination of Se and major ions in saline waters for the three basic types of samples analyzed in the laboratory: ground water, surface water, and soil extracts. These methods were adapted from American Public Health Association and others (1985), Methods for Determination of Inorganic Substances in Water and Fluvial Sediments (Fishman and Friedman, 1989), and manufacturer's operation manuals (Perkin-Elmer Corporation, 1986; Dionex Corporation, 1985a). Methods for individual constituents are outlined in the appendixes.

Occasionally, methods need to be modified. If so, any changes are documented in the instrument logbook. For example, when analyzing some of the experimental samples for Na and K on the ion chromatograph, the concentration of K can be extremely high (10,000 mg/L K) and the Na concentration can be low (10 mg/L Na). The standard ion chromatography method is inadequate for this matrix because a clean separation between the peaks of Na and K is not possible. The separator column becomes overloaded, and an increase in the resolution between the two peaks is necessary. This is usually accomplished by diluting the eluent fourfold, to increase the separation and decrease the sensitivity on the conductivity detector for K, or by diluting the sample and increasing the sensitivity for Na (Smith and Chang, 1983). The modified method is tested with duplicate, spiked, and reference samples, and must be within the criteria outlined in the "Internal Quality Control" section of this report.

INSTRUMENT MAINTENANCE

Each instrument is maintained according to the manufacturer's recommendation plus other maintenance requirements necessary, as indicated in appendixes F and H. Each instrument has its own logbook that contains information regarding instrument conditions, problems, maintenance, and repairs. Proper operation will be enhanced by following the maintenance practices listed for each instrument.

INTERNAL QUALITY CONTROL

DUPLICATE SAMPLES

Randomly selected duplicate samples are included with each set (average 30 samples per set) of samples analyzed. Duplicates are obtained by taking two aliquots of the sample from the same container, remixing the contents after retrieving the first aliquot. The duplicate samples are not analyzed consecutively; otherwise, they are treated identically throughout the process. Ten to fifteen percent of the samples are duplicates.

The reproducibility of repetitive analysis is a measure of precision. Precision is reported as the relative percent difference between sample duplicates and is calculated as follows:

$$\text{Relative percent difference} = \frac{|C1 - C2|}{(C1 + C2)/2} \times 100 \qquad (1)$$

where

C1 = concentration of the first analysis, and
C2 = concentration of the second analysis.

As a general guide, a relative difference of 10 percent or less is acceptable; 10 to 20 percent is at the warning limit. Greater than 20 percent is considered unacceptable; see the "Corrective Action" section for proper steps to resolve the problem. For samples at or below the detection limit, the relative percent difference is not calculated, and the notation "below detection limit" is recorded.

SPIKED SAMPLES

The addition of a known standard quantity of analyte into a sample (spiking) is a way to check the accuracy of an analysis. Accuracy is defined as the difference between the measured value and the true or expected value. After the accuracy has been established, any biases or sample matrix problems can be determined through evaluation of data and observation of any positive or negative deviations (Friedman and Erdmann, 1982; Taylor, 1987).

Routinely, 10 to 15 percent of the sample set is spiked. Addition of the spike solution does not significantly change the final volume of the sample. Samples are spiked prior to digestion or other sample preparation to check on the procedure and the effect of the sample matrix on the analysis.

For the major ions, the spike concentration is 10 to 20 percent of the highest standard. The spike for total Se usually results in a final increase in Se concentration of 10 µg/L. For Se speciation, two

aliquots of one sample are spiked with a mixed standard of 10 µg/L SeO_4^{2-} and 10 µg/L SeO_3^{2-}. One spiked aliquot is processed through the resin column, the same as unspiked samples. The other aliquot is undigested and analyzed for selenite by direct aspiration into the VGA and AAS. This is necessary to check the chromatography procedure.

The concentration of the spike is calculated as follows:

$$\text{Spike concentration} = \frac{(C1) \times (V1)}{V2}, \qquad (2)$$

where

C1 = concentration of the spike,
V1 = volume of the spike, and
V2 = volume of spiked sample.

The artificial analyte in spiked solutions is assumed to have the same recovery efficiency as a natural analyte (Taylor, 1987). To calculate spike recovery efficiency, the following equation is used:

$$\text{Percent spike recovery} = \frac{(C3 - C2)}{C1} \times 100, \qquad (3)$$

where

C1 = concentration of the spike,
C2 = concentration of the unspiked sample, and
C3 = concentration of the spiked sample.

Spike recoveries of 90 to 110 percent are acceptable. Recoveries of 80 to 120 percent are at the warning limit; procedures should be examined closely to avoid problems. If the recovery of the spike is not within allowable limits, matrix interferences are indicated, and corrective measures are taken, as described in the "Corrective Action" section.

When values of the unspiked sample are less than detection limits, the concentration of the sample is assumed to be zero, to calculate the spike recovery. If the sample requires dilution and the concentration of the constituent being analyzed is negligible, the spike value is considered invalid and is recorded in the quality-control notebook as an overdiluted spike.

REFERENCE SAMPLES

Another method to check analytical accuracy is to analyze samples with known concentrations. Standard reference water samples are prepared and distributed by the USGS, as described by Janzer (1985). They are also available through the U.S. Environmental Protection Agency and the National Institute of Standards and Technology.

At least two standard reference water samples are analyzed with every set of 30 samples, if reference samples are available for the constituent being determined. One reference sample is analyzed after the standard curve is determined, as an immediate monitor of the system. The other reference sample is interspersed with the sample set and is treated like a sample. When possible, reference samples should have a similar sample matrix and have a concentration close to the concentrations being determined.

Percentage of deviation from the accepted value is calculated as follows:

$$\text{Percentage of deviation} = \frac{(C1 - C2)}{C1} \times 100, \qquad (4)$$

where

C1 = concentration of the accepted value, and
C2 = concentration of the analytical value.

Ten percent deviation is acceptable, 10 to 20 percent is at the warning limit, and greater than 20 percent is considered unacceptable. For sample values 10 times the detection limit or less, a control limit of 15 percent deviation is acceptable; greater than 25 percent is considered unacceptable. Unacceptable samples are handled according to the corrective measures described in the "Corrective Action" section.

EXTERNAL QUALITY CONTROL

The research laboratory in Sacramento, California, participates twice a year in round-robin analyses of water samples, sponsored by the USGS. This program compares values from all participating

laboratories and establishes a most-probable value for each constituent. Analyses from each laboratory are compared with the most-probable value calculated for each constituent analyzed, and each laboratory is given a rating based on their results relative to the most-probable value. A summary report of each round-robin study is distributed to each participating laboratory, and the results are reviewed by the laboratory personnel.

The research laboratory also participated in the annual Se round-robin program sponsored by the San Joaquin Valley Drainage Program. This program was designed to ensure that data from laboratories analyzing drainage water, soil, and biota from the San Joaquin Valley are reliable. A report summarizing the Se results and the various laboratory methods was sent to all participating laboratories and reviewed by laboratory personnel.

LABORATORY RECORDS

QUALITY-CONTROL DATA

Quality-control data for all analyses are recorded in the appropriate notebook for each constituent. Quality-control data include results of duplicate sampling and percentage difference from the mean, spike concentration and percentage recovery values, and reference samples and percentage deviation from the most-probable value. These data are recorded shortly after the sample set is analyzed and quality-control charts are made to show trends not evident from data tabulation (fig. 2). Any problems regarding the quality-control data are documented in the appropriate notebook and the appropriate corrective actions are taken, as described in the "Corrective Action" section.

EXPERIMENTS

All data for research experiments performed in the laboratory are recorded in a bound notebook. The concentration and date of preparation of all reagents prepared for the experiment, meter and probe calibrations for pH, specific conductance, and redox potential also are recorded in the notebook. Data for the determination of total alkalinity by incremental titration (appendix I) for water samples and soil

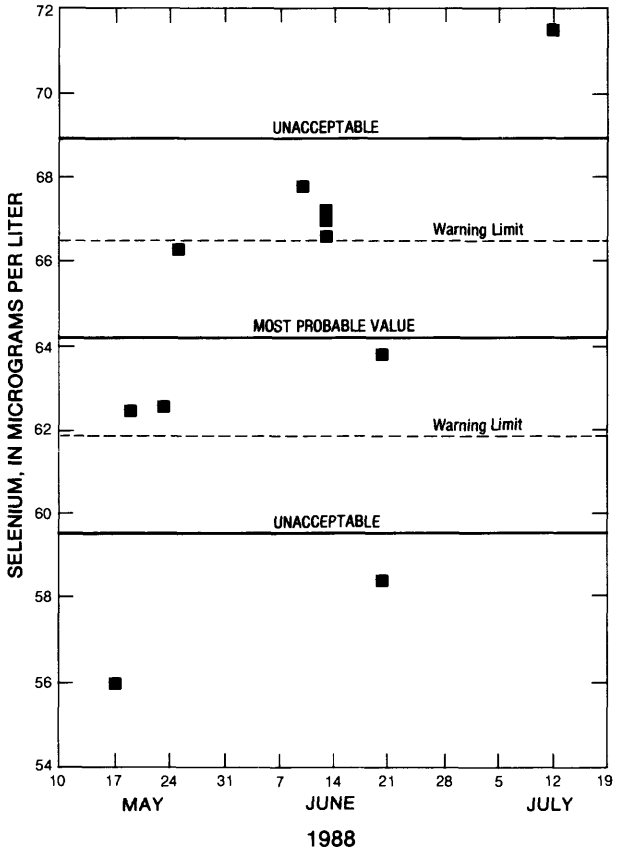

Figure 2. Quality-control chart for total selenium. Data are recorded by date of measurements and amount of selenium.

extracts are also recorded in the notebook. Soil and solution weights for saturation extracts (appendix J) and all calculations are included, along with observations, time schedules, and temperatures.

SELENIUM SPECIATION

A bound notebook of samples analyzed for Se species is kept in the laboratory. Column identification, sample identification, sample and reagent volumes, and calculations are recorded in the given order. All quality-control data are documented in this notebook, along with observations of unusual sample appearance or problems. Dates when columns were repacked and reagents prepared and by whom also are noted in the notebook.

SOIL EXTRACTS

All soil extract records are kept in a bound notebook. Soil weights and water volumes, calculations, redox potential, pH and specific conductance measurements, and calibration notes also are recorded in the notebook.

INSTRUMENT LOGBOOK

Each instrument has a logbook that contains information regarding instrument maintenance and problems, standard preparation, and instrument performance. For example, EDL energy is recorded for every run of the AAS, along with absorbance readings for each standard used. For the ion chromatograph, information such as eluent or regenerant modifications, column cleaning and replacements, and methods modification is recorded in the ion chromatography logbook.

DATA HANDLING

DATA REVIEW

Data are reviewed within one week of the analysis. The analyst first reviews the data and calculations. Next, the senior technician reviews the data and evaluates the quality-control data to ensure the data are acceptable. The readings and calculations for each sample also are checked for any calculation errors. If there is a problem with the data, or the data are questionable, the problem is resolved and the samples are reanalyzed as soon as possible.

DATA REPORTING

The data are reviewed and tabulated. The table includes data not corrected for dilution, the dilution factor, and the data corrected for dilution. All data are stored in the laboratory file and a copy is given to the requestor. If major ion analysis was requested, a cation-anion equivalent balance is calculated. Generally, a difference of less than 5 percent is acceptable. But, in water with a dissolved-solids concentration greater than 1,000 mg/L, high concentrations of a few constituents are usually found, and the cation-anion equivalent balance is not always an accurate check of the values of the lesser constituents (Hem, 1985). If the cation-anion equivalent balance exceeds 5 percent, the reason must be investigated. A list of corrective actions is given by Friedman and Erdmann (1982).

CORRECTIVE ACTION

Corrective action is required when analytical errors and poor performances are detected during the review of the internal quality-control samples or external quality-control programs. There may be several reasons why a quality-control sample is unacceptable, and the problem must be discerned. Steps to identify the problem are outlined on the flowchart (fig. 3); table 3 lists some specific problems encountered at the various steps. If after performing all of the appropriate checks, the problem still has not been determined, the manufacturer or personnel from other laboratories using similar instrumentation and procedures are consulted to help resolve the problem.

Table 3. Common problems

Blunders	**Instrument or Procedural Problems**
Mislabelled sample	Weak or misaligned lamp
Wrong spike solution	Obstructions in lines
Wrong spike volume	Insufficient warm-up time (unstable system)
Calculation error	Bad standard and/or reagents
Dilution error	
Transcription error	
Sample Problems	
Matrix effects	
Sample variability	
Sample contamination	

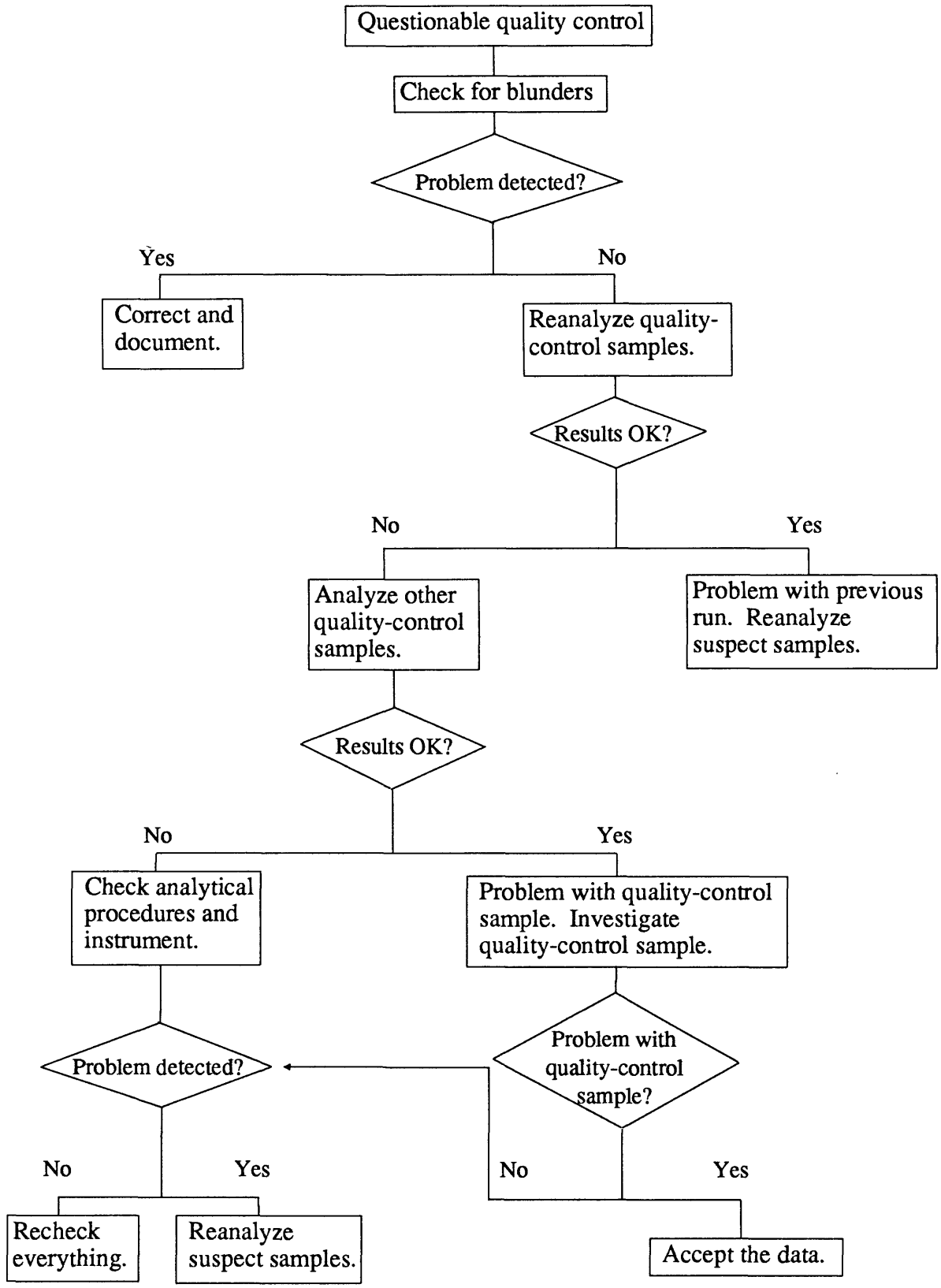

Figure 3. Corrective action sequence.

SUMMARY

This report describes the quality-assurance practices currently used by the U.S. Geological Survey laboratory in Sacramento, California, to assure that data are valid and can be used with confidence. As research studies change and other projects develop, the analytical focuses of the laboratory may change and the quality-assurance plan may need to be adjusted to reflect these changes. As these changes are implemented, the overall objective of providing quality analyses remains unchanged.

REFERENCES CITED

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1985, Standard methods for the examination of water and wastewater (16th ed.): Washington, D.C., American Public Health Association, 1268 p.

Cutter, G.A., 1986, Selenium speciation, v. 1 *of* Speciation of selenium and arsenic in natural waters and sediments: Palo Alto, California, Electric Power Research Institute Report EA-4641, variously paged.

Dionex Corporation, 1985a, Eluant preparation and use for Dionex columns: Sunnyvale, California, Dionex Technical Note 16, 4 p.

-----1985b, Routine maintenance and reconditioning of columns: Sunnyvale, California, Dionex Technical Note 2R, 8 p.

-----1986, Anion micro membrane suppressor instructions: Sunnyvale, California, Dionex Document No. 032477, variously paged.

-----1987, Cation micro membrane suppressor installation instructions and trouble-shooting guide: Sunnyvale, California, Dionex Document No. 032632, 13 p.

Fio, J.L., and Fujii, Roger, 1990, Selenium speciation methods and application to soil saturation extracts from San Joaquin Valley, California: Soil Science Society of America Journal, v. 54, no. 2, p. 363-369.

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 545 p.

Friedman, L.C., and Erdmann, D.E., 1982, Quality assurance practices for the chemical and biological analyses of water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A6, 181 p.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 264 p.

Janzer, V.J., 1985, The use of natural waters as U.S. Geological Survey reference samples, *in* Taylor, J.K., and Stanley, T.W., eds., Quality assurance for environmental measurements: Philadelphia, Pennsylvania, American Society for Testing and Materials Special Technical Publication, v. 867, p. 319-333.

Leenheer, J.A., and Huffman, W.D., Jr., 1976, Classification of organic solutes in water by using macroreticular resins: U.S. Geological Survey Journal of Research, v. 4, no. 6, p. 737-751.

Ohlendorf, H.M., Hothem, R.L., Bunck, C.M., Aldrich, T.W., and Moore, J.F., 1986, Relationships between selenium concentrations and avian reproduction: North American Wildlife and Natural Resources Conference, 51st, Reno, Nevada, 1986, Transactions, p. 330-342.

Perkin-Elmer Corporation, 1986, Reference manual--Model 5100 atomic absorption spectrophotometer: Norwalk, Connecticut, variously paged.

Presser, T.S., and Barnes, Ivan, 1984, Selenium concentrations in waters tributary to and in the vicinity of the Kesterson National Wildlife Refuge, Fresno and Merced Counties, California: U.S. Geological Survey Water-Resources Investigations Report 84-4122, 26 p.

Roden, D.R., and Tallman, D.E., 1982, Determination of inorganic selenium species in groundwaters containing organic interferences by ion chromatography and hydride generation/atomic spectrometry: Analytical Chemistry, v. 54, no. 2, p. 307-309.

Smith, F.C., and Chang, R.C., 1983, Practice of ion chromatography: New York, John Wiley, 218 p.

Taylor, J.K., 1985, The quest for quality assurance: American Laboratory, October 1985, p. 67-75.

-----1987, Quality assurance of chemical measurements: Chelsea, Michigan, Lewis Publishers, 328 p.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: Cincinnati, Ohio, Environmental Monitoring and Support Laboratory, Research and Development, EPA-600/4-79-019, variously paged.

Varian Corporation, 1984, VGA-76 Vapor generation accessory, operation manual: Mulgrave, Victoria, Australia, Publication No. 85-100577-00, 26 p.

Wood, W.W., 1976, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 1, Chapter D2, 24 p.

APPENDIXES

APPENDIX A--Procedure for Analyzing Total Selenium in Water by Hydride Generation Atomic Absorption Spectrometry

1. PREPARATION OF STANDARDS

1.1 *Selenium standard solution I*, 1,000 mg/L: Baker Analyzed Reagent.

1.2 *Selenium standard solution II*, 10.0 mg/L: Combine 10.00 mL selenium standard solution I and 4 mL concentrated nitric acid (HNO_3); dilute to 1,000 mL with deionized water. Store refrigerated; discard after 3 months.

1.3 *Selenium standard solution III*, 0.100 mg/L: Combine 5.0 mL selenium standard solution II and 2 mL concentrated HNO_3; dilute to 500 mL with deionized water. Store refrigerated; discard after 2 weeks.

1.4 *Working standard solution*, 2 µg/L, 6 µg/L, 10 µg/L, 15 µg/L: Pipet 2, 6, 10, or 15 mL of selenium standard solution III into a 250-mL Erlenmeyer flask. Dilute to 60 mL with 0.4 percent HNO_3. Prepare additional 10 µg/L selenium standard solution III to use as a reslope solution. Working standard solutions are prepared fresh for each batch and go through the same digestion procedure as the samples, with a final dilution to 100 mL.

2. PREPARATION OF REAGENTS

2.1 *Oxalic acid*: Dissolve 35 g oxalic acid powder reagent in deionized water; dilute to 1 L.

2.2 *Potassium persulfate ($K_2S_2O_8$)*, 2 percent: Dissolve 20 g $K_2S_2O_8$ in deionized water; dilute to 1 L.

2.3 *Sodium borohydride ($NaBH_4$)*: Dissolve 2.5 g NaOH in deionized water. Add 3 g $NaBH_4$; dilute to 500 mL.

2.4 *Hydrochloric acid (HCl), 7 M*: Dissolve 290 mL concentrated HCl in deionized water; dilute to 500 mL.

3. PREPARATION OF SAMPLE

3.1 Wash all glassware with phosphate-free laboratory detergent and warm water. Rinse well, acid rinse, and then rinse three times with deionized water.

3.2 Shake sample bottle thoroughly and pipet 20 mL of sample into a 250-mL Erlenmeyer flask. Dilute to 40 mL with 0.4 percent HNO_3.

3.3 Prepare two reference samples of 20 mL each, and dilute to 40 mL with 0.4 percent HNO_3.

3.4 For every fifth sample, alternate a duplicate or spiked sample. Spiked samples are prepared by adding 50 µL of selenium standard solution II.

3.5 Prepare two blank samples by measuring 60 mL of 0.4 percent HNO_3.

3.6 Add 3.3 mL of 50 percent HCl and 4 mL of 2 percent $K_2S_2O_8$ to each sample; add 5 mL of 50 percent HCl and 6 mL of 2 percent $K_2S_2O_8$ to each standard and blank. Cover with "tuttle" caps. Boil on hot plate for 15 to 20 minutes and let cool.

3.7 Add 4 mL oxalic acid reagent to each sample and 6 mL oxalic acid reagent to each standard and blank. Boil on hot plate for 15 to 20 minutes and let cool.

3.8 Add 15 mL concentrated HCl to each sample and 23 mL concentrated HCl to each standard and blank. Boil on hot plate for 35 to 40 minutes; watch carefully to prevent overboiling and let cool.

3.9 Dilute samples in 50 mL volumetric flasks with deionized water; dilute standards and blanks in 100 mL volumetric flasks with deionized water. Analyze within 48 hours, if possible.

3.10 To determine the final sample concentration, multiply the concentration of the output by the dilution factor.

$$\text{Dilution factor} = \frac{50\ \text{mL}}{X},$$

where

X = volume of sample used.

4. OPERATION OF PERKIN ELMER 5100 ATOMIC ABSORPTION SPECTROMETER (AAS) WITH VARIAN VAPOR GENERATOR ACCESSORY (VGA-76)

4.1 Turn on EDL power supply and rotate knob approximately one-third. To light the EDL, place the lamp lighter in front of the EDL for a few seconds. Set the power to 6 watts.

4.2 Turn on the computer, AAS, printer, autosampler, and the hood over the AAS in the order given.

4.3 Type "idris" on the computer. Type "5100" at the next prompt.

4.4 Turn on the gases at the cylinders. Set the acetylene flow to 12 lb/in^2 and the argon flow to 46 lb/in^2. If the pressure in the acetylene tank is 100 lb/in^2 or less, replace the acetylene tank.

4.5 Clean the sampling probe of AAS by running a thin wire through the hole. Set up the VGA-76 and pump deionized water through the reagent tubes and oxalic acid reagent through the sample tube.

4.6 Verify that the quartz tube is out of the light path. Turn on the flame using the "flame on/off" key. Set the quartz tube in the light path and let it heat at least 30 minutes.

4.7 Enter sample labels by pressing the "program id/wt" key and the "recall" key. Select "labeltmplt" followed by the "enter" key. Press the "section 2" soft key and the "skip weight" soft key. Type the sample labels and dilution factors, and save with the "store" key.

4.8 Check flow rates of the sample and reagent tubes. Replace the sample tube if the rate is less than 7.0 mL/min and the combined flow rate of the two reagent tubes is less than 2.0 mL/min. Place the tubes in their respective reagent containers.

4.9 In the "continuous graphics" mode, autozero the AAS; check the absorbance with the 15 µg/L standard. If the absorbance is less than 0.350, adjust the vertical, horizontal, and rotational knobs to optimize the AAS. Recalibrate to zero and check with the 15 µg/L standard. Repeat this process until the absorbance reads 0.400 with the 15 µg/L standard.

4.10 Autozero the AAS with the probe in the blank sample. Call up the Se program with the "run samples" key. Move the pointer to the "Se-hydride" program and press the "enter" key.

4.11 To start the analyses, press the "execute obey" key and select the "LACA 0211" program. Wait a few seconds for the program to be recalled. During the analysis, make sure the blank sample, standard solution III (reslope solution), and rinse (oxalic acid reagent) containers are filled.

4.12 After the run is completed, press the "display calibration" key to print the calibration curve.

5. SHUTDOWN PROCEDURE

5.1 Turn flame off.

5.2 Run deionized water through reagent tubes and 0.4 percent HNO_3 through sample tube for 10 minutes.

5.3 Turn off VGA-76 and disconnect tubing. Turn on VGA and allow argon gas to flow through the system for 5 to 10 minutes.

5.4 Turn argon and acetylene gases off at the tank and open regulator valve. In the "control atomizer" mode, press "bleed gases" key. Rotate the regulator valves slightly and press the "bleed gases" key again. When the light stops blinking, press the "quit" key on the computer. Turn off autosampler, EDL power supply, printer, AAS, computer, and fan above the AAS in the order given.

5.5 Immerse the liquid gas separator and quartz tube in dilute HNO_3, and empty waste reservoir after each set of analyses.

APPENDIX B--Selenium Speciation Using XAD-8 Resin

1. PREPARATION OF REAGENTS

1.1 0.1N sodium hydroxide (NaOH): Dissolve 4.0 g NaOH in deionized water; dilute to 1,000 mL.

1.2 0.1N hydrochloric acid (HCl): Dissolve 8.3 mL of Baker Insta-Analyzed HCl in deionized water; dilute to 1,000 mL.

2. PREPARATION AND CLEANUP OF XAD-8 RESIN COLUMN

2.1 Rinse XAD-8 resin with deionized water. Prepare columns by packing glass wool at the ends of a column and filling column with XAD-8 resin.

2.2 Put 40 mL 0.1N NaOH solution through the packed column at a flow rate of 1.0 mL/min; discard the effluent.

2.3 Put 40 mL 0.1N HCl solution through the column at a flow rate of 1.0 mL/min; discard the effluent.

2.4 Repeat steps 2.2 and 2.3 two times.

3. PREPARATION OF SAMPLE

3.1 Put 25 to 30 mL of sample through the cleaned resin column at a flow rate of 0.5 mL/min; record weight of solution put through column (original solution). Collect the effluent (solution 1) in an empty tared bottle and weigh; record weight of effluent in appropriate notebook.

3.2 Put an equal volume of 0.1N HCl reagent through the column at the same flow rate to flush out the remaining solution. Add the effluent (solution 2) to the bottle containing solution 1, and record the weight. The resulting solution (solution 3) is the combination of solutions 1 and 2.

3.3 Reverse the column and put 40 mL 0.1N NaOH through the column at a flow rate of 0.5 mL/min. Collect the effluent (solution 4) in an empty tared bottle and weigh; record weight in appropriate notebook.

3.4 Reverse the column again and follow clean-up procedure in steps 2.2 through 2.4.

4. SAMPLE ANALYSES AND CALCULATIONS

4.1 Digest an aliquot of the untreated sample and analyze for total Se.

4.2 Digest an aliquot of solution 3 and analyze for $SeO_4^{2-} + SeO_3^{2-}$.

4.3 Analyze an aliquot of undigested solution 3 for SeO_3^{2-}.

4.4 Multiply the results of 4.1, 4.2, and 4.3 by the following correction factor to obtain concentrations of SeO_3^{2-} and $SeO_4^{2-} + SeO_3^{2-}$ in the original, untreated solution:

$$CF = \frac{\text{weight of solution 3}}{\text{weight of original solution}},$$

where

CF = correction factor for $SeO_4^{2-} + SeO_4^{2-}$ or SeO_4^{2-}

4.5 Digest solution 4 and analyze for organic Se.

4.6 Calculation of concentration of organic Se in the original solution:

$$\text{organic Se} = \frac{\text{(Total Se concentration in solution 4)(weight of solution 4)}}{\text{weight of original solution}}$$

5. QUALITY ASSURANCE

5.1 Pipet two 25 mL samples into test tubes. Spike each sample with 10 µg/L SeO_3^{2-} and 10 µg/L SeO_4^{2-} (0.25 mL of 1,000 µg/L SeO_3^{2-} and 1,000 µg/L SeO_4^{2-} mixed standard). Ten percent of the samples should be spiked.

5.2 Put one spiked sample through the resin column and analyze as the other samples. Another spiked sample is set aside and analyzed for SeO_3^{2-} by direct aspiration.

5.3 Duplicate 10 percent of the samples by taking two aliquots from one container, shaking the bottle between aliquots, and putting them through the resin columns.

APPENDIX C--Procedure for Analyzing Chloride, Nitrate, and Sulfate in Water by Ion Chromatography

1. PREPARATION OF STANDARDS

1.1 *Chloride standard solution I*, 10,000 mg/L Cl: Dissolve 16.4846 g NaCl crystals (dried for 1 hour at 180 °C) in deionized water; dilute to 1,000 mL.

1.2 *Nitrate standard solution I*, 1,000 mg/L NO_3-N: Dissolve 0.7218 g KNO_3 (dried overnight at 105 °C) in deionized water; dilute to 1,000 mL.

1.3 *Sulfate standard solution I*, 50,000 mg/L SO_4: Dissolve 7.394 g Na_2SO_4 (dried for 2 hours at 180 °C) in deionized water; dilute to 1,000 mL.

1.4 *Mixed standard solution I*, 100 mg/L Cl, 10 mg/L NO_3-N, 250 mg/L SO_4: Combine 1.0 mL chloride standard solution I, 1.0 mL nitrate standard solution I, and 2.5 mL sulfate standard solution I; dilute to 100 mL with deionized water. Use a micropipet to dispense the 1.0 mL volumes.

1.5 *Mixed standard solution II*, 250 mg/L Cl, 50 mg/L NO_3-N, 500 mg/L SO_4: Combine 2.5 mL chloride standard solution I, 5.0 mL nitrate standard solution I, and 5.0 mL sulfate standard solution I; dilute to 100 mL with deionized water.

1.6 *Mixed standard solution III*, 500 mg/L Cl, 75 mg/L NO_3-N, 750 mg/L SO_4: Combine 5.0 mL chloride standard solution I, 7.5 mL nitrate standard solution I, and 7.5 mL sulfate standard solution I; dilute to 100 mL with deionized water.

1.7 *Mixed standard solution IV*, 750 mg/L Cl, 100 mg/L NO_3-N, 1,000 mg/L SO_4: Combine 7.5 mL chloride standard solution I, 10.0 mL nitrate standard solution I, and 10.0 mL sulfate standard solution I; dilute to 100 mL with deionized water.

1.8 *Working standard solution I*, 10 mg/L Cl, 1 mg/L NO_3-N, 25 mg/L SO_4: Dilute 10.0 mL mixed standard solution I to 100 mL with deionized water.

1.9 *Working standard solution II*, 25 mg/L Cl, 5 mg/L NO_3-N, 50 mg/L SO_4: Dilute 10.0 mL mixed standard solution II to 100 mL with deionized water.

1.10 *Working standard solution III*, 50 mg/L Cl, 7.5 mg/L NO_3-N, 75 mg/L SO_4: Dilute 10.0 mL mixed standard solution III to 100 mL with deionized water.

1.11 *Working standard solution IV*, 75 mg/L Cl, 10 mg/L NO_3-N, 100 mg/L SO_4: Dilute 10.0 mL mixed standard solution IV to 100 mL with deionized water.

2. PREPARATION OF REAGENTS

2.1 *Regenerant stock solution H_2SO_4*, 0.75 mol/L H_2SO_4: Dilute 41.67 mL of Baker Insta-Analyzed H_2SO_4 to 1,000 mL with carbonate-free deionized water.

2.2 *Regenerant working solution*, 0.0125 mol/L H_2SO_4: Dilute 50.0 mL regenerant stock solution H_2SO_4 to 3.0 L with carbonate-free deionized water.

2.3 *Eluent stock solution*: Dissolve 4.41 g $NaHCO_3$ and 16.32 g Na_2CO_3 in carbonate free deionized water; dilute to 1,000 mL.

2.4 *Eluent working solution*: Dilute 50 mL eluent stock solution to 3.5 L with carbonate-free deionized water.

3. OPERATION OF DIONEX 2010i ION CHROMATOGRAPH

3.1 Verify that all ribbon cables and connectors on the back of the AutoIon 100 controller are connected to system 1. The front panel should be on system 1.

3.2 Turn on nitrogen gas, and set the pressure at 80 to 100 lb/in^2.

3.3 Verify that valve A on the chromatography module (CMA) is turned off, and the eluent line and sample loop are connected to the system 1 portfaces.

3.4 Select the appropriate eluent on the pump module, and prime the pump. Set the eluent flow rate to 2.0 mL/min and the regenerant flow rate to 3 mL/min. Let the system equilibrate at least 30 minutes.

3.5 Fill 5.0 mL sample vials with sample and set the vials in the sample cassettes. Place the sample cassettes in the autosampler and advance vials to the first sample.

3.6 Recall file 1 on the integrator and go through the dialog. Reset the run number to zero (RN=0).

3.7 Program the execution sequence on the controller to start with program 4 and end with program H (halt program).

3.8 Put the conductivity detector, pump module, and CMA on "remote" in the given order. Press "start" on the controller.

APPENDIX D--Procedure for Analyzing Calcium and Magnesium in Water by Ion Chromatography

1. PREPARATION OF STANDARDS

1.1 *Calcium standard solution I*, 1,000 mg/L Ca: Baker Analyzed Reagent.

1.2 *Magnesium standard solution I*, 1,000 mg/L Mg: Baker Analyzed Reagent.

1.3 *Working standard solution I*, 10 mg/L Ca, 5 mg/L Mg: Combine 1.0 mL calcium standard solution I and 0.5 mL magnesium standard solution I; dilute to 100 mL with deionized water. Use a micropipet to dispense the 1.0 mL and 0.5 mL volumes.

1.4 *Working standard solution II*, 25 mg/L Ca, 10 mg/L Mg: Combine 2.5 mL calcium standard solution I and 1.0 mL magnesium standard solution I; dilute to 100 mL with deionized water. Use a micropipet to dispense the 1.0 mL volume.

1.5 *Working standard solution III*, 50 mg/L Ca, 20 mg/L Mg: Combine 5.0 mL calcium standard solution I and 2.0 mL magnesium standard solution I; dilute to 100 mL with deionized water.

1.6 *Working standard solution IV*, 75 mg/L Ca, 30 mg/L Mg: Combine 7.5 mL calcium standard solution I and 3.0 mL magnesium standard solution I; dilute to 100 mL with deionized water.

2. PREPARATION OF REAGENTS

2.1 *Regenerant solution*, 0.04 mol/L tetramethylammonium hydroxide pentahydrate (TMAOH): Dissolve 26.229 g TMAOH in carbonate-free deionized water; dilute to 3.5 L.

2.2 *Eluent solution*, 1.5 mmol/L HCl and 1.5 mmol/L phenylenediamine dihydrochloride (m-PDA•2HCl): Dissolve 0.95 g m-PDA•2HCl and 0.438 mL HCl in carbonate free deionized water; dilute to 3.5 L.

3. OPERATION OF DIONEX 2010i ION CHROMATOGRAPH

3.1 Verify that all ribbon cables and connectors on the back of the controller are connected to system 2. The front panel should be on system 2.

3.2 Turn on nitrogen gas, and set the pressure at 80 to 100 lb/in^2.

3.3 Verify that the eluent line from the pump to the CMA and the sample loop from the autosampler to the CMA are connected to the system 2 portfaces. Turn off valve A on system 2, and turn on valve A on system 1.

3.4 Select the appropriate eluent on the pump module, and prime the pump. Set the eluent flow rate to 2.0 mL/min and the regenerant flow rate to 3 mL/min. Let the system equilibrate at least 30 minutes.

3.5 Fill 0.5 mL sample vials with sample and set the vials in the sample cassettes. Place the sample cassettes in the autosampler and advance vials to the first sample.

3.6 Recall file 7 on the integrator and go through the dialog. Reset the run number to zero (RN=0).

3.7 Program the execution sequence on the controller to start with program 7 and end with program H (halt program).

3.8 Put the conductivity detector, pump module, and CMA on "remote" in the given order. Press "start" on the controller.

APPENDIX E--Procedure for Analyzing Sodium and Potassium in Water by Ion Chromatography

1. PREPARATION OF STANDARDS

1.1 *Sodium standard solution I*, 1,000 mg/L: Baker Analyzed Reagent.

1.2 *Potassium standard solution I*, 1,000 mg/L: Baker Analyzed Reagent.

1.3 *Working standard solution I*, 10 mg/L Na, 1 mg/L K: Combine 1.0 mL sodium standard solution I and 0.1 mL potassium standard solution I; dilute to 100 mL with deionized water.

1.4 *Working standard solution II*, 25 mg/L Na, 3 mg/L K: Combine 2.5 mL sodium standard solution I and 0.3 mL potassium standard solution I; dilute to 100 mL with deionized water.

1.5 *Working standard solution III*, 50 mg/L Na, 5 mg/L K: Combine 5.0 mL sodium standard solution I and 0.5 mL potassium standard solution I; dilute to 100 mL with deionized water.

1.6 *Working standard solution IV*, 75 mg/L Na, 7.5 mg/L K: Combine 7.5 mL sodium standard solution I and 0.75 mL potassium standard solution I; dilute to 100 mL with deionized water.

2. PREPARATION OF REAGENTS

2.1 *Regenerant solution*, 0.04 mol/L TMAOH: Dissolve 26.229 g TMAOH in carbonate-free deionized water; dilute to 3.5 L.

2.2 *Eluent solution*, 5 mmol/L HCl: Dilute 1.44 mL HCl to 3.5 L with carbonate-free deionized water.

3. OPERATION OF DIONEX 2010i ION CHROMATOGRAPH

3.1 Verify that all ribbon cables and connectors on the back of the controller are connected to system 2. The front panel should be on system 2.

3.2 Turn on nitrogen gas, and set the pressure at 80 to 100 lb/in^2.

3.3 Verify that the eluent line from the pump to the CMA and the sample loop from the autosampler to the CMA are connected to the system 2 portfaces. Turn on valve A on system 2 and valve A on system 1.

3.4 Select the appropriate eluent on the pump module and prime the pump. Set the eluent flow rate to 2.0 mL/min and the regenerant flow rate to 3 mL/min. Let the system equilibrate at least 30 minutes.

3.5 Fill 0.5 mL sample vials with sample and set the vials in the sample cassettes. Place the sample cassettes in the autosampler and advance vials to the first sample.

3.6 Recall file 6 on the integrator and go through the dialog. Reset the run number to zero (RN=0).

3.7 Program the execution sequence on the controller to start with program 6 and end with program H (halt program).

3.8 Put the conductivity detector, pump module, and CMA on "remote" in the given order. Press "start" on the controller.

APPENDIX F--Operation of Radiometer pH/Millivolt Meter to Measure pH

1. Switch the meter to the pH mode.

2. Rinse pH electrode thoroughly with deionized water. Measure the temperature of the buffer solution and record; discard solution.

3. To condition the probe, immerse in an aliquot of pH 7 buffer solution; discard solution. Repeat two times.

4. Obtain a fresh aliquot of pH 7 buffer solution and immerse the pH electrode in the solution. Press the "cal" key and calibrate the temperature to the temperature of the buffer solution.

5. Press the "cal" key again and enter the actual pH value of the buffer solution.

6. Wait for a stable reading and then press the "cal" key.

7. Rinse pH electrode with deionized water. Repeat steps 2 through 6 with the pH 10 buffer solution.

8. If a 3-point calibration is desired, use a third buffer solution and proceed with steps 2 through 6.

9. Record the sensitivity of the instrument after calibration. If sensitivity is not at least 98.5 percent, recalibrate the meter and check the freshness of the buffers.

10. When calibration is complete, press the "pH" key. The meter is now ready to measure samples. Immerse the cleaned pH electrode in the sample and wait for a stable reading before recording pH.

APPENDIX G--Measurement of Redox Potential

1. PLATINUM ELECTRODE CALIBRATION

1.1 Calibrate pH electrode using pH 7 and pH 4 buffers (see appendix F).

1.2 Place enough Quinhydrone in buffers so there is excess solid, and allow to equilibrate. Record pH values for the pH 7 and pH 4 buffers containing Quinhydrone.

1.3 Turn pH/millivolt meter off, replace pH electrode with a platinum electrode to measure redox potential, and turn the meter setting to mV.

1.4 Immerse platinum electrode in the pH 7 buffer with Quinhydrone. Record the electromotive force (EMF) value in mV, $EMF_{(pH7)}$.

1.5 Rinse platinum electrode with deionized water.

1.6. Repeat steps 1.4 and 1.5, using the pH 4 buffer with Quinhydrone, $EMF_{(pH4)}$.

2. CALCULATION OF REDOX POTENTIAL

2.1 The redox potential relative to the standard hydrogen electrode potential (Eh) is calculated as:

$$Eh = EMF + E(ref)$$

where

EMF = electromotive force measured using the platinum electrode, and

E(ref) = potential of the reference half cell (theoretically, 202 mV for Ag/AgCl, saturated KCl; 244 mV for $Hg/HgCl_2$, saturated KCl at 25 °C).

2.1a For a saturated solution of Quinhydrone at a given pH:

$$EMF = E^0(Quinhydrone) - E(ref) - EN(pH)$$

where

E^0(Quinhydrone) = the standard half-cell potential (700 mV) for a saturated solution of Quinhydrone, and

EN = the Nernst potential (theoretically, 59.2 mV at 25 °C)

2.1b Solve for E(ref) and EN, from the EMF and pH measurements of saturated Quinhydrone solutions in pH 7 and pH 4 buffers:

$$EMF_{(pH7)} = E^0(Quinhydrone) - E(ref) - EN_{(pH7)}$$

$$EMF_{(pH4)} = E^0(Quinhydrone) - E(ref) - EN_{(pH4)}$$

2.2 An example:

2.2a Electrode calibration using saturated Quinhydrone solution:

Quinhydrone	pH	EMF (mV)
pH 7 buffer	7.00	86
pH 4 buffer	3.99	264

$EMF_{(pH7)} = 86 = 700 - E(ref) - EN(7.00)$
$EMF_{(pH4)} = 264 = 700 - E(ref) - EN(3.99)$

Subtracting equations:

$178 = EN(3.01)$

$EN = 59.14$

Solving for E(ref):

$86 = 700 - E(ref) - 59.14(7.00)$
$E(ref) = 200$ mV

2.2b Calculation of Eh and pE (negative logarithm of the electron activity)

Sample reading:

EMF = 262 mV
Eh = EMF + E(ref) (calculation 2.1)
Eh = 262 + 200
Eh = 462 mV

$$pE = \frac{Eh}{59.2} = \frac{462}{59.2} = 7.80.$$

APPENDIX H--Instrument Maintenance

1. RADIOMETER CONDUCTIVITY METER

1.1 Verify that the conductivity cell is clean by flushing it with deionized water three times. Take the temperature of a conductivity standard close to the sample value and adjust to this temperature by pressing the "t" key and using the up or down arrow key.

1.2 Condition the conductivity cell by flushing it three times with the conductivity standard, being careful not to pipet any solution into the bulb. When measurements are made, the solution must cover the three metal bands inside the cell, and there must not be any air bubbles on the glass surfaces.

1.3 Correct the conductivity reading of the standard by adjusting the readout with the up or down arrow key.

1.4 Before reading the conductivity of a sample, rinse the conductivity cell three times with deionized water. Shake the sample bottle thoroughly, and flush the cell three times with the sample. After the third flush, wait for the signal to stabilize before recording the reading.

1.5 The conductivity of the standard should be read after every five samples; recalibrate the meter if necessary.

1.6 When not in use, the conductivity cell should be stored in deionized water.

2. ATOMIC ABSORPTION SPECTROMETER AND HYDRIDE GENERATOR

2.1 Check and/or drain moisture trap on the air line to the instrument monthly.

2.2 Clean autosampler surface after each use.

2.3 Check flow rates of each pump tube on the hydride generator before each run. Change sample tubing every week and reagent tubing every month; change sample tubing and reagent tubing more frequently if they do not meet the operating procedures criteria in appendix A.

2.4 Assess the performance of each quartz-tube absorption cell by regularly monitoring absorbance measurements of standards and by recording the hours of use. When the absorbance measurement of the highest standard falls below 0.350 absorbance units, the cell should be discarded (Varian Corporation, 1984). The number of hours a quartz-tube absorption cell has been used is monitored because it has been observed that the performance of the tube begins to degrade after about 40 hours of use.

3. ION CHROMATOGRAPH

3.1 Oil pump monthly or bimonthly, depending on use.

3.2 Check daily for liquid leaks along the element, suppressor, and sample lines and valves.

3.3 Replace bed supports on the separator columns when the pump pressure exceeds the manufacturer's recommended pressure limit (Dionex Corporation, 1985b).

3.4 Clean separator columns if column contamination is suspected (Dionex Corporation, 1985b).

3.5 Clean suppressors if contamination is suspected and/or pump pressure on the suppressor exceeds 50 lb/in^2 (Dionex Corporation, 1986, 1987).

APPENDIX I--Total Alkalinity by Incremental Titration[1]

1. Standardize radiometer pH/millivolt meter according to instructions given in appendix F.

2. Fill micrometer buret (2.0 capacity) with 0.01639N H_2SO_4.

3. Rinse pH electrode 3 times with sample.

4. Take a 4 mL aliquot of sample, dispense in a 10 mL microbeaker, and insert pH electrode. Measure and record the pH value.

5. Insert Teflon-coated star stirring bar and turn on magnetic stirrer.

6. Titrate directly to pH 5.0 with H_2SO_4, and record volume of titrate used. Then add H_2SO_4 in 0.002 mL increments, recording the pH and volume of titrant. Allow 5 to 10 seconds for equilibration between additions of H_2SO_4. Continue until pH 4.0 is reached.

7. Determine the endpoint of the titration by either (1) plotting the change in pH divided by the change in volume of titrant as a function of the volume of titrant; the endpoint occurs at the maximum change, or (2) plotting the pH as a function of titrant volume; the endpoint occurs at the inflection point of the resulting curve.

8. To calculate total alkalinity:

$$\text{Total alkalinity as } CaCO_3\,(mg/L) = \frac{1{,}000}{mL(sample)} \times \left[mL(H_2SO_4) \times 0.8202\right]$$

APPENDIX J--Saturation Extracts

1. Wash all items (plastic container and lid, spatula, Buchner funnel, test tubes, filtering apparatus, and sample bottles) with phosphate-free laboratory detergent and warm water. Rinse well. Acid-rinse items, except the spatula, with 10 percent HCl, and rinse three times with deionized water. Set in drying rack and dry completely.

2. Weigh plastic container and weigh out approximately 400 g of air-dried soil; record weight in notebook.

3. Add deionized water to soil and stir to obtain a homogenous, saturated soil-water paste. When the soil paste glistens and slides freely off the spatula in one lump, it is considered saturated.

4. When soil is saturated, weigh container and paste mixture.

5. Cover with snaptight lid, and allow sample to stand overnight.

6. Recheck paste mixture for saturation before use. If paste is too wet, add additional soil to the paste mixture (record the amount of soil added); if paste is too dry, add more deionized water.

7. Transfer paste mixture to Buchner funnel covered with a 11.0 cm ashless filter paper. Connect to vacuum filtration system, and collect filtrate in test tube.

8. Measure pH and specific-conductance of filtrate.

9. Pour filtrate into filtering apparatus and filter through 0.45 µm membrane filter; divide solution as follows:
   a. for major ion analyses, 20 mL of unacidified sample.
   b. for Se analyses, remaining solution to be acidified with 1 drop (0.05 mL) HCl per 10 mL of sample or until pH <2.

10. Store all samples at 4 °C.

[1]General theory and procedure for larger sample volumes is given by Wood (1976).

☆U.S. GOVERNMENT PRINTING OFFICE: 1992 - 686-025/79050

This report was prepared by the U.S. Geological Survey in cooperation with the San Joaquin Valley Drainage Program and as part of the Regional Aquifer-System Analysis (RASA) Program of the U.S. Geological Survey.

The San Joaquin Valley Drainage Program was established in mid-1984 and is a cooperative effort of the U.S. Bureau of Reclamation, U.S. Fish and Wildlife Service, U.S. Geological Survey, California Department of Fish and Game, and California Department of Water Resources. The purposes of the program are to investigate the problems associated with the drainage of agricultural lands in the San Joaquin Valley and to develop solutions to those problems. Consistent with these purposes, program objectives address the following key concerns: (1) public health, (2) surface- and ground-water resources, (3) agricultural productivity, and (4) fish and wildlife resources.

Inquiries concerning the San Joaquin Valley Drainage Program may be directed to:

San Joaquin Valley Drainage Program
Federal-State Interagency Study Team
2800 Cottage Way, Room W-2143
Sacramento, California 95825-1898

The RASA Program of the U.S. Geological Survey was started in 1978 following a congressional mandate to develop quantitative appraisals of the major ground-water systems of the United States. The RASA Program represents a systematic effort to study a number of the Nation's most important aquifer systems, which in aggregate underlie much of the country and which represent an important component of the Nation's total water supply. In general, the boundaries of these studies are identified by the hydrologic extent of each system, and accordingly transcend the political subdivisions to which investigations were often arbitrarily limited in the past. The broad objectives for each study are to assemble geologic, hydrologic, and geochemical information, to analyze and develop an understanding of the system, and to develop predictive capabilities that will contribute to the effective management of the system. The Central Valley RASA study, which focused on the hydrology and geochemistry of ground water in the Central Valley of California, began in 1979. Phase II of the Central Valley RASA began in 1984 and is in progress. The focus during this second phase is on more detailed study of the hydrology and geochemistry of ground water in the San Joaquin Valley, which is the southern half of the Central Valley.