Methods of Analysis by the U.S. Geological Survey
National Water Quality Laboratory—Determination of
Whole-Water Recoverable Arsenic, Boron, and Vanadium
Using Inductively Coupled Plasma–Mass Spectrometry

By John R. Garbarino

U.S. GEOLOGICAL SURVEY

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U.S. GEOLOGICAL SURVEY

Charles G. Groat, Director

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
liter (L)	2.64×10^{-1}	gallon
microgram (μg)	3.53×10^{-8}	ounce, avoirdupois
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter (mL)	2.64×10^{-4}	gallon

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5 \ (°C) + 32.$$

Abbreviated water-quality units used in this report are as follows:

mg/L	milligram per liter
μg/L	microgram per liter
μS/cm	microsiemens per centimeter at 25°C

Other abbreviations also used in this report:

amu	atomic mass unit
ASTM	American Society for Testing and Materials
DCP–AES	direct current plasma–atomic emission spectrometry
FEP	fluorinated ethylene propylene (Teflon)
GF–AAS	graphite furnace–atomic absorption spectrophotometry
HCl	hydrochloric acid
HG–AAS	hydride generation–atomic absorption spectrophotometry
HNO_3	nitric acid
ICP–AES	inductively coupled plasma–atomic emission spectrometry, also known as inductively coupled plasma–optical emission spectrometry (ICP–OES)
ICP–MS	inductively coupled plasma–mass spectrometry
MDL(s)	method detection limit(s)
MRL(s)	minimum reporting level(s)
MPV(s)	most probable value(s)
NWQL	National Water Quality Laboratory
SRWS(s)	U.S. Geological Survey Standard Reference Water Sample(s)
USGS	U.S. Geological Survey
<	less than
$\leq$	less than or equal to
$\pm$	plus or minus

Definitions:

MDL The method detection limit (MDL) is defined as the minimum concentration of an element that can be measured and reported with 99-percent confidence that the concentration is greater than zero and is determined from analysis of a sample in a given matrix that contains the element of interest (U.S. Environmental Protection Agency, 1997).

MPV The most probable value (MPV) is equal to the median value for numerous interlaboratory analyses that use multiple analytical methods.

Whole-water recoverable. Pertains to the constituents in solution after a representative water-suspended-sediment sample is digested (usually by using dilute acid solution). Complete dissolution of particulate matter often is not achieved by the digestion treatment, and thus the determination represents something less than the "total" amount (that is, less than 95 percent) of the constituent present in the dissolved and suspended phases of the sample. Equivalent digestion procedures would be required of all laboratories that perform such analyses to achieve comparability of analytical data, because different digestion procedures are likely to produce different analytical results.

Inventory of Selected Freshwater-Ecology Studies from the New England Coastal Basins (Maine, New Hampshire, Massachusetts, Rhode Island), 1937-97

By Steven Tessler, James F. Coles, and Karen M. Beaulieu

Abstract

An inventory of published studies that address freshwater ecology within the New England Coastal Basins was created through computerized bibliographic literature searches and consultation with environmental agencies. Assembled papers were classified to associate their contents with one or more states, ecoregions, river basins, and ecological topics. Full references and their classifications were entered into a bibliographic software program and then exported to a data-base application to generate a checklist summary of study contents. This report presents a listing and classification of 154 selected studies, published between 1937 and 1997, that provide background knowledge and serve as general aquatic-ecology references for the New England Coastal Basins study area.

INTRODUCTION

The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) is designed to assess the status and trends in the quality of the Nation's water resources and to develop an understanding of the major factors that affect water quality (Hirsch and others, 1988; Leahy and others, 1990). To achieve these goals, the NAWQA program uses an integrated approach of investigating physical, chemical, and biological components of an aquatic system to assess water quality on a basinwide scale (Gurtz, 1994). Nationally, the NAWQA program consists of 59 river basins or aquifer systems, termed "study units," that collectively account for about two-thirds of the Nation's population served by public water supply (Leahy and Wilber, 1991). The New England Coastal Basins (NECB) Study Unit encompasses 23,000 mi^2 in western and central Maine, central and eastern New Hampshire, eastern Massachusetts, most of Rhode Island, and a small part of Connecticut (fig. 1). The study unit includes the drainage basins of the Kennebec, Androscoggin, Saco, Merrimack, Charles, Blackstone, Taunton, and Pawcatuck Rivers, as well as small coastal drainages between these larger river basins (fig. 2).

One of the tasks in the planning stages for the NECB study was to identify and review previous studies that are relevant to understanding water quality and aquatic ecosystems within the study unit. This information is used to help identify prevailing water-quality issues, to assess the status of water-quality conditions and biological communities in streams, and to allocate NAWQA resources to complement previous or existing studies. These previous studies can be identified through a combination of computerized literature searches and consultation with agencies and researchers in the region. Organizing and classifying references by their relevance to particular geographic regions or subject areas allows the references to be used more efficiently.
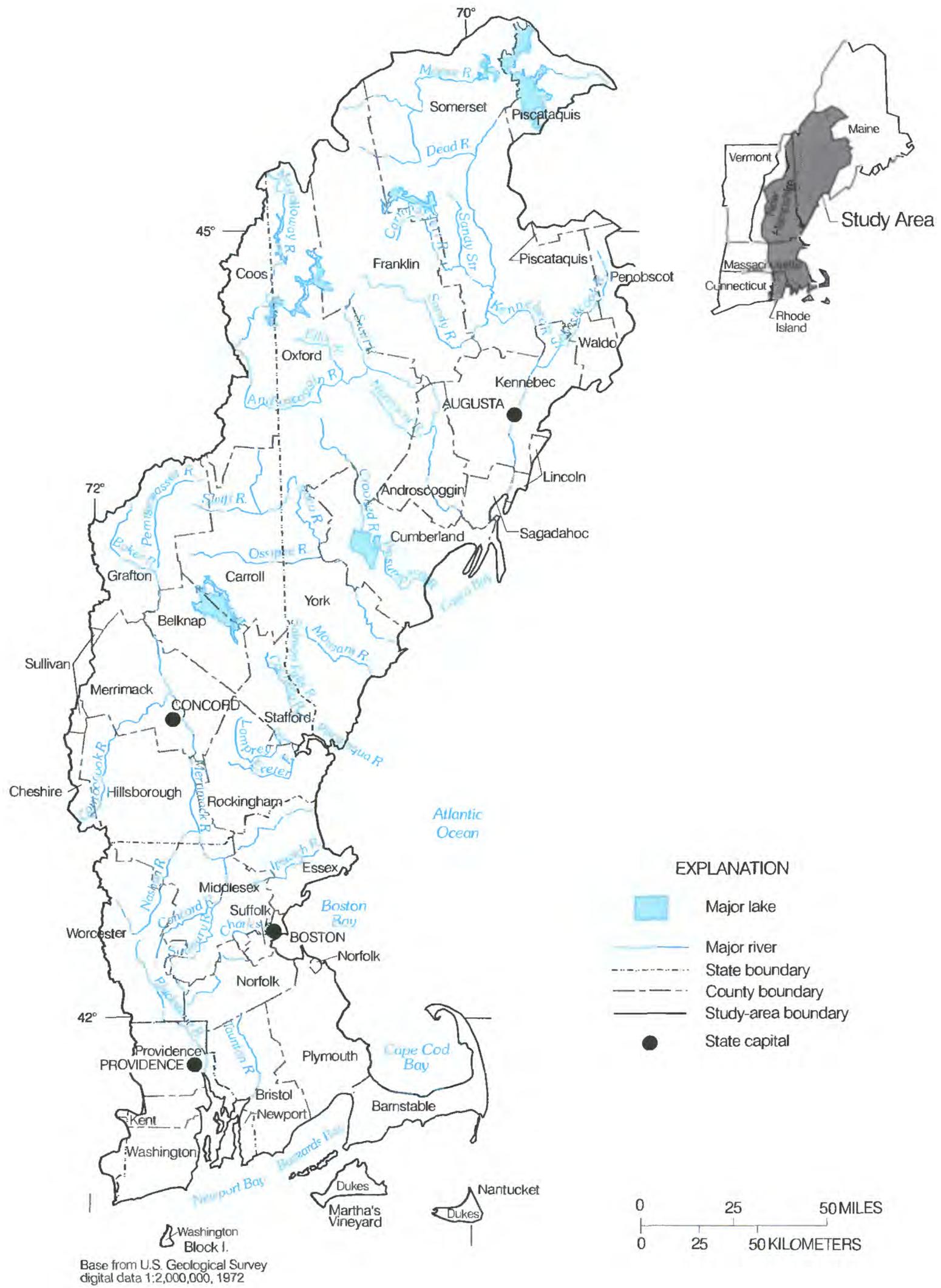
Figure 1. Location and major rivers of the New England Coastal Basins Study Unit.
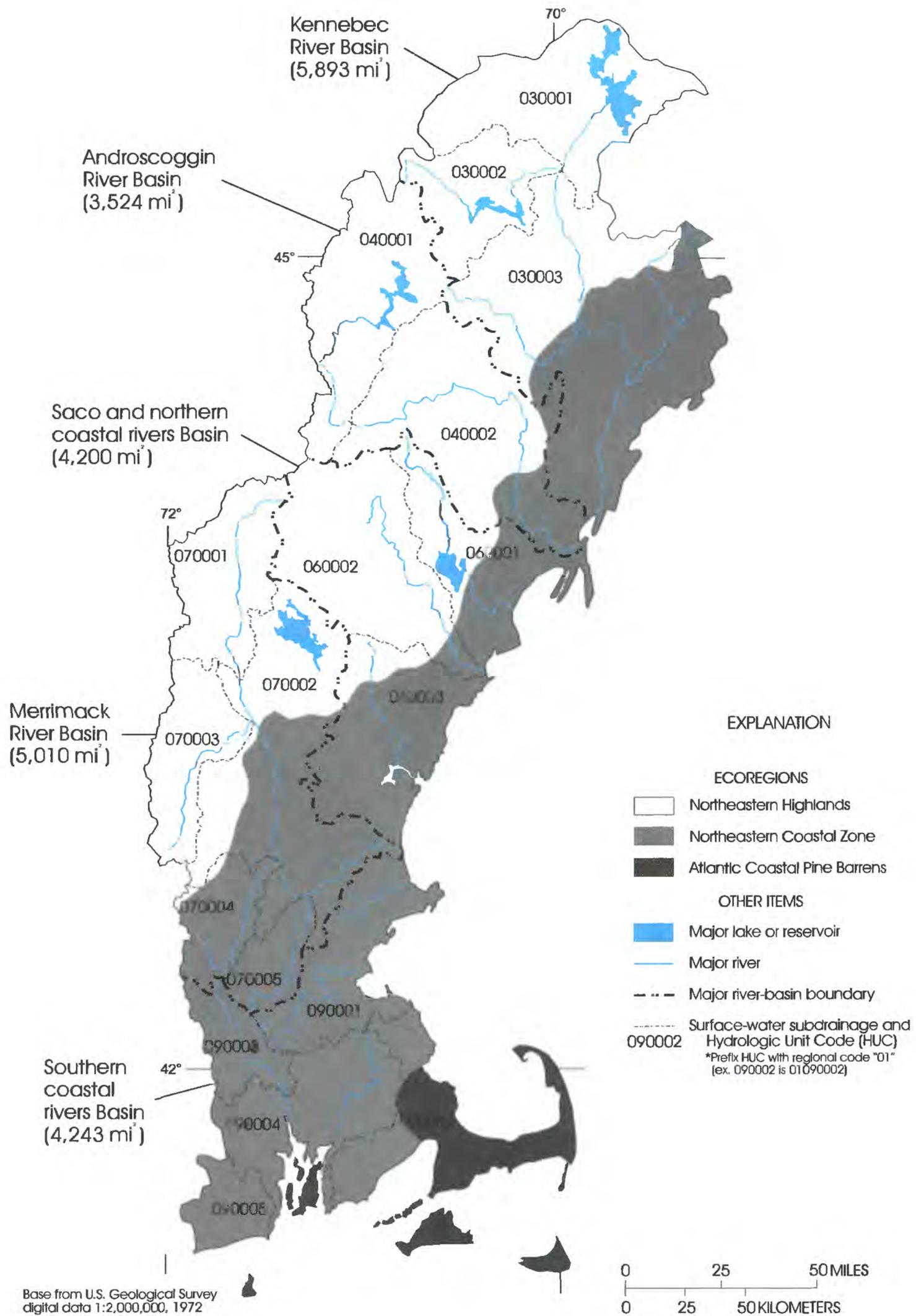
Figure 2. Ecoregions and river basins of the New England Coastal Basins Study Unit.

Purpose and Scope

This report presents an inventory of selected published freshwater ecological studies within the NECB Study Unit. Selection of a citation for inclusion in this report required that the work had been done in a freshwater system (river, stream, lake, or pond) and focused on at least one of the following ecological subjects of field study relevant to the NAWQA program: algae, macroinvertebrates, fish, habitat, and tissue or sediment contaminants. Therefore, studies focused solely on wetlands, estuarine or marine coastal waters, microbiology, or nonfish vertebrates were not targeted. Studies were identified through a computerized literature search and by contacting state and Federal agencies and researchers who collect freshwater ecological data in the NECB Study Unit. Citation and classification information for the studies was entered into a computerized reference library and then processed to create tables that facilitate quick identification of the scope of each study. The general methods used to assemble the bibliography and classify citations are presented in this report, along with tables that summarize the collection of references found and the information in each reference by state, ecoregion, major river basin, and ecological topic. The listings in this report provide NECB staff and others with a means to (1) quickly identify previous or ongoing studies with a focus on particular water-quality issues in geographic, ecoregion, or hydrologic-basin areas, (2) identify references reporting the known status of biological communities and contaminant conditions, (3) identify researchers with a working knowledge of the area and issues, and (4) assess the potential for allocation of field personnel and laboratory resources to complement previous and ongoing studies.

Methods Used to Assemble the Bibliography

Most of the references were identified by means of data-base searches over the Internet, although direct contacts with state- and Federal-agency personnel resulted in useful and important references that otherwise would have been overlooked. Although bibliographic data bases provide a rapid means of assembling lists of citations that are candidates for a focused reference collection, the process of assembling a useful list of uniformly formatted references from those available is challenging and involves several additional steps. An appendix in this report provides a more detailed explanation of the strategy and some of the methods and mechanics that were used to assemble the computerized bibliography and produce the citation tables for this report, including search-string development, a listing of the bibliographic data bases that contributed citations to this report, use of bibliographic software for basic citation management, and a custom data-base application to enable other uses and format options for the bibliography that are not supported in the citation-management tool.

Acknowledgments

CLASSIFICATION OF ECOLOGICAL STUDIES

For all citations to be included in our bibliographic data base, the states, ecoregions, and river basins in which the studies took place were identified, as well as the ecological topics addressed in the studies. By assigning each ecological study to multiple categories, studies can be identified as relevant to a specific topic and location.

Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Whole-Water Recoverable Arsenic, Boron, and Vanadium Using Inductively Coupled Plasma–Mass Spectrometry

By John R. Garbarino

ABSTRACT

Analysis of in-bottle digestate by using the inductively coupled plasma–mass spectrometric (ICP–MS) method has been expanded to include arsenic, boron, and vanadium. Whole-water samples are digested by using either the hydrochloric acid in-bottle digestion procedure or the nitric acid in-bottle digestion procedure. When the hydrochloric acid in-bottle digestion procedure is used, chloride must be removed from the digestate by subboiling evaporation before arsenic and vanadium can be accurately determined. Method detection limits for these elements are now 10 to 100 times lower than U.S. Geological Survey (USGS) methods using hydride generation–atomic absorption spectrophotometry (HG–AAS) and inductively coupled plasma–atomic emission spectrometry (ICP–AES), thus providing lower variability at ambient concentrations. The bias and variability of the methods were determined by using results from spike recoveries, standard reference materials, and validation samples. Spike recoveries in reagent-water, surface-water, ground-water, and whole-water recoverable matrices averaged 90 percent for seven replicates; spike recoveries were biased from 25 to 35 percent low for the ground-water matrix because of the abnormally high iron concentration. Results for reference material were within one standard deviation of the most probable value. There was no significant difference between the results from ICP–MS and HG–AAS or ICP–AES methods for the natural whole-water samples that were analyzed.

INTRODUCTION

The U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) offers several methods for the determination of recoverable arsenic, boron, and vanadium in whole-water samples. Former USGS methods use single-element quantification, such as graphite furnace– (GF–AAS), and hydride generation–atomic absorption spectrophotometry (HG–AAS), direct current plasma–atomic emission spectrometry (DCP–AES), or the simultaneous multielement technique of inductively coupled plasma–atomic emission spectrometry (ICP–AES). This report provides data that validates the addition of the aforementioned elements to the existing inductively coupled plasma–mass spectrometric (ICP–MS) method.

Elements that are being added to the existing multielement ICP–MS method and their corresponding former USGS methods of analysis are listed in the following table. Arsenic, boron, and vanadium have been added to method I-4471-97 (see Garbarino and Struzeski, 1998).

Element	GF–AAS	HG–AAS	DCP–AES	ICP–AES
Arsenic	✓	✓		
Boron			✓	✓
Vanadium				✓

ICP–MS is compared to one former method from the list in the preceding table. In all comparisons, the most current (as of January 1998) former method is used. Whole-water recoverable arsenic by ICP–MS is compared to the former HG–AAS method. The digestion of whole-water samples for recoverable arsenic by the former HG–AAS method uses an online sulfuric acid/potassium persulfate digestion. In contrast, the ICP–MS method uses an in-bottle digestion procedure to determine whole-water recoverable concentrations. Whole-water recoverable boron and vanadium by ICP–MS is compared to the former ICP–AES method.

Ambient concentrations of recoverable arsenic and vanadium cannot be accurately measured by ICP–MS in digestates prepared by using the hydrochloric acid (HCl) in-bottle digestion procedure (Hoffman and others, 1996) because of interferences from chloride. When whole-water recoverable arsenic and vanadium are being determined by ICP–MS, either the HCl must be removed from the HCl in-bottle digest through subboiling evapora-tion (see Appendix in Garbarino and Hoffman, 1999) or nitric acid (HNO3) in-bottle digestion must be used (Garbarino and Hoffman, 1999).

The expanded method was developed by the USGS for use at the NWQL. The expanded method supplements other official USGS inorganic methods (Fishman, 1993; Fishman and Friedman, 1989; Garbarino, and Struzeski, 1998). The new elements will be available in the whole-water recoverable ICP–MS schedules.

ANALYTICAL METHOD

Application

The determination of whole-water recoverable arsenic, boron, and vanadium have been added to ICP–MS method I-4471-97. Details of this method are provided in Garbarino and Struzeski (1998). Whole water is digested using either the HCl in-bottle procedure described by Hoffman and others (1996) or the HNO_3 in-bottle procedure described by Garbarino and Hoffman (1999). Whenever whole-water recoverable arsenic and vanadium are being determined in the HCl in-bottle digest, however, the HCl must be removed from the digest by subboiling evaporation (see Appendix in Garbarino and Hoffman, 1999). The new laboratory code, parameter code, method code, and reporting unit for each element are listed in table 1.

Table 1. Inorganic constituents and codes

Metals, Acid Digestion, Whole-Water Recoverable Method I-4471-97

[µg/L, microgram per liter]

Element	Lab code	Parameter and method codes
Arsenic, µg/L	2500	01002F
Boron, µg/L	2501	01022C
Vanadium, µg/L	2502	01087B

The short-term method detection limits (MDLs) and analytical concentration ranges are listed in table 2. The elemental linear dynamic range for ICP–MS is greater than 1 mg/L when calibrating both the pulse and analog measurement modes. Short-term MDLs were calculated by using U.S. Environmental Protection Agency's (1997) definition and represent pooled averages on the basis of four MDLs determined on

Table 2. Former methods and inductively coupled plasma–mass spectrometric method detection limits for new elements determined in whole-water digestate

[All concentrations are in micrograms per liter; MRL, minimum reporting level; MDL, method detection limit; DCP–AES, direct current plasma–atomic emission spectrometry; GF–AAS, stabilized temperature graphite furnace–atomic absorption spectrophotometry; HG–AAS, hydride generation–atomic absorption spectrophotometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry]

Element	Former methods			ICP–MS
	Technique	MRL	Upper concentration limit (without dilution)	Short-term MDL
Arsenic	GF–AAS	0.9	50	0.07
	HG–AAS	1	20	
Boron	DCP–AES	10	10,000	[1] 0.5
	ICP–AES	13	10,000	
Vanadium	ICP–AES	10	10,000	0.08

[1]Method detection limit for boron is limited by reagent blank concentration.

different days over several weeks. The MDLs have not been established for former methods, therefore, minimum-reporting levels (MRLs) are listed that are probably within a factor of 5 of the MDL.

Summary of Method

The ICP–MS method has been described previously in Garbarino and Struzeski (1998). The following sections only provide additional information specific to the elements that are being added to the method.

Interferences

Physical and spectral interference associated with the determination of arsenic, boron, and vanadium by ICP–MS are documented in Horlick and Shao (1992), Garbarino and Taylor (1994), Garbarino and Struzeski (1998), and Garbarino (1999).

3.1 *Physical interferences.* Internal standards are used to minimize effects from sample transport, instrumental drift, and

matrix-induced fluctuations in plasma characteristics. Typical internal standard elements are $^{72}Ge^+$, $^{115}In^+$, and $^{209}Bi^+$ (see Garbarino and Struzeski, 1998; Garbarino, 1999). Alternative isotopes may be substituted after ensuring that there are no spectral interferences associated with the new selections.

Memory effects related to sample transport are negligible for most elements normally present in whole-water digestate. Carryover from samples that have arsenic and boron concentrations less than or equal to 200 µg/L is negligible when the sample introduction described in Garbarino and Struzeski (1998) is used. Vanadium, however, did not recover to reagent-blank intensity levels within the rinse period; vanadium intensities were 2 times greater than reagent-blank level. Fortunately, vanadium concentrations rarely exceed 100 µg/L. Nevertheless, the analyst must review all analytical results to ensure that errors from carryover are minimized.

Sample matrix composition could also affect the bias and variability of ICP–MS determinations. The use of internal standardization compensates for most matrix effects, however, some matrix interferences remain problematic. Matrix composition can suppress the ionization efficiency of the plasma and result in negatively biased elemental concentrations, especially for lighter elements (see Garbarino, 1999). This suppression can be significant for whole-water matrices because of the level of dissolved solid concentrations.

3.2 *Spectral interferences.* There are no isobaric interferences on arsenic, boron, or vanadium. Chloride-associated molecular-ion interferences have been documented on arsenic ($^{75}As^+$) and vanadium ($^{51}V^+$). The molecular ions $^{40}Ar^{35}Cl^+$ and $^{35}Cl^{16}O^+$ interfere with $^{75}As^+$ and $^{51}V^+$, respectively. The standard equation used to correct for chloride interference on arsenic uses a term based on a measurement made at 82 amu. If the bromide concentration in a sample exceeds about 100 µg/L, the standard correction equation will give positively biased arsenic results. All the equations used to correct molecular-ion interference on arsenic and vanadium are described by Garbarino (1999). Interference corrections on arsenic and vanadium have been shown to be acceptable for sample solutions that have chloride concentrations less than 5,000 mg/L. There are no significant interferences on arsenic, boron, or vanadium from doubly charged ions.

Apparatus, Instrumentation, and Operating Conditions

Instrumentation previously described in a whole-water recoverable method by Garbarino and Struzeski (1998) has been replaced with a Perkin-Elmer Elan 6000 ICP–MS. Details of instrument operation are fully documented in the NWQL Standard Operating Procedure IM0011.1 (T.M. Struzeski, U.S. Geological Survey, written commun., 1998) and by Garbarino (1999). The standard Perkin-Elmer cross-flow nebulizer and spray chamber is used to introduce samples. The cross-flow nebulizer resists clogging (≤ 0.5 percent total dissolved solids) and is chemically inert. Other nebulizer designs can be used but must be resistant to clogging and capable of providing MDLs that are within a factor of two of those listed in table 2.

Primary isotopes used to determine recoverable concentrations for the new elements are as follows (amu, atomic mass unit):

Arsenic	75 amu	Boron	11 amu
Vanadium	51 amu		

Reagents and Calibration Standards

A report by Garbarino and Struzeski (1998) describes the preparation of calibration standards, internal standard solution, and the performance check solution. New elements are calibrated by including them in the multielement standards described in method I-4471-97 at the same concentrations. Multielement standards are prepared in a matrix that is matched to the acid concentration of the samples being analyzed. Arsenic and vanadium must not be included in a multielement standard that contains bromide or chloride. The interference solution has been added to verify the accuracy of interference corrections on arsenic and vanadium.

ASTM Type I reagent water (American Society for Testing and Materials, 1995, p. 122–124), spectroscopic grade commercial standards, and ultrapure acids must be used to prepare all solutions.

All percentages represent volume-to-volume ratios. All concentrated acids and commercial standards must be verified to contain concentrations of concomitant elements that are less than the MDLs after the prescribed dilution. Every solution must be stored in a designated FEP Teflon bottle. Use clean Type A glass volumetric flasks to prepare all solutions except for those containing boron. Regularly verify the accuracy of all pipets and volumetric flasks for preparing standard solutions.

5.1   *Nitric acid* (HNO_3): Concentrated, specific gravity 1.41.

5.2   *Hydrochloric acid* (HCl): Concentrated, specific gravity 1.19.

5.3   *Calibration blank*: Reagent water is acidified to either 3 percent HNO_3 when using the HNO_3 in-bottle procedure or 1 percent HNO_3 when using the HCl in-bottle procedure.

5.4   *Commercial single-element standard solutions*, 1.00 mL = 10 mg preserved in HNO_3 for each of the following: As, B (in water), and V.

Chloride: 1.00 mL = 100 mg in water and
Bromide: 1.00 mL = 1.0 mg in water

5.6   *Multielement stock solution I*, 1.00 mL = 0.010 mg of As, B (in water), and V: Dilute 1.0 mL of each commercial single-element standard to 1,000 mL in a volumetric flask with 1 percent HNO_3. Store in a clean designated FEP Teflon bottle.

5.7   *Multielement calibration standard I*, 1.00 mL = 0.025 μg of As, B (in water), and V: Include new elements in an existing calibration standard by diluting 0.250 mL of multielement stock solution I in a 100-mL volumetric flask with the suitable calibration blank.

5.8   *Multielement calibration standard II*, 1.00 mL = 0.100 μg of As, B (in water), and V: Include new elements in an existing calibration standard by diluting 1.0 mL of multielement stock solution I in a 100-mL volumetric flask with the suitable calibration blank.

5.9   *Multielement calibration standard III*, 1.00 mL = 0.200 μg of As, B (in water), and V: Include new elements in an existing calibration standard by diluting 2.0 mL of multielement stock solution I in a 100-mL volumetric flask with the suitable calibration blank.

5.10   *Interference check standard*, 1.00 mL = 0.50 mg Cl, 0.005 mg Br, and 0.025 μg As and V: Dilute 5.0 mL of the commercial chloride standard solution, 0.50 mL of commercial bromide standard solution, and 2.5 mL of multielement stock solution I in a 1,000-mL volumetric flask with the suitable calibration blank. Store in a clean designated FEP Teflon bottle.

Sample Preparation

Whole-water recoverable arsenic, boron, and vanadium. Nonfiltered, acidified whole-water samples analyzed by ICP–MS for recoverable arsenic, boron, vanadium, and other elements must be digested by using either the HCl in-bottle procedure (Hoffman and others, 1996) or the HNO_3 in-bottle procedure (Garbarino and Hoffman, 1999). When the HCl in-bottle digestion is used, the HCl must be removed by subboiling evaporation if arsenic and vanadium are determined (see Appendix in Garbarino and Hoffman, 1999).

Analytical Procedure

Refer to Perkin Elmer (1997a, 1997b) and NWQL Standard Operating Procedure IM0011.1 (T.M. Struzeski, U.S. Geological

Survey, written commun., 1998) for details of the analytical procedure. In addition, verify the accuracy of interference correction equations by analyzing the interference check standard (see section 5.10) with every batch of samples. The Elan software automatically verifies that the results meet acceptance criteria.

Calculations

No additional calculations are required in this method.

Reporting Results

The number of significant figures reported varies with element and is a function of concentration. Whenever the concentration is less than the MDL for an element, the result is reported as less than the MDL (< MDL). All other elemental results should be reported by using the criteria listed below. These criteria are based on the uncertainty suggested in the following Discussion of Results section. Alternatively, the variability in the mean concentration could be used to establish the appropriate number of significant figures to report for each individual sample matrix. This procedure would provide the most accurate estimate of the uncertainty associated with each sample.

For arsenic and vanadium—

* If the concentration is greater than the MDL, but less than 10 μg/L, report result to two decimal places.

* If the concentration is greater than 10 μg/L, but less than 100 μg/L, report result to one decimal place.

* If the concentration is greater than 100 μg/L, report result to three significant figures.

For boron—

* If the concentration is greater than or equal to the MDL, but less than 100 μg/L, report result to one decimal place.

* If the concentration is greater than 100 μg/L, report result to three significant figures.

DISCUSSION OF RESULTS

The bias of the ICP–MS methods for the determination of whole-water recoverable concentrations is established by comparing results to former USGS methods of analysis. ICP–MS method variability was determined from replicate analyses over a range of elemental concentrations prepared in a calibration-blank matrix. All whole-water samples analyzed by ICP–MS were prepared by using subboiling evaporation of the HCl in-bottle digestate (Garbarino and Hoffman, 1999). Results for standard reference material, spiked samples, and whole-water digestates are used to evaluate the determination of recoverable arsenic, boron, and vanadium by ICP–MS. All former methods are U.S. Geological Survey approved methods (Fishman and Friedman, 1989; Fishman, 1993).

Results for Standard Reference Material

U.S. Geological Survey SRWS T145 was analyzed repetitively for 3 weeks to determine the long-term bias and variability of the ICP–MS method (see table 3). Results for all elements are within one standard deviation of the most probable value (MPV). The average long-term variability is 4±2

percent for elemental concentrations ranging from 10 to 46 µg/L. The paired Student *t*-Test was used to test the null hypothesis that the ICP–MS method gives mean elemental concentrations that are not significantly different from the MPVs. P-values were calculated for each element to provide a level of confidence in accepting the null hypothesis. The larger the p-value the greater the confidence in accepting the null hypothesis. When the p-value exceeds 0.05, the null hypothesis is acceptable at the 95-percent confidence level. The Student *t*-Test indicated that only the boron experimental results are not significantly different from the MPV. Nevertheless, the difference

between the MPV and the experimental mean for arsenic and vanadium is analytically insignificant.

The short-term variability of ICP–MS over an extended concentration range is listed in table 4. The variability is based on three replicate determinations (an acquisition time of about 1 minute) at each elemental concentration in the calibration blank matrix. The short-term variability was less than or equal to 5 percent at 0.5 µg/L for arsenic and vanadium; variability for boron was about 5 percent at 1 µg/L.

Table 3. Statistical analysis of long-term inductively coupled plasma–mass spectrometric results for U.S. Geological Survey's Standard Reference Water Sample T145

[ICP–MS, inductively coupled plasma–mass spectrometry; element results are in micrograms per liter; MPV, the published most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation at 1σ in the experimental mean column; n, number of replicates used to calculate the experimental mean; p-value, level of significance; <, less than]

Element	MPV	Experimental mean, *n*=12	*t*-Test statistic	p-value
Arsenic	10 ± 1	10.3 ± 0.2	9.00	<0.0001
Boron	46 ± 6	45 ± 3	-0.23	0.8253
Vanadium	12 ± 2	10.6 ± 0.5	-7.86	<0.0001

Table 4. Short-term analytical variability as a function of elemental concentration for inductively coupled plasma–mass spectrometry

[ICP–MS, inductively coupled plasma–mass spectrometry; %RSD, percent relative standard deviation on the basis of three sequential determinations in a 0.4-percent solution of concentrated nitric acid in deionized water; <MDL, less than the method detection limit; nd, not determined]

Element	Concentration, in micrograms per liter							
	0.05 %RSD	0.1 %RSD	0.5 %RSD	1.0 %RSD	10 %RSD	50 %RSD	100 %RSD	250 %RSD
Arsenic	<MDL	30	3	4	2	nd	1	0.6
Boron	nd	10	nd	5	2	0.4	0.2	nd
Vanadium	8	10	2	0.6	0.7	nd	0.5	0.5

Spike Recoveries in Natural-Water Samples

Spike recovery percentages listed in table 5 were determined for the new elements in matrices representative of reagent-water, surface-water, ground-water, and whole-water digests. Seven replicate recoveries at 5 to 10 times the MDL (the low-level spike) and 75 μg/L (the high-level spike) were determined in each matrix over a period of about 1 week. Average recoveries in the reagent-water matrix ranged from 77 to 105. Recovery variability for the low-level spike ranged from 4 to 9 percent, depending on the element.

Recoveries of the high-level spike in the surface-water matrix were similar to those of the reagent-water matrix. Ambient concentrations of vanadium in the surface water, however, hindered the recovery of the low-level spike. Recovery of low-level arsenic and boron ranged from 88 to 112 percent. The variability in the recovery of 1 μg/L boron in the presence of 40 μg/L boron was 52 percent; the variability for arsenic was less than 6 percent at about the same spike concentration.

The ground-water matrix used for spike recoveries was selected to examine the effects of interferent species on elemental determinations. The ground water had a relatively high concentration of iron (340 mg/L) that exceeds the concentration found in over one-half of the whole-water digestates analyzed by NWQL. Ambient concentrations of boron precluded the recovery of the low-level spike, however, recoveries for arsenic and vanadium averaged 70 percent. High-level spike recoveries averaged 67±3 percent. The low percent recoveries for the lighter elements confirm the effects from ionization suppression.

Table 5. Average percent spike recoveries in reagent-water, surface-water, ground-water, and in-bottle digest matrices by using inductively coupled plasma–mass spectrometry

[μg/L, micrograms per liter; number following the plus or minus symbol (±) is the standard deviation on the basis of seven determinations accrued on separate days; high spike, 75 μg/L for all elements; na, not applicable because the difference between the spike concentration and ambient concentration was greater than a factor of 10; <MDL, concentration is less than the method detection limit; %, percent]

Element	Low-spike, in μg/L	Reagent-water matrix			Surface-water matrix		
		Ambient concentration, in μg/L	Low-spike recovery, in %	High-spike recovery, in %	Ambient concentration, in μg/L	Low-spike recovery, in %	High-spike recovery, in %
Arsenic	0.5	<MDL	102±4	101±1	1	112±6	105±2
Boron	1	<MDL	77±9	103±2	40	88±52	102±4
Vanadium	0.6	<MDL	98±4	105±4	60	na	104±4
		Ground-water matrix			Synthetic whole-water recoverable digest matrix		
Arsenic	0.5	1	75±8	68±4	7	100±10	95±22
Boron	1	350	na	70±20	8	na	97±9
Vanadium	0.6	<MDL	64±20	64±10	7	na	97±10

The whole-water digest matrix was prepared by weighing 200 mg of National Institute of Standards and Technology's 2704 Buffalo River sediment into 400 mL of calibration blank, digesting the mixture using the HCl in-bottle digestion, removing the HCl by subboiling evaporation, and reconstituting the residue in 3 percent HNO_3. The boron and vanadium low-level spikes were not recovered because the matrix concentration exceeded their concentration by about a factor of 10; the arsenic recoveries averaged 100±10 percent. High-level spike recoveries for arsenic, boron, and vanadium were nearly 100 percent with variability of less than or equal to 10 percent.

Comparison of Inductively Coupled Plasma–Mass Spectrometry to Former Methods of Analysis

The ICP–MS results are compared to former methods of analysis, such as hydride generation–atomic absorption spectro-photometry (HG–AAS) and inductively coupled plasma–atomic emission spectrometry (ICP–AES). Whole-water digest samples were selected from the population of such samples submitted to the NWQL. The samples have a wide range of element concentrations and specific conductance. Surface-water and ground-water samples are included in the sample set; the number of each type is about proportional to its fraction of the total submitted for analysis during an average year. Other chemical characteristics that often influence the performance of analytical methods, such as sulfate and chloride concentrations, were also considered in the selection process (see table 6 for the chemical characteristics of the samples).

Results were evaluated by using several different approaches. Because the data extend over a wide concentration range, it is inappropriate to use the paired Student t-test to evaluate the null hypothesis because errors, whether random or systematic, are independent of the concentration. Consequently, linear regression analysis is used to calculate the slope, y-intercept, and coefficient of determination (R^2) for the equation that describes the relation between ICP–MS and a former USGS method. A

Table 6. Chemical characteristics of natural-water samples used to evaluate inductively coupled plasma–mass spectrometry

[ICP–MS, inductively coupled plasma–mass spectrometry; μg/L, microgram per liter; mg/L, milligram per liter; <MDL, less than the method detection limit; SC, specific conductance]

Element, in μg/L	25th percentile	Median	75th percentile	Maximum
Arsenic	1.7	2.9	7.4	104
Boron	52	120	210	1,700
Vanadium	1.8	4.7	9.7	1,530
Constituent				
Chloride, in mg/L	9.8	68	501	9,176
SC, in μS/cm[1]	455	944	2,490	52,600
Sulfate, in mg/L	108	309	1,306	16,832

[1]Specific conductance in microsiemens per centimeter at 25°C (μS/cm); includes measurements for whole-water samples prior to digestion.

slope coefficient of one and a y-intercept of zero indicate exact correlation. The corresponding p-values indicate the degree of confidence in each coefficient. Box plots also are provided to show the distribution of the results for each method. The nonparametric Wilcoxon Signed Rank Test also is used to evaluate whether there is a significant difference between results from the ICP–MS and former USGS methods. Data that were less than the highest MDL or MRL were omitted from the data set prior to statistical analysis. Statistical analysis results are summarized in the following paragraphs and are listed in table 7. Results of the statistical tests are shown in figures 1 through 3.

Linear regression results show acceptable correlation between ICP–MS and former USGS methods for the determination of whole-water recoverable arsenic, boron, and vanadium (see table 7). The p-values for all the slope coefficients indicate that the slope is not significantly different from 1.0 at the 95-percent confidence level. In addition, the y-intercept p-values for all elements indicate that the intercepts are not significantly different from zero. The p-values from the Wilcoxon Signed Rank Test support the linear regression results for arsenic and vanadium. The p-value for boron was probably influenced by several high-level concentrations in selected whole-water digestates.

Table 7. Statistical analysis of inductively coupled plasma–mass spectrometry and former methods of analysis for the determination of whole-water recoverable arsenic, boron, and vanadium
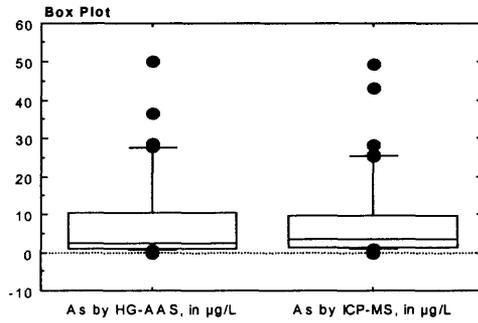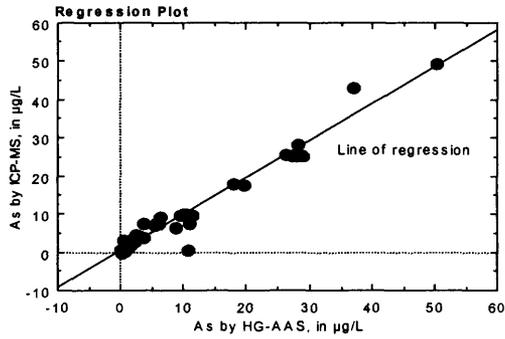
[Coef., the slope coefficient of the regression line; Const., the y-intercept constant of the regression line; p-value, level of significance; R^2, coefficient of determination; HG–AAS, hydride generation–atomic absorption spectrophotometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; <, less than]

| Element | Former method | Slope | | y-intercept | | R^2 | Wilcoxon Signed Rank Test p-value [c] |
		Coef.	p-value [a]	Const.	p-value [b]		
Arsenic	HG–AAS	0.96	<0.0001	0.42	0.2895	0.959	0.1660
Boron	ICP–AES	0.89	<0.0001	-5.0	0.6206	0.927	<0.0001
Vanadium	ICP–AES	1.1	<0.0001	-1.8	0.6436	0.988	0.1138

[a]The null hypothesis: slope is not equal to one.
[b]The null hypothesis: y-intercept is equal to zero.
[c]The null hypothesis: the difference in concentration between the new inductively coupled plasma–mass spectrometric method and the former USGS method is equal to zero.

Regression Plot

As by ICP-MS, in µg/L (y-axis: -10 to 60)
As by HG-AAS, in µg/L (x-axis: -10 to 60)

Line of regression

Box Plot

(y-axis: -10 to 60)

As by HG-AAS, in µg/L   As by ICP-MS, in µg/L

Descriptive Statistics

	As by HG-AAS, in µg/L	As by ICP-MS, in µg/L
Mean	8.16	8.27
Std. Dev.	11.13	10.94
Std. Error	1.56	1.53
Count	51	51
Minimum	0	0.01
Maximum	50.30	49.57
# Missing	0	0

**Wilcoxon Signed Rank Test for As by HG-AAS, in µg/L, As by ICP-MS, in µg/L**

# 0 Differences	1
# Ties	0
Z-Value	-1.39
P-Value	0.1660
Tied Z-Value	-1.39
Tied P-Value	0.1660

Wilcoxon Rank Info for As by HG-AAS, in µg/L, As by ICP-MS, in µg/L

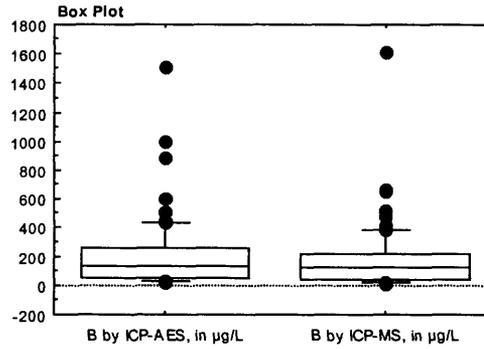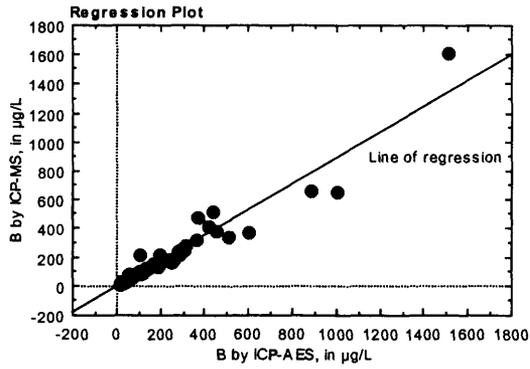|	Count	Sum Ranks	Mean Rank
# Ranks < 0	33	781.00	23.67
# Ranks > 0	17	494.00	29.06

EXPLANATION

Hydride generation-atomic absorption spectrophotometry (HG-AAS);
Inductively coupled plasma-mass spectrometry (ICP-MS); micrograms
per liter (µg/L); Std. Dev., standard deviation; Std. Error, standard error;
<, less than; >, greater than; #, number

Percentile
— 90th
— 75th
— 50th
— 25th
— 10th
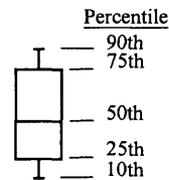
Figure 1. Statistical analysis of **arsenic** results for 50 natural whole-water in-bottle digestates from inductively coupled plasma–mass spectrometry and hydride generation–atomic absorption spectrophotometry.

Regression Plot — B by ICP-MS, in µg/L (y-axis) vs B by ICP-AES, in µg/L (x-axis); Line of regression

Box Plot — B by ICP-AES, in µg/L; B by ICP-MS, in µg/L

Descriptive Statistics

	B by ICP-AES, in µg/L	B by ICP-MS, in µg/L
Mean	209.72	182.18
Std. Dev.	248.34	230.30
Std. Error	30.57	28.35
Count	66	66
Minimum	14.90	9.57
Maximum	1511.20	1612.00
# Missing	0	0

Wilcoxon Signed Rank Test for B by ICP-AES, in µg/L, B by ICP-MS, in µg/L

# 0 Differences	0
# Ties	0
Z-Value	-4.90
P-Value	<0.0001
Tied Z-Value	-4.90
Tied P-Value	<0.0001

**Wilcoxon Rank Info for B by ICP-AES, in µg/L, B by ICP-MS, in µg/L**

	Count	Sum Ranks	Mean Rank
# Ranks < 0	9	338.00	37.56
# Ranks > 0	57	1873.00	32.86

EXPLANATION

Inductively coupled plasma-atomic emission spectrometry (ICP-AES);
inductively coupled plasma-mass spectrometry (ICP-MS); micrograms
per liter (µg/L); Std. Dev., standard deviation; Std. Error, standard error;
<, less than; >, greater than; #, number

Percentile
— 90th
— 75th
— 50th
— 25th
— 10th
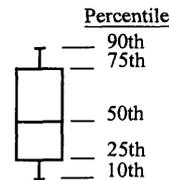
Figure 2. Statistical analysis of **boron** results for 66 natural whole-water in-bottle digestates from inductively coupled plasma–mass spectrometry and inductively coupled plasma–atomic emission spectrometry.

Regression Plot

Box Plot
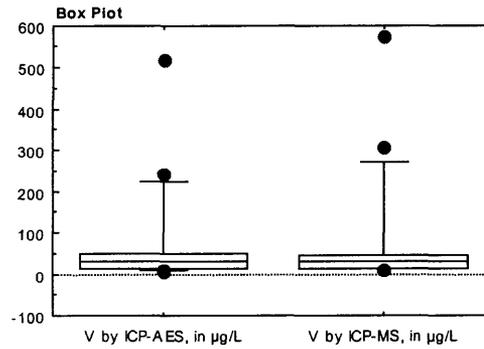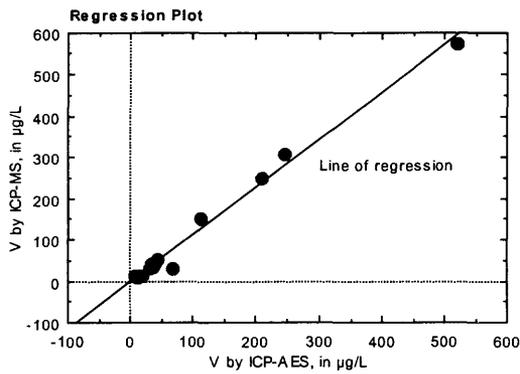
Descriptive Statistics

	V by ICP-AES, in µg/L	V by ICP-MS, in µg/L
Mean	72.69	81.39
Std. Dev.	120.32	138.81
Std. Error	26.26	30.25
Count	21	21
Minimum	7.24	10.35
Maximum	518.58	573.30
# Missing	0	0

**Wilcoxon Signed Rank Test for V by ICP-AES, in µg/L, V by ICP-MS, in µg/L**

# 0 Differences	0
# Ties	0
Z-Value	-1.58
P-Value	0.1138
Tied Z-Value	-1.58
Tied P-Value	0.1138

Wilcoxon Rank Info for V by ICP-AES, in µg/L, V by ICP-MS, in µg/L

	Count	Sum Ranks	Mean Rank
# Ranks < 0	13	181.00	12.38
# Ranks > 0	8	70.00	8.75

EXPLANATION

Inductively coupled plasma-atomic emission spectrometry (ICP-AES);
Inductively coupled plasma-mass spectrometry (ICP-MS); micrograms
per liter (µg/L); Std. Dev., standard deviation; Std. Error, standard error;
<, less than; >, greater than; #, number

Percentile

— 90th
— 75th
— 50th
— 25th
— 10th
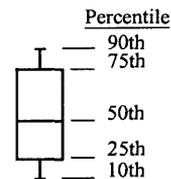
Figure 3. Statistical analysis of **vanadium** results for 21 natural whole-water in-bottle digestates from inductively coupled plasma–mass spectrometry and inductively coupled plasma–atomic emission spectrometry.

CONCLUSIONS

Results from reference material, spike recoveries, and the analysis of natural-water samples were used to evaluate the overall bias and variability of the determination of whole-water recoverable arsenic, boron, and vanadium by inductively coupled plasma–mass spectrometry (ICP–MS). All test results provide an accurate estimate of the expected analytical performance. The following list outlines the major conclusions of this report. In addition to analytical performance comparisons, suggestions are provided for selecting appropriate methodology and the potential impact of the use of ICP–MS on long-term trend analysis in water-quality studies.

- Method detection limits (MDLs) for ICP–MS are between about 10 and 100 times lower than hydride generation–atomic absorption spectrophotometry (HG–AAS) and inductively coupled plasma–atomic emission spectrometry (ICP–AES) methods. Therefore, ICP–MS is the method of choice whenever elemental concentrations are less than 10 µg/L.

- The short- and long-term accuracy for the determination of the new elements by ICP–MS were acceptable; all the elements were within one standard deviation of the most probable value.

- Data for whole-water digestates indicated that there was no significant method bias for the determination of arsenic, boron, and vanadium by ICP–MS. However, matrix interferences from high concentrations of concomitant constituents, for example iron, can affect the determination of some elements. Concomitant concentrations that cause significant interference are usually much greater than concentrations found in most samples submitted to NWQL.

- Preparation of whole-water samples requires using either the HCl in-bottle digestion procedure or the HNO_3 in-bottle digestion procedure. Whenever the HCl in-bottle procedure is used, the HCl must be removed from the digest by using subboiling evaporation. This step is not required if the HNO_3 in-bottle digestion procedure is used. However, there are potential differences between the HNO_3 in-bottle and HCl in-bottle procedures in the solubilization of sediment material. Such differences depend on the mineral composition of the sediment in the whole-water sample.

- Data from ICP–MS will impact long-term trends in water-quality studies because of the improved bias and variability at elemental concentrations less than 10 µg/L.

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