# Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory-- Determination of Dissolved Aluminum and Boron in Water by Inductively Coupled Plasma—Atomic Emission Spectrometry

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# CONVERSION FACTORS, ABBREVIATED WATER-QUALITY UNITS, ADDITIONAL ABBREVIATIONS, AND DEFINITIONS

| *Multiply* | *By* | *To obtain* |
|---|---|---|
| liter (L) | 2.64 X10$^{-1}$ | gallon |
| meter (m) | 3.94 X 10$^{1}$ | inch |
| microgram (~tg) | 3.53 X 10$^{-8}$ | ounce, avoirdupois |
| micrometer (itm) | 3.94 X 10$^{-5}$ | inch |
| milliliter (mL) | 2.64 X 10$^{-4}$ | gallon |
| millimeter (mm) | 3.94 X 10$^{-2}$ | inch |
| nanometer (nm) | 3.94 x 10$^{-8}$ | inch |

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

$$^{\circ}F = 9/5\,(^{\circ}C) + 32$$

Abbreviated water-quality units used in this report:

| | |
|---|---|
| L/min | liter per minute |
| mg/L | milligram per liter |
| mg/mL | milligram per milliliter |
| µg/L | microgram per liter |
| µL | microliter |
| µS/cm | microsiemens per centimeter |

Other abbreviations used in this report:

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| DCP—AES | direct current plasma—atomic emission spectrometry |
| °C | degree Celsius |
| ICP—AES | inductively coupled plasma—atomic emission spectrometry |
| kPa | kiloPascal |
| lb/in$^2$ | pound per square inch |
| MDL | method detection limit |
| MPV | most probable value |
| MRL | method reporting limit |
| NIST | National Institute of Standards and Technology |
| SRWS | U.S. Geological Survey Standard Reference Water Samples |
| USGS | U.S. Geological Survey |
| W | watt |
| < | less than |

Definitions:

| | |
|---|---|
| MDL | The method detection limit is defined as the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (U.S. Environmental Protection Agency, 1992). |
| MPV | The 95-percent most probable value. |
| MRL | The method reporting limit is equal to the lowest reported concentration of an analyte by a given method. |

# METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY—DETERMINATION OF DISSOLVED ALUMINUM AND BORON IN WATER BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

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*By* Tedmund M. Struzeski, W. Jack DeGiacomo, and Edward J. Zayhowski

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## ABSTRACT

Inductively coupled plasma—atomic emission spectrometry is a sensitive, rapid, and accurate method for determining the dissolved concentration of aluminum and boron in water samples. The method detection limits are 5 micrograms per liter for aluminum and 4 micrograms per liter for boron. For aluminum, lower-level (about 30 micrograms per liter) short-term precision (single-operator, seven days) is about 5-percent relative standard deviation, and the lower-level long-term precision (single-operator, nine months) is about 8-percent relative standard deviation. For boron, the lower-level short-term precision is about 4-percent relative standard deviation, and the lower-level long-term precision is about 5-percent relative standard deviation. Spike recoveries for aluminum ranged from 86 to 100 percent, and recoveries for boron ranged from 92 to 109 percent.

## INTRODUCTION

The National Water Quality Laboratory (NWQL) has determined dissolved concentrations of aluminum and boron by direct current plasma—atomic emission spectrometry (DCP—AES). A widely used alternative technique, inductively coupled plasma—atomic emission spectrometry (ICP—AES), is now available and allows for the analysis of dissolved aluminum and boron simultaneously with other trace metals (Fishman, 1993). Virtually no additional analytical time nor operator time is required. Furthermore, the overall precision of aluminum and boron determinations by ICP—AES provides improvement over the present DCP—AES method in Fishman (1993).

This report describes a method tested by the U.S. Geological Survey (USGS) for use in the Survey's NWQL for determining dissolved aluminum and boron in water samples. The method supplements other methods of the USGS for determination of inorganic substances in water that are described by Fishman and Friedman (1989). The ICP--AES method was implemented in the NWQL in May 1996.

This report provides a detailed description of all aspects of the method including application, method detection limits, and interferences. Accuracy and precision and recovery data are also presented.

The authors. wish to thank the following people for their assistance in making this project possible: Gary Austin for analyzing samples, Chuck Millhollin for analyzing samples and researching historical data, John Garbarino and Charles Patton for guidance and comments, and Ed Gilroy and Jeff Pritt for their assistance with the statistical comparison of the two methods.

# ANALYTICAL METHOD

## Inorganic Constituents and Parameter Codes:

Aluminum and boron, inductively coupled plasma—atomic emission spectrometry
Aluminum, dissolved, I-1472-95 (µg/L as Al): 01106
Boron, dissolved, I-1472-95 (µg/L as B): 01020

## 1. Application

This method is suitable for the single-element or multielement determination of dissolved aluminum and boron in precipitation samples and surface-, ground-, and drinking-water samples that have a measured specific conductance of less than 2,000 µS/cm at 25°C. Samples that have a measured specific conductance greater than or equal to 2,000 µS/cm may be diluted by the minimum factor possible to adjust the sample to the specified limit; however, the method reporting limit (MRL) of all reported analytes will increase by the factor of dilution. The concentration limits are listed in table 1.

Table 1 .--*Method reporting limits and wavelengths used to determine aluminum and boron*

[MRL, method reporting limit; µg/L, microgram per liter; nm, nanometer]

| Element | MRL (µg/L) | Maximum limit (µg/L) | Wavelength (nm) |
|---|---|---|---|
| Aluminum | 5 | 100,000 | 167.081[a] |
| Boron | 4 | 10,000 | 249.773[a] |

[a] Second order.

## 2. Summary of Method

Dissolved aluminum and boron are determined simultaneously on a single sample by using an inductively coupled plasma emission spectrometer. Sample solution is pumped into a crossflow pneumatic nebulizer that produces a liquid aerosol. This aerosol is subsequently transported by argon gas through a spray chamber and torch assembly into an inductively coupled plasma source where the aerosol is desolvated and atomized, and the resultant atoms or ions are excited. The emission, which results as excited state atoms or excited state ions relax to their ground state, is measured and the signal integrated. Each result is determined on the basis of the mean of three replicate integrations. The results then are converted to concentration.

## 3. Interferences

3.1 Interelement interferences on aluminum and boron were evaluated; the interferences are listed in table 2.

Table 2.--*Constituents and concentrations evaluated for interferences on aluminum (167.081 nanometers) and boron (249.773 nanometers) emission*

[µg/L, microgram per liter; <MRL, less than method reporting limit]

| Constituent | Concentration (µg/L) | Apparent aluminum concentration (µg/L) | Apparent boron concentration (µg/L) |
|---|---|---|---|
| Barium | 10,000 | <MRL | <MRL |
| Beryllium | 10,000 | <MRL | <MRL |
| Cadmium | 10,000 | <MRL | <MRL |
| Calcium | 100,000 | <MRL | <MRL |
| Carbonate | 100,000 | <MRL | <MRL |
| Chromium | 10,000 | <MRL | <MRL |
| Cobalt | 10,000 | <MRL | <MRL |
| Copper | 10,000 | <MRL | <MRL |
| Iron | 100,000 | 243 | 36 |
| Lead | 10,000 | <MRL | <MRL |
| Lithium | 10,000 | <MRL | <MRL |
| Magnesium | 100,000 | <MRL | <MRL |
| Manganese | 100,000 | <MRL | <MRL |
| Molybdenum | 10,000 | <MRL | <MRL |
| Nickel | 10,000 | <MRL | <MRL |
| Phosphorus | 10,000 | <MRL | <MRL |
| Silica | 200,000 | <MRL | <MRL |
| Silver | 2,000 | <MRL | <MRL |
| Sodium | 100,000 | <‘MRL | <MRL |
| Strontium | 10,000 | <MRL | <MRL |
| Sulfate | 500,000 | <MRL | <MRL |
| Vanadium | 10,000 | <MRL | <MRL |
| Zinc | 100,000 | <MRL | <MRL |

The apparent aluminum and boron concentration caused by the emission of iron is corrected by using an interelement correction factor.

3.2 Samples containing high dissolved solids can exhibit unidentified interference effects. These effects can be minimized by analyzing only samples that have a measured specific conductance less than 2,000 µS/cm at 25°C (Fishman, 1993).

## 4. Apparatus

4.1 *Emission spectrometry system* consisting of the following:

4.1.1 Autosampler.
4.1.2 Computer (286 or more powerful).
4.1.3 Peristaltic pump.
4.1.4 Quartz torch assembly.
4.1.5 Spectrometer, Thermo Jarrell Ash argon or nitrogen purged spectrometer, 0.75-m focal curve with spectrum shifter background correction, crossflow pneumatic nebulizer, and radio frequency generator.

4.2 Operating conditions are approximate and will vary from instrument to instrument. Refer to manufacturer's instrument manual to optimize operating conditions and instrument performance.

| | |
|---|---|
| Incident radio frequency power …... | 950-1,350 W |
| Reflected radio frequency power…. | <10 W |
| Horizontal observation position …. | Approximately 15 mm above load coil |
| Vertical observation position ……. | Center |
| Argon head pressure ……………… | 55 lb/in$^2$ (379 kPa) |
| Sample argon rate for crossflow nebulizer ……………… | 1.2 L/min |
| Sample pumping rate for crossflow nebulizer ……………… | 10 percent greater than aspiration rate |
| Refractor plate position …………… | Optimized for mercury profile |
| Spectrum shifter …………………... | 12 spectrum shift units to the right side of wavelength. |

## 5. Reagents

5.1 *Water:* All references to water shall be understood to mean ASTM Type I Reagent Water (American Society for Testing and Materials, 1994).

5.2 *Nitric acid* ($HNO_3$): Concentrated, specific gravity 1.41, Ultrex grade or equivalent.

5.3 *Aluminum standard solution:* 100 mg/L aluminum. Add 10 mL concentrated Ultrex (or equivalent) $HNO_3$ to a 1,000-mL, class A volumetric flask containing approximately 500 mL of Type I water. To this add 10.0 mL of National Institute of Standards and Technology (NIST) 10.00 mg/mL aluminum Standard Reference Material (or equivalent). Dilute to mark to make a 100 mg/L aluminum standard solution in a 1-percent $HNO_3$ matrix. Avoid using Standard Reference Materials made in a hydrochloric acid matrix because the acid might cause incompatibilities with other analytes in the final standardization mixes. Transfer the standard to a Teflon or polyethylene bottle (preferably Teflon) for storage.

5.4 *Boron standard solution:* 100 mg/L boron. Add 20.0 mL NIST 5.00 mg/mL boron Standard Reference Material (or equivalent) to a 1,000-mL, class A volumetric flask containing approximately 500 mL of Type I water. Dilute to mark to make a 100 mg/L boron standard solution in a water matrix. Avoid using Standard Reference Materials made in a hydrochloric acid matrix because the acid might cause incompatibilities with other analytes in the standardization mixes. Transfer the standard to a Teflon or polyethylene bottle (preferably Teflon) for storage.

5.5 *Mixed working standard solution IV:* Prepare mixed working standard solution as follows. Pipet 50.0 mL of each appropriate standard solution into a 1,000-mL, class A volumetric flask. Mix aluminum and boron with cobalt, chromium, and lithium. Dilute to mark to make mixed standard solution *IV*. The final concentration of all elements in standard solution *IV* is 5 mg/L. Transfer the standard to a Teflon or polyethylene bottle (preferably Teflon) for storage.

## 6. Sample preparation

Filter the surface- or ground-water samples through a 0.45-µm filter and acidify to a pH less than 2.0 with ultrapure-grade nitric acid immediately after collection. Collect and store samples in acid-rinsed Teflon, polytetrafluoroethylene, fluorinated ethylene propylene, high-density polyethylene, or similar containers (Faires, 1993). Samples are stable for at least 6 months at room temperature.

## 7. Instrument performance

7.1 *Analytical productivity:* Each sample requires about 3 minutes to analyze. This 3-minute process includes line-flushing, three 10-second integrations, and a final rinse. It takes about 4 hours for the instrument to analyze mixed working standard solutions, the on-line USGS Standard Reference Water Samples (SRWS), and 50 water samples.

7.2 Refer to manufacturer’s instrument manual to optimize operating conditions and instrument performance.

## 8. Procedure

8.1 Set up instrument with proper operating conditions (paragraph 4.2) and ignite plasma. Allow the instrument to warm up for at least 30 minutes prior to optimization.

8.2 Initiate the operation sequence in the software.

8.3 Turn on the instrument-mounted mercury pen lamp, then initiate the profile option in the ThermoSPEC software. Profile until peak position is within ± 0.1 spectrum shift units.

8.4 Standardize the instrument using a standardization blank and standard solution IV. Pump rinse solution for 30 to 45 seconds between standards. Allow 45 to 60 seconds for equilibration each time a new solution is introduced.

8.5 Verify standardization by analyzing a check standard solution consisting of aluminum and boron at approximately one-half the concentration used in the standardization mix. Determined concentrations are not to deviate from the theoretical concentrations by more than ±5 percent. If the results deviate by more than ±5 percent, then restandardize.

8.6 Verify standardization by analyzing certified reference samples in a natural-water matrix. The determined concentrations need to be within specified control limits

8.7 Analyze samples allowing 70 to 80 seconds for rinsing the line with sample and for equilibration of sample introduction. Pump rinse solution for 15 to 30 seconds between samples. Verify standardization after analyzing 8 to 10 samples by reanalyzing a reference sample. The determined concentrations need to be within specified control limits. If the determinations are outside of the limits, restandardize the instrument (see paragraphs 8.3 through 8.6).

## 9. **Calculations**

9.1 All calculations are performed internally by instrument manufacturer’s computer hardware and software. Headings are used to identify results.

9.2 If samples were diluted, multiply results by appropriate dilution factor using the computer software.

## 10. Reporting of results

Report concentrations of dissolved aluminum (01106) as follows: if concentration is less than 5 µg/L report as <5 µg/L if concentration is greater than or equal to 5 µg/L but less than 10 µg/L, report results using two significant figures; if concentration is greater than or equal to 10 µg/L, report results using three significant figures.

Report concentrations of dissolved boron (01020) as follows: if concentration is less than 4 µg/L, report as <4 µg/L; if concentration is greater than or equal to 4 µg/L but less than 10 µg/L, report results using two significant figures; if concentration is greater than or equal to 10 µg/L, report results using three significant figures.

# DISCUSSION OF RESULTS

## Method Detection Limits and Method Reporting Limits

The method detection limits (MDLs) for aluminum and boron were studied using five inductively coupled plasma—atomic emission spectrometry (ICP—AES) instruments. Ten consecutive aliquots of a laboratory-prepared solution were analyzed following the procedure listed in the U.S. Code of Federal Regulations (U.S. Environmental Protection Agency, 1992). The test solution contained approximately 13 µg/L of aluminum and 11 µg/L of boron in a 0.4-percent $HNO_3$ matrix. The mean MDLs from the five ICP instruments were found to be 4.5 µg/L for aluminum and 3.8 µg/L for boron using the Student's t value appropriate for a 99-percent confidence level. The decision was made to report no lower than the MDL; thus, the method reporting limits (MRLs) were set at 5 µg/L for aluminum and 4 µg/L for boron.

## Accuracy and Precision

The accuracy and precision of the ICP—AES method were determined in two studies using USGS Standard Reference Water Samples (SRWSs). First, in a short-term study, SRWSs were analyzed for aluminum and boron on seven different days using the same instrument and operator. Second, long-term accuracy and precision were determined from historical on-line quality-control data. (See figs. 1 and 2.) Multiple SRWSs at various concentrations of analyte were analyzed over a 9-month period by a single operator (except for boron in SRWS T-113, which was analyzed over a 4-month period). The number of replicates used in this study varies from 150 to 550. Results from both studies for aluminum and boron are listed in tables 3 through 6.

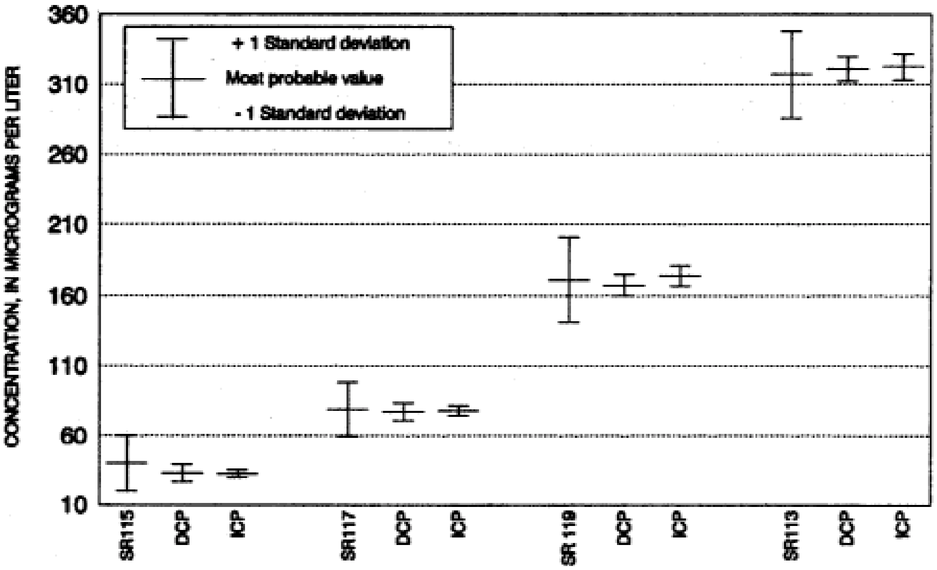

**Figure 1.--Long-term accuracy and precision of direct current plasma–atomic emission spectrometry and inductively coupled plasma–atomic emission spectrometry for aluminum determinations relative to Standard Reference Water Samples.**

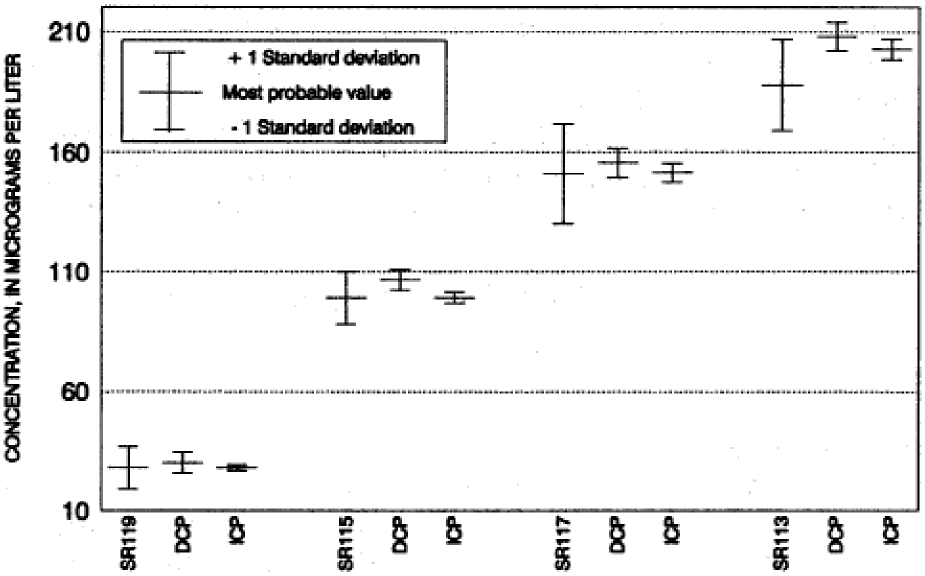

Figure 2. – Long-term accuracy and precision of direct current plasma-atomic emission spectrometry and inductively coupled plasma-atomic emission spectrometry for boron determinations relative to standard Reference Water Samples.

Table *3.--Short-term accuracy and precision for aluminum by inductively coupled plasma—atomic emission spectrometry (ICP—AES)*

[SRWS, Standard Reference Water Sample; MPV, most probable value; µg/L, microgram per liter]

| | | | ICP-AES | | |
|---|---|---|---|---|---|
| SRWS number | SRWS MPV (µg/L) | SRWS F-pseudosigma (µg/L) | Mean measured[1] (µg/L) | Standard deviation[1] (µg/L) | Relative standard deviation[1] (percent) |
| 107 | 220 | 45 | 222 | 2.0 | 09 |
| 109 | 113 | 32 | 115 | 2.0 | 1.7 |
| 113 | 317 | 31 | 328 | 4.0 | 1.2 |
| 115 | 40 | 20 | 32.7 | 1.5 | 4.5 |
| 117 | 79 | 19 | 78.7 | 1.7 | 2.1 |
| 119 | 171 | 30 | 165 | 3.2 | 1.9 |
| 121 | 86 | 13 | 87.5 | 2.5 | 2.8 |

[1] From seven determinations.

**Table 4.** --*Short-term accuracy and precision for boron by inductively coupled plasma—atomic emission spectrometry (ICP—AES)*

[SRWS, Standard Reference Water Sample; MPV, most probable value; µg/L, microgram per liter]

| | | | ICP-AES | | |
|---|---|---|---|---|---|
| SRWS number | SRWS MPV (µg/L) | SRWS F-pseudosigma (µg/L) | Mean measured[1] (µg/L) | Standard deviation[1] (µg/L) | Relative standard deviation[1] (percent) |
| 107 | 130 | 21 | 139 | 1.5 | 1.1 |
| 109 | 115 | 19 | 119 | 2.1 | 1.8 |
| 113 | 188 | 19 | 202 | 3.3 | 1.7 |
| 115 | 99 | 11 | 99.1 | 1.2 | 1.2 |
| 117 | 151 | 21 | 150 | 1.7 | 1.1 |
| 119 | 28 | 8.9 | 28.0 | 1.0 | 3.6 |
| 121 | 90 | 9.0 | 90.9 | 2.0 | 2.2 |

[1] From seven determinations.

**Table** 5. --*Long-term accuracy and precision for aluminum by inductively coupled plasma—atomic emission spectrometry (ICP—AES)*

[SRWS, Standard Reference Water Sample; MPV, most probable value;
µg/L, microgram per liter]

| SRWS number | SRWS MPV (µg/L) | SRWS F-pseudosigma (µg/L) | ICP—AES<br>Mean measured[1] (µg/L) | ICP—AES<br>Standard deviation[1] (µg/L) | ICP—AES<br>Relative standard deviation[1] (percent) |
|---|---|---|---|---|---|
| 113 | 317 | 31 | 322 | 9.3 | 2.9 |
| 115 | 40 | 20 | 32.6 | 2.8 | 8.5 |
| 117 | 79 | 19 | 78.1 | 3.5 | 4.5 |
| 119 | 171 | 30 | 174 | 7.2 | 4.2 |

[1] The number of determinations used varies from 150 to 550.

**Table** 6.--*Long-term accuracy and precision for boron by inductively coupled plasma—atomic emission spectrometry (ICP—AES)*

[SRWS, Standard Reference Water Sample; MPV, most probable value;
µg/L, microgram per liter]

| SRWS number | SRWS MPV (µg/L) | SRWS F-pseudosigma (µg/L) | ICP—AES<br>Mean measured[1] (µg/L) | ICP—AES<br>Standard deviation[1] (µg/L) | ICP—AES<br>Relative standard deviation[1] (percent) |
|---|---|---|---|---|---|
| 113 | 188 | 19 | 203 | 4.1 | 2.0 |
| 115 | 99 | 11 | 99.1 | 2.4 | 2.4 |
| 117 | 151 | 21 | 151 | 3.9 | 2.5 |
| 119 | 28 | 8.9 | 28.1 | 1.4 | 5.0 |

[1] The number of determinations used varies from 150 to 550.

Figure 1 shows that dissolved aluminum determinations by the proposed method were in agreement with the interlaboratory most probable values (MPVs) for the SRWSs. The study also indicated that not only is the precision of the ICP— AES method well within the limits established using the interlaboratory Fpseudosigma, but it is also generally superior to that of the present direct current plasma—atomic emission spectrometry (DCP—AES) method in Fishman (1993).

The SRWSs also were used to evaluate the accuracy and precision of the ICP—AES method for the determination of dissolved boron at various concentrations. The ICP—AES results shown in figure 2 are consistent with the interlaboratory MPV and demonstrate improved accuracy over the method in Fishman (1993). The improved accuracy is consistent with the findings discussed in the following Comparison of Methods section, which indicate an overall 8.8-percent positive bias in the DCP—AES method. In addition, the precision of the proposed method is well within the limits established using the interlaboratory F-pseudosigma and will offer an improvement compared to the precision of the DCP—AES method in Fishman (1993).

## Spike Recoveries

Measured recoveries in the spiked samples were favorable for the aluminum and boron determinations (see tables 7 and 8). A variety of conductances and concentrations was chosen to test recoveries in several matrices. In all cases, recoveries were between the expected limits of 85 to 115 percent. Recoveries were calculated using unrounded data and the following equation:

$$\textbf{Percent Recovery} = \frac{\textbf{Determination after spike} - \textbf{Determination before spike}}{\textbf{Amount of spike added}} \times 100$$

**Table** *7.--Spike recovery data for aluminum in filtered-acidified water samples using inductively coupled plasma—atomic emission spectrometry*

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; µg/L, microgram per liter; µg, microgram]

| Sample number | Specific conductance (µ.S/cm) | Determination before spike (µg/L) | Spike added (µg) | Determination after spike (µg/L) | Recovery (percent) |
|---|---|---|---|---|---|
| Matrix Blank | 0 | 0 | 54.1 | 50.9 | 94.1 |
| 1 | 1.9 | 2.0[a] | 54.1 | 50.8 | 90.2 |
| 2 | 78 | 83.4 | 150 | 229 | 97.4[b] |
| 3 | 154 | 70.8 | 54.1 | 117 | 86.1[b] |
| 4 | 243 | 68.5 | 54.1 | 121 | 96.9[b] |
| 5 | 370 | 14.2 | 54.1 | 65.7 | 95.2 |
| 6 | 547 | 8.5 | 54.1 | 59.6 | 94.4 |
| 7 | 1,000 | 2.0[a] | 54.1 | 53.8 | 95.7 |
| 8 | 1,670 | 14.5 | 54.1 | 67.1 | 97.2 |
| 9 | 2,930 | 7.5 | 54.1 | 61.6 | 99.9[b] |

[a] Less than 4 µg/L was replaced by 2.0.

[b] Unrounded numbers used for all calculations. Only rounded numbers listed in table.

**Table** *8.--Spike recovery data for boron in filtered-acidified water samples using inductively coupled plasma—atomic emission spectrometry*

[µS/cm, microsiemens per centimeter at 25 degrees Celsius;
µg/L, microgram per liter; fig, microgram]

| Sample number | Specific conductance (µS/cm) | Determination before spike (µg/L) | Spike added (µg) | Determination after spike (µg/L) | Recovery (percent) |
|---|---|---|---|---|---|
| Matrix Blank | 0 | 0 | 54.1 | 56.2 | 104 |
| 1 | 1.9 | 5.5[a] | 54.1 | 55.1 | 91.6[b] |
| 2 | 78 | 5.5[a] | 54.1 | 64.5 | 109 |
| 3 | 154 | 33.7 | 54.1 | 86.4 | 97.4 |
| 4 | 243 | 13.6 | 54.1 | 68.7 | 102 |
| 5 | 370 | 63.3 | 54.1 | 116.0 | 97.3 |
| 6 | 547 | 40.9 | 54.1 | 91.2 | 93.0 |
| 7 | 1,000 | 114 | 54.1 | 172.0 | 107 |
| 8 | 1,670 | 1,680 | 4,000 | 5,560 | 97.1[b] |
| 9 | 2,930 | 185 | 1,000 | 1,190 | 101 |

[a] Less than 11 µg/L was replaced by 5.5.

[b] Unrounded numbers used for all calculations. Only rounded numbers listed in table.

## Comparison of Methods

Aluminum and boron were determined in a large set of natural-water samples using the DCP—AES and ICP—AES methods. Most samples were analyzed within weeks of each other. The results for aluminum are shown in figure 3.

### *Aluminum*

Aluminum was determined in 131 filtered-acidified samples. The DCP—AES and ICP—AES results were log transformed and the resulting distribution confirmed for normality. The paired Student’s t test, applied at the 95-percent confidence level, indicated no statistical basis to reject the assumption that both methods yield equivalent results.

A high degree of scatter is shown in figure 3. This scatter may be a result of the imprecision inherent in the analysis of dissolved aluminum (aluminum determinations made from water filtered through a 0.45-µm membrane). Several factors have been shown to influence the determination of aluminum in samples of natural, filtered water. Most important among these include the pore size of the membrane used, for filtration (Kennedy and others, 1974); the time between filtration and analysis (Smith and Hem, 1972); the presence of other cations (Brown and Hem, 1975) or anions, or both (Roberson and Hem, 1969); and the presence of organic solutes (Lind and Hem, 1975).

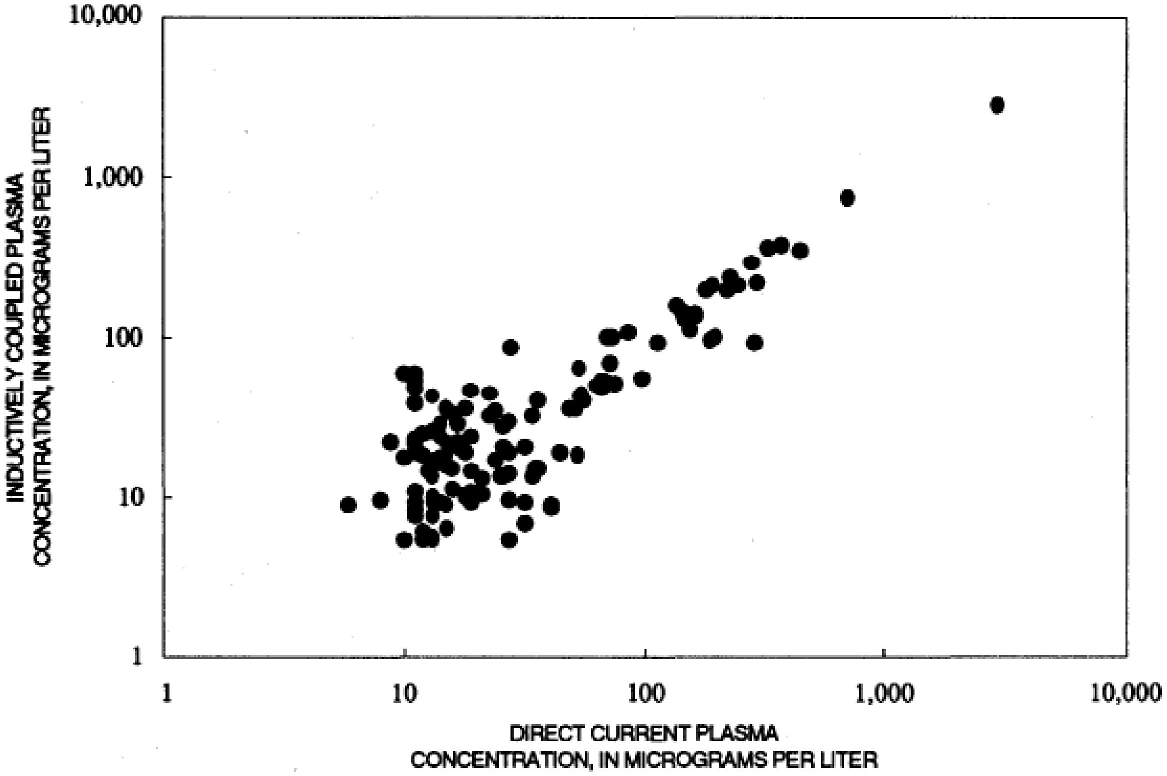

Figure 3.--Filtered-acidified sample results for aluminum determinations by the direct current plasma—atomic emission spectrometry method and inductively coupled plasma—atomic emission spectrometry method..

Kennedy and others (1974) found that colloidal particulate matter can pass through a 0.45-µm filter, thereby affecting the homogeneity of the filtrate. The colloidal particulate matter can be present in quantities significant enough to influence the reported concentration of aluminum in filtered-acidified samples by an order of magnitude or more. The fluctuating results for the concentration of dissolved aluminum may also be a result of a reaction between the acid used for sample preservation and the fine colloidal particles. Over time, this reaction can lead to increasing concentrations of dissolved aluminum (Smith and Hem, 1972). This result and the presence of solvated silica and other major cations in natural water samples have also been found to affect the aluminum concentration by complexation and precipitation (Brown and Hem, 1975). Roberson and Hem (1969) demonstrated that the concentration of complexing ligands, such as fluoride and sulfate, can affect the solubility of aqueous dissolved species of aluminum as well. Organic matter, common in natural water, can form numerous aluminum complexes. Under certain conditions, where concentrations of organic matter are higher, this process can have a significant effect on measured aluminum concentrations (Lind and Hem, 1975).

Aluminum contamination, especially in the concentration range from 0 to 100 µg/L, also may have enhanced the amount of scatter at lower concentrations as shown in figure 3. Aluminum results have a tendency to be affected by contamination.

Aluminum results from 10 samples (three replicates each) of various specific conductances (427-1,370 µS/cm) exhibited poor reproducibility by the ICP—AES method as well as the DCP—AES method. Removal of particulates by refiltration through a 0.45-µm filter resulted in more than a six-fold improvement in the average precision (24-percent relative standard deviation in relation to 4.2-percent relative standard deviation) for the ICP—AES determinations and a one and one-half-fold improvement in the average precision (14-percent relative standard deviation in relation to 9.5-percent relative standard deviation) for the DCP—AES determinations. In comparison, good overall precision (2.2-percent relative standard deviation for the ICP—AES method and 7.1-percent relative standard deviation for the DCP—AES method) is achieved upon analysis of SRWSs. (See fig. 1.) These reference standards, however, need to be considered *clean* samples because they have been filtered a minimum of four times through a variety of filter sizes down to at least 0.2 µm (Long and Farrar, 1993). Thus, some of the scatter shown in figure 3 is probably a result of the filtration technique being used as opposed to a characteristic of the ICP—AES or the DCP—AES methodology.

### *Boron*

Boron determinations by DCP—AES were made from filtered-unacidified samples whereas boron determinations by ICP—AES were made from filtered-acidified samples. Results for boron are shown in figure 4. The distribution of the unprocessed and the transformed boron data could be confirmed neither for normality nor for symmetry. Therefore, the one-sample sign test was used to test for a difference between the results of the two methods. At the 95-percent confidence interval, there was sufficient evidence to reject the null hypothesis, thereby indicating a bias between the two methods. Further analysis showed that the DCP—AES method, on average, gives results approximately 8.8-percent higher than the ICP—AES method. Contribution to the bias may be a result of filtered-acidified and filtered-unacidified samples being compared; however, as indicated in the Accuracy and Precision section, the ICP—AES method is capable of improved accuracy over that of the DCP—AES method. (See fig. 2.)

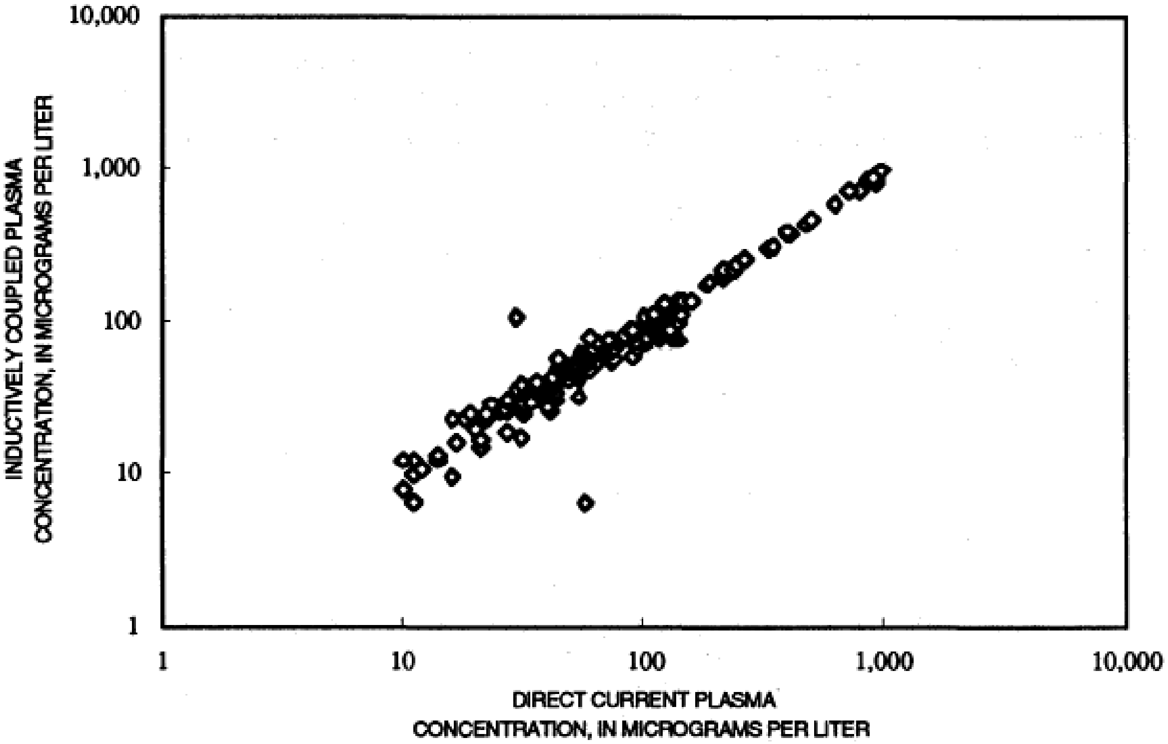

Figure 4.--Filtered sample results for boron determinations by the direct current plasma—atomic emission spectrometry method (unacidified matrix) and inductively coupled plasma—atomic emission spectrometry method (acidified matrix).

## CONCLUSIONS

The multielement ICP—AES method is far more efficient and cost-effective than the single-element DCP-AES method. This report has shown that ICP-AES is a reliable alternative method for the determination of dissolved aluminum that exhibits a lower MRL and better precision than offered by the present (1996) DCP— AES technique. For dissolved boron, the ICP—AES technique offers improved precision and accuracy over that of the DCP—AES method.

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