METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY— USE OF A MODIFIED ULTRASONIC NEBULIZER FOR THE ANALYSIS OF LOW IONIC-STRENGTH WATER BY INDUCTIVELY COUPLED OPTICAL EMISSION SPECTROMETRY

By Carl M. Harris, Charles J. Litteral, and Donna L. Damrau

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	*By*	*To obtain*
centimeter (cm)	3.94×10^{-1}	inch
gram (g)	3.53×10^{-2}	ounce, avoirdupois
liter (L)	2.64×10^{-1}	gallon
microgram (µg)	3.53×10^{-8}	ounce
microliter (µL)	2.64×10^{-7}	gallon
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter (mL)	2.64×10^{-4}	gallon
millimeter (mm)	3.94×10^{-2}	inch
nanometer (nm)	3.94×10^{-8}	inch

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

$$°F = 9/5\ (°C) + 32$$

Abbreviated units of measurement used in report:

L/min	liter per minute
mL/min	milliliter per minute
mg/L	milligram per liter
mg/mL	milligram per milliliter
µg/L	microgram per liter
µg/mL	microgram per milliliter
µS/cm	microsiemens per centimeter at 25 degrees Celsius
kW	kilowatt

Other abbreviations are as follows:

AES	atomic emission spectrometry
ASTM	American Society for Testing and Materials
IC	ion chromatography
ICP	inductively coupled plasma
ICP–OES	inductively coupled plasma–optical emission spectrometry
ICP–IC	inductively coupled plasma–ion chromatography
ICP–MS	inductively coupled plasma–mass spectrometry
MDL	method detection limit
NIST	National Institute of Standards and Technology
NWQL	National Water Quality Laboratory
RSD	relative standard deviation
SRWS	Standard Reference Water Sample
UDX	ultrasonic nebulizer
USGS	U.S. Geological Survey
USEPA	U.S. Environmental Protection Agency
v/v	volume per volume
w/v	weight per volume

METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY—USE OF A MODIFIED ULTRASONIC NEBULIZER FOR THE ANALYSIS OF LOW IONIC-STRENGTH WATER BY INDUCTIVELY COUPLED OPTICAL EMISSION SPECTROMETRY

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ABSTRACT

The U.S. Geological Survey National Water Quality Laboratory has developed a method for the determination of dissolved calcium, iron, magnesium, manganese, silica, and sodium using a modified ultrasonic nebulizer sample-introduction system to an inductively coupled plasma–optical emission spectrometer. The nebulizer's spray chamber has been modified to avoid carryover and memory effects common in some conventional ultrasonic designs. The modified ultrasonic nebulizer is equipped with a high-speed rinse cycle to remove previously analyzed samples from the spray chamber without excessive flush times. This new rinse cycle decreases sample washout times by reducing carryover and memory effects from salt or analytes in previously analyzed samples by as much as 45 percent. Plasma instability has been reduced by repositioning the argon carrier gas inlet on the spray chamber and by directly pumping waste from the chamber, instead of from open drain traps, thereby maintaining constant pressure to the plasma. The ultrasonic nebulizer improves signal intensities, which are 8 to 16 times greater than for a conventional cross-flow pneumatic nebulizer, without being sensitive to clogging from salt buildup as in cross-flow nebulizers. Detection limits for the ultrasonic nebulizer are 4 to 18 times less than detection limits achievable using a cross-flow pneumatic nebulizer, with equivalent sample analysis time.

INTRODUCTION

The National Water Quality Laboratory (NWQL) purchased an ultrasonic nebulizer for use with a newly acquired Thermo-Jarrell Ash inductively coupled plasma–optical emission spectrometer (ICP–OES). The authors intended to investigate the capabilities of the nebulizer and determine the usefulness of this technology to the NWQL. It was hoped that this nebulizer could be used to improve the overall performance of the methods in use at the NWQL. The first phase of the project was to adapt the nebulizer for use in evaluating a low ionic-strength method to determine calcium, iron, magnesium, manganese, silica, and sodium in acid-rainwater samples. The second phase of the project was to adapt the nebulizer for use with the general 20-element ICP–OES scan for whole-water recoverable samples. The third phase would evaluate its possible use with the inductively coupled plasma–mass spectrometer systems used for ultratrace element scans. Because the ultrasonic nebulizer was to be used on a variety of systems and applications, a detailed description of all aspects of the nebulizer's performance was needed. Signal intensities, detection limits, method precision and bias, sample interferences, and sample carryover effects were investigated but a complete study was not possible. Budget cutbacks and a laboratory reorganization precluded completion of the second and third phases of the project. Only a small part of the second phase of the project was finished, consisting primarily of establishing fundamental instrument settings and preliminary detection limit data for the 20-element scan. No data were collected for the inductively coupled mass spectrometer. On the basis of the present (1997) research, the

ultrasonic nebulizer could improve the performance of the mass spectrometer as well. However, much information was gained before the project was terminated. This report summarizes the results.

Purpose and Scope

This report describes a method for determining calcium, iron, magnesium, manganese, silica, and sodium in samples of low ionic-strength water. The method was developed by the U.S. Geological Survey (USGS) for use in the National Water Quality Laboratory (NWQL). The method uses a modified ultrasonic nebulizer sample introduction system to an ICP–OES. The method supplements other methods of the USGS for determination of inorganic substances in water that are described by Fishman and Friedman (1989). At the present time (1997), this method has not been implemented at the NWQL.

Modifications to the Commercial Ultrasonic Nebulizer System

After completing several analytical tests using the Baird ultrasonic nebulizer (UDX), it was clear that the system could not obtain the expected detection limits published by the manufacturer. The manufacturer claimed detection limits 10 to 40 times better than that of a cross-flow system. Design flaws prevented the nebulizer from operating at maximum potential. For example, the factory claimed a detection limit for iron of 0.3 µ/L. However, problems with the system prevented it from detecting iron at less than 10 µ/L. The system had to be corrected to operate it near the expected performance claimed by Baird. First, the position of the sample guide tube and argon carrier inlet (fig. 1) disrupted the sample flow. Water droplets produced by the vibrating transducer blocked the argon inlet and condensed on the sample guide tube, eventually dribbling down onto the transducer. Both results severely disrupted the stability of the plasma. Second, the heater tube running at nearly 300 degrees Celsius (^{o}C) was too hot, and as constructed, was not adjustable. The extreme heat overloaded the small condenser used to remove water from the sample and allowed too much water vapor to enter the plasma (fig. 2). This overload caused the plasma to surge and oscillate violently. The third problem was the use of drain traps at atmospheric pressure. The pressure of the argon carrier flow caused water in the traps to oscillate. This oscillation disrupted the continuous flow of sample aerosol into the plasma.

To correct these problems, the glass spray chamber was reconstructed with the sample input tube and argon carrier inlet in positions that would prevent droplets from interrupting the flow of sample aerosol to the inductively coupled plasma (ICP) (fig. 3). The design of the spray chamber was influenced by designs from Olson and others (1977), Goulden and Anthony (1984), Fassel and Bear (1986), and Browner and Boorn (1984). Additionally, a sample wash port at the top of the spray chamber was added so that high-conductance samples could be washed quickly from the spray chamber with the aid of two high-speed water pumps. This rinse system was added to the nebulizer because some researchers were concerned that adverse carryover problems were inherent with an ultrasonic nebulizer system (Olson and others, 1977), and they were skeptical of the nebulizer's use with high-conductance samples. The heater tube circuit was rewired through a Variac autotransformer so that the temperature of the tube could be controlled. The temperature for optimum nebulizer performance ranges from 100 to 150^{o}C. This temperature range concurs with the findings of other authors (Fassel

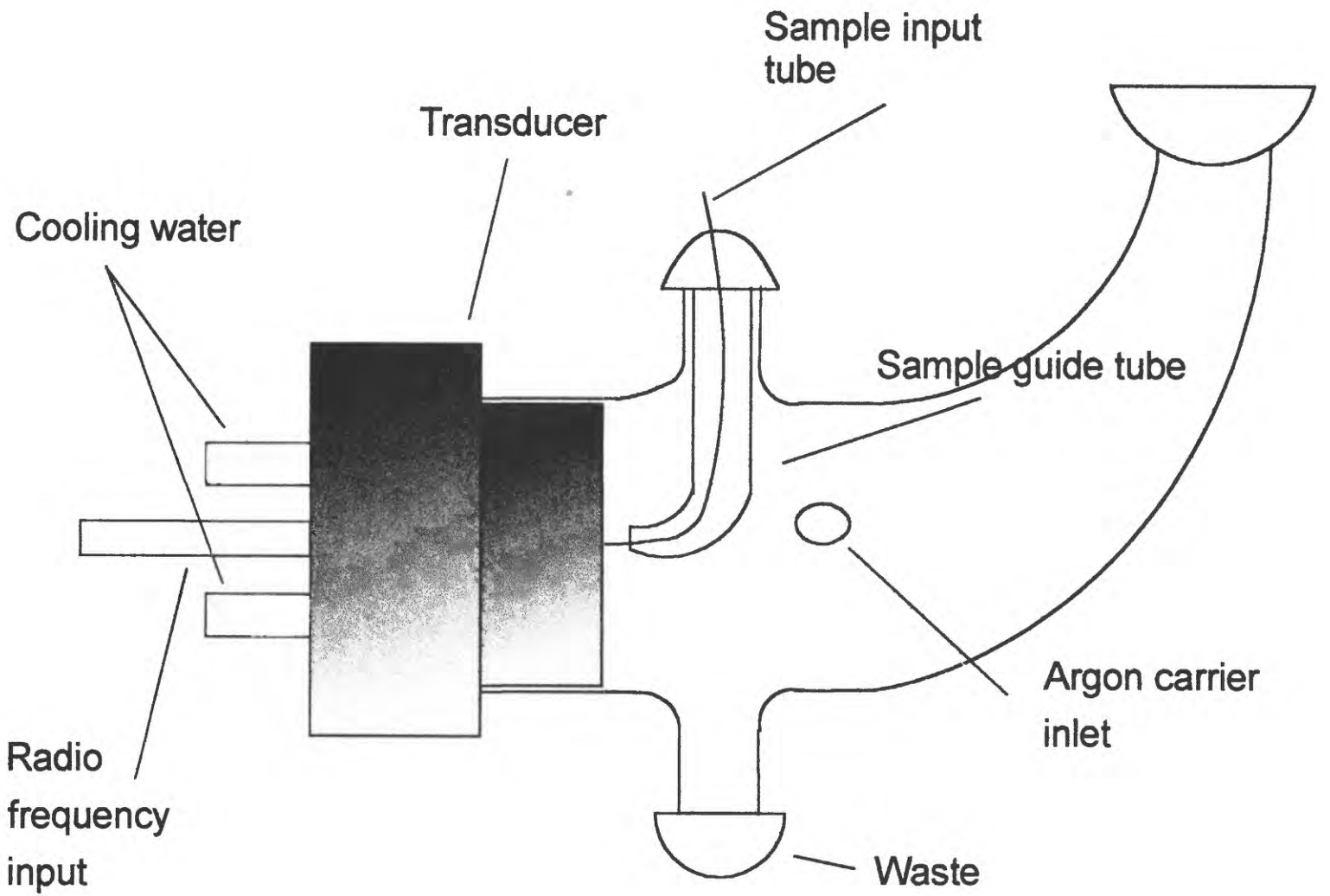

Figure 1.–Baird UDX ultrasonic nebulizer.

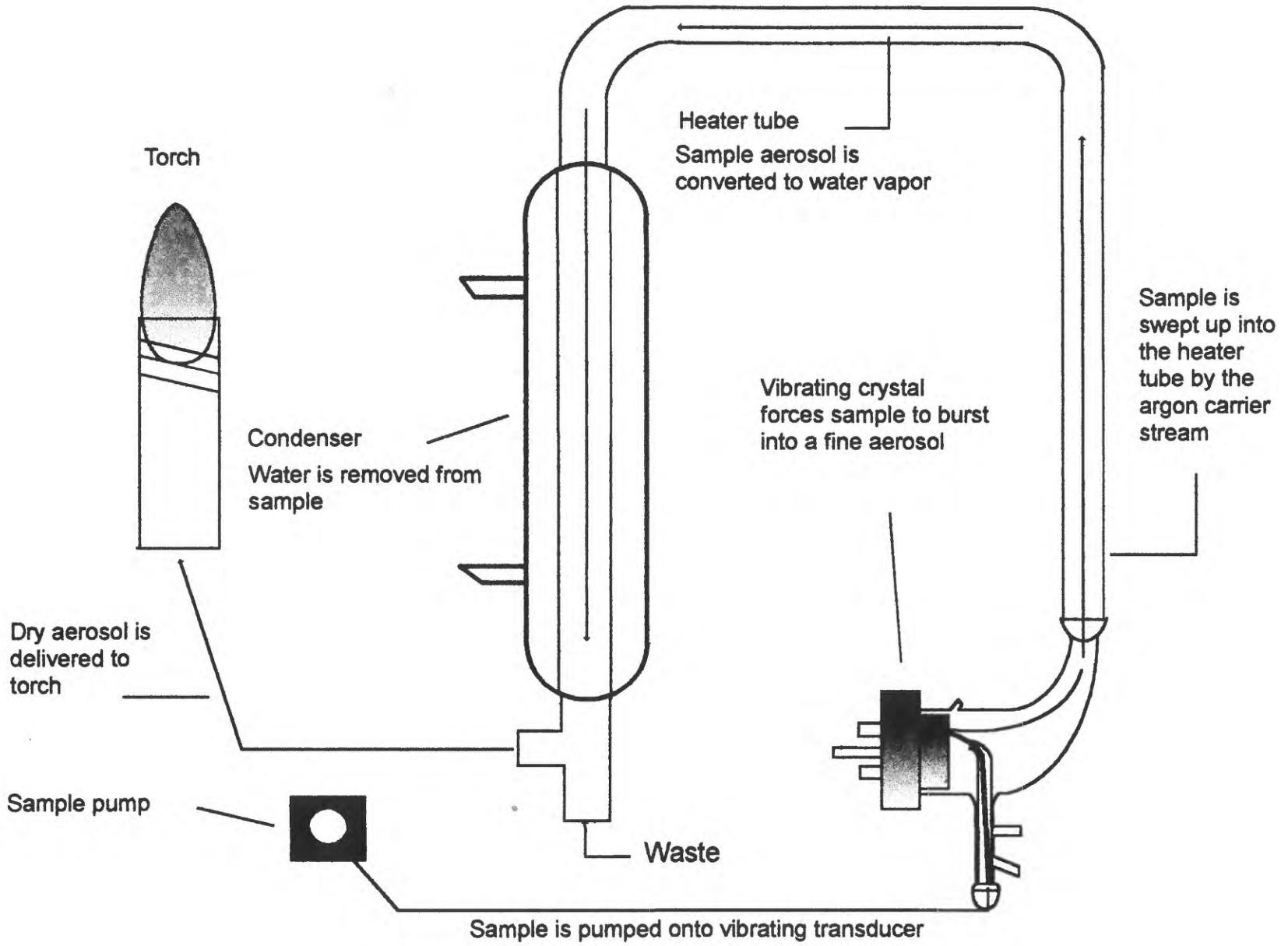

Figure 2.–Inductively coupled plasma–ultrasonic nebulizer system with modified spray chamber.

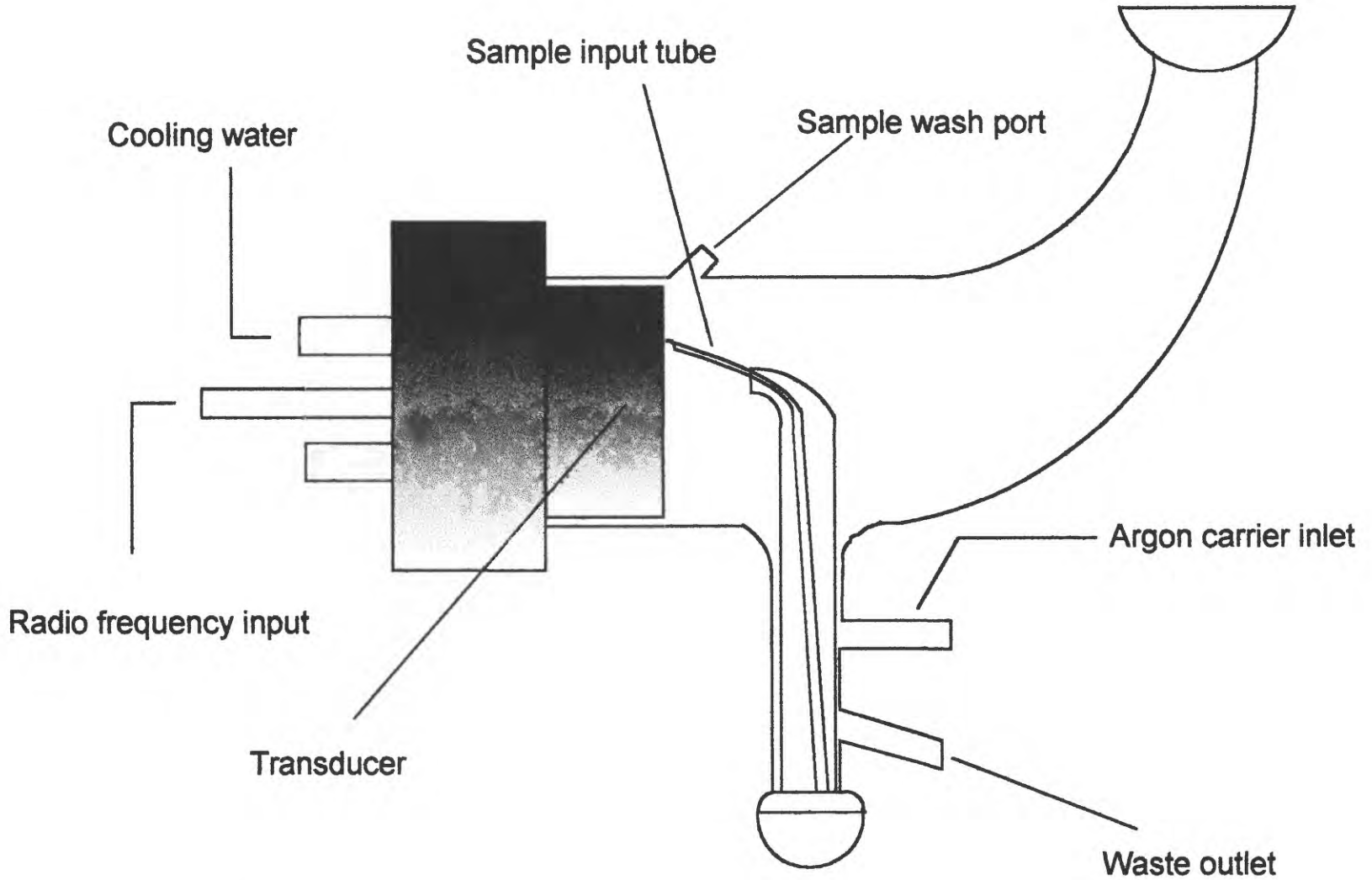

Figure 3.—Modified ultrasonic nebulizer spray chamber.

and Bear, 1986; Petrucci and Van Loon, 1990; Anderson, 1992). The optimum temperature was determined by analyzing a 10-mg/L standard of caldium at different heater tube temperatures and tabulating the results (fig. 4).

Since the waste is being pumped out of the spray chamber at a constant rate, it does not pool at the base of the input stem. This procedure prevents the argon inlet from being clogged by a puddle of water. The waste flow is controlled by a peristaltic pump that pumps water at a much higher pressure than the input pressure of the argon gas (fig. 5). This large pressure gradient prevents argon from backing up into the waste outlet. The waste traps were disconnected from the nebulizer, and drain tubes were connected through another pump to provide a smooth flow of waste from the nebulizer.

ANALYTICAL METHOD

1. Application

Samples analyzed using this method must have a specific conductance of less than 100 µS/cm as a prerequisite for determining calcium, iron, magnesium, manganese, silica, and sodium. The suitability of this method for determining trace metals in high-conductance water samples was not investigated fully. However, partial data were collected for whole-water samples that were used as test samples for the second phase 20-element scan. Results indicated that higher conductance samples (for example, samples greater than 100 µS/cm) could be analyzed by the nebulizer depending on the background matrix composition. These data are not included in this report, but current (1997) findings suggest further study would be appropriate. The concentration limits are listed in table 1. Samples with specific conductances greater than 100 µS/cm require appropriate dilution and duplicate analysis as a precaution against salt interferences that are enhanced by the ultrasonic nebulizer.

Table 1.--Working ranges of constituents for inductively coupled plasma–optical emission spectrometer
[nm, nanometer; µg/L, microgram per liter; mg/L, milligram per liter]

Major ion, trace metal, or constituent	Lower limit	Upper limit	Wavelength (nm)
Calcium	0.005 mg/L	10 mg/L	396.8
Iron	.33 µg/L	5,000 µg/L	259.9
Magnesium	.0014 mg/L	5 mg/L	279.5
Manganese	.14 µg/L	5,000 µg/L	257.6
Silica	.019 mg/L	5 mg/L	288.1
Sodium	.011 mg/L	10 mg/L	589.0

2. Summary of method

The water sample to be analyzed is pumped from a test tube onto the surface of a vibrating transducer. The transducer is constructed of lead-zirconate-titanate ceramic that is bonded to

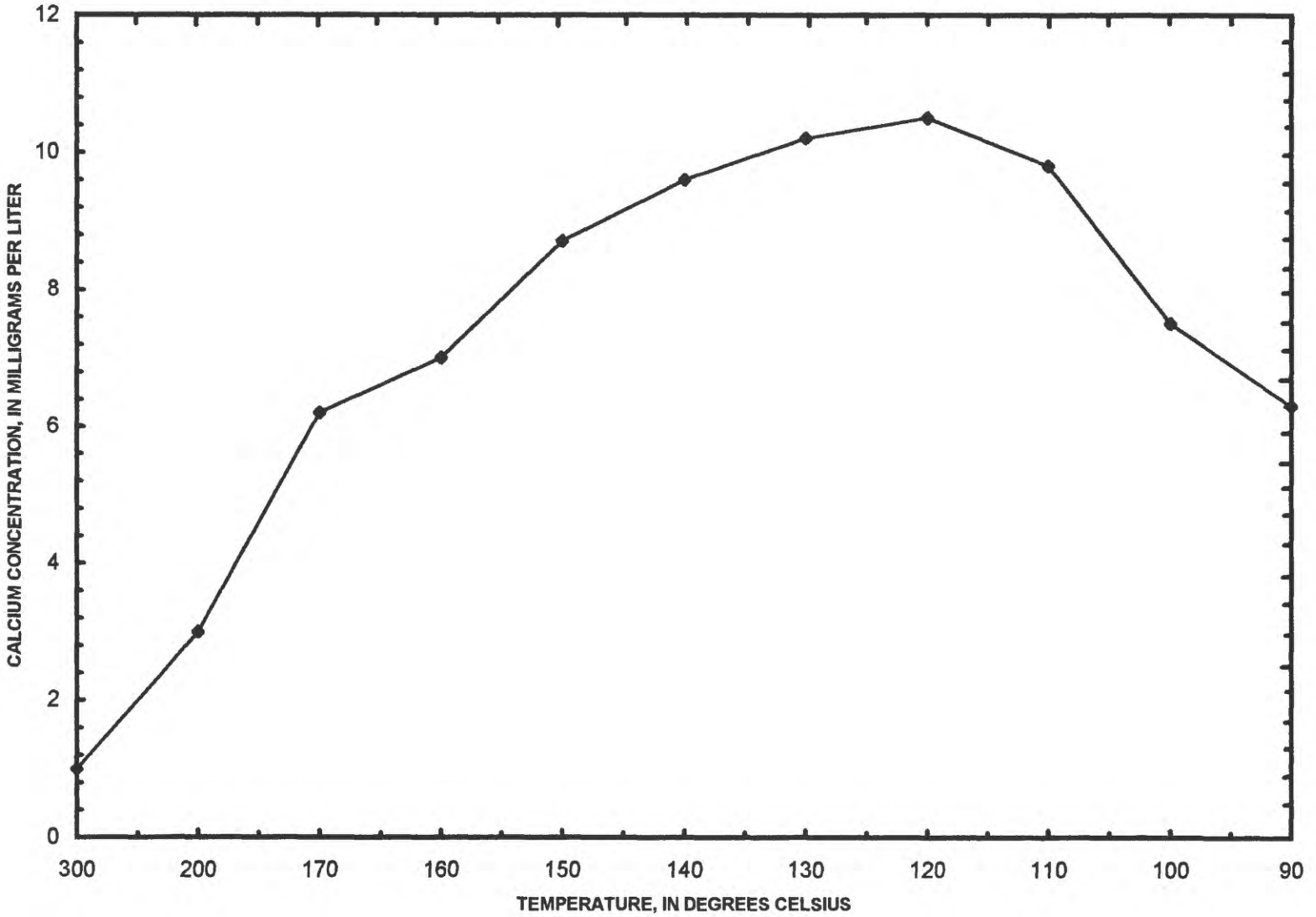

Figure 4.—Calcium concentration with respect to heater tube temperature.

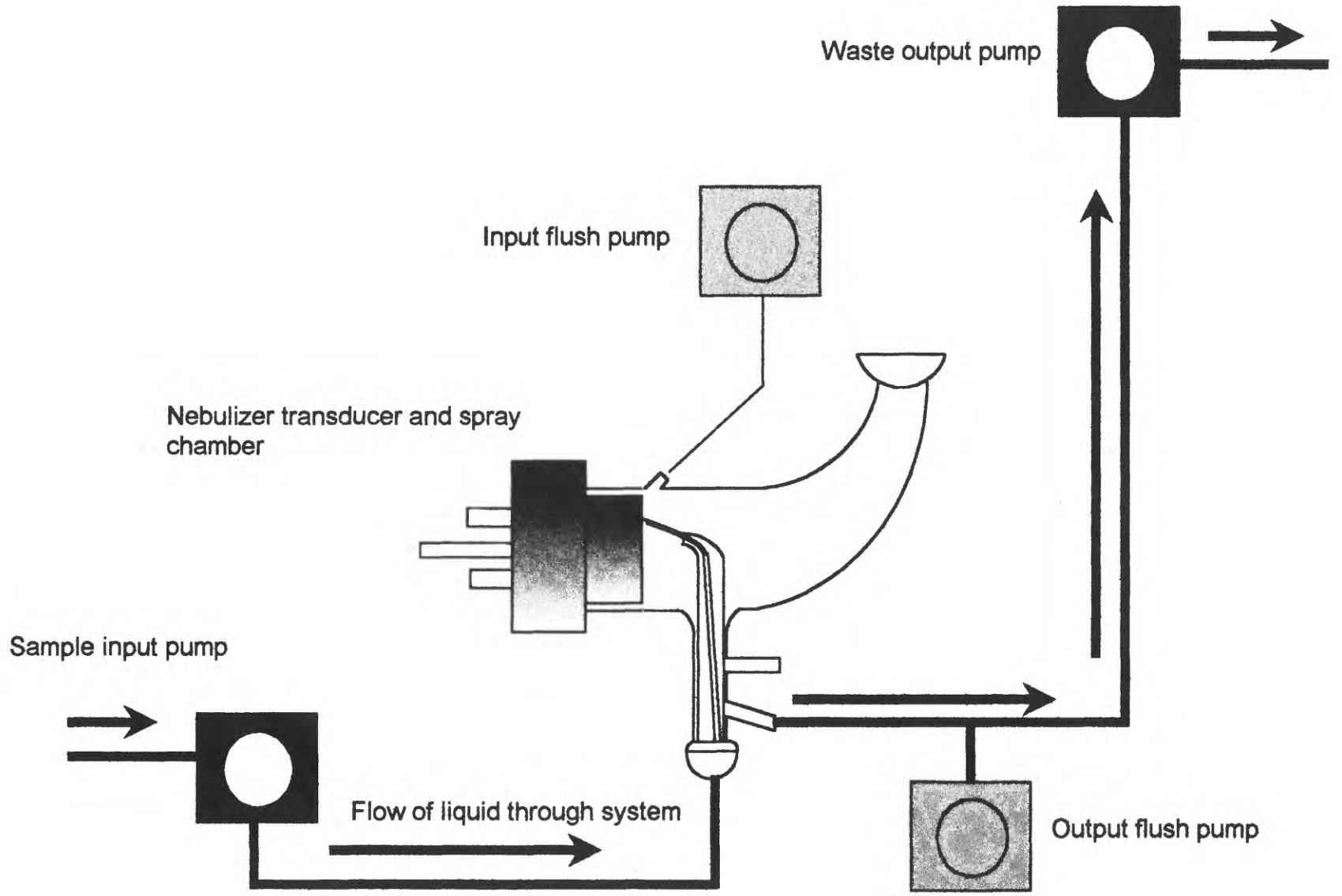

Figure 5.—Operation of the ultrasonic nebulizer's sample input and waste output system.

a polished quartz plate to protect the transducer from corrosion. The transducer is water cooled and is driven by a radio frequency generator. The transducer vibrates at a frequency of 1.35 MHz (fig. 3). The acoustic energy supplied by the transducer causes the sample flowing across the transducer surface to burst into a fine aerosol (Nygaard and Bulman, 1990; Tarr and others, 1991). Unlike cross-flow nebulizers that have a transport efficiency of 1 to 2 percent, the ultrasonic nebulizer has a transport efficiency greater than 85 percent, that is, 85 percent of the sample delivered to the nebulizer reaches the plasma (Olson and others, 1977; Petrucci and Van Loon, 1990). The volume of aerosol produced by the nebulizer is so large that it contains enough water to extinguish the plasma; therefore, desolvation is required. The aerosol is swept into a quartz tube that has been wrapped with an electric heating tape. The tube is heated to a temperature of 120°C to convert the water contained in the aerosol to water vapor. The vapor and analyte stream then are passed through a glass condenser maintained at 1°C to remove a large portion of the water vapor from the analyte stream ("analyte" is a substance being determined in an analysis). The "dried" aerosol is then introduced to the plasma for analysis (fig. 2).

After the sample has been analyzed, the autosampler then returns to its home position. This activates two small high-speed water pumps that pump approximately 170 mL of ASTM type I reagent water across the face of the transducer (fig. 6).

One of the pumps sprays water across the transducer face while the other pump sucks this waste water out of the spray chamber through the waste outlet. This cycle of pushing and then pulling the water out of the spray chamber allows a large amount of cleaning water to be flushed through the nebulizer without significantly disrupting the gas flow to the plasma.

The thickness of the water column passing across the transducer is sufficient to completely absorb the acoustic energy produced by the vibrating transducer. This result momentarily stops the generation of aerosol in the spray chamber, allowing any excess aerosol to be swept out of the spray chamber before the next sample is introduced. It also washes away any material deposited on the quartz end plate, avoiding memory effects produced by re-nebulizing previous samples.

The photons produced from the atomic emission of sample after it has been injected into the plasma are isolated, quantified, and analyzed by the spectrometer's hardware and software. The spectrometer's software compares "unknowns" to a two-point calibration curve and calculates a concentration for each "unknown."

3. Interferences

Samples with specific conductances greater than 100 µS/cm may contain interferences. No interfering matrices were found when analyzing low-conductance samples. A 100-mg/L standard for each of 20 elements was analyzed to determine interelement interferences. For example, a sample containing 100 mg/L of sodium was analyzed and the impact of that sample was recorded for each of the 20 elements the instrument was programmed to detect. The results are shown in table 2. Other types of interferences such as high chloride or sulfate concentrations were not investigated prior to termination of the project.

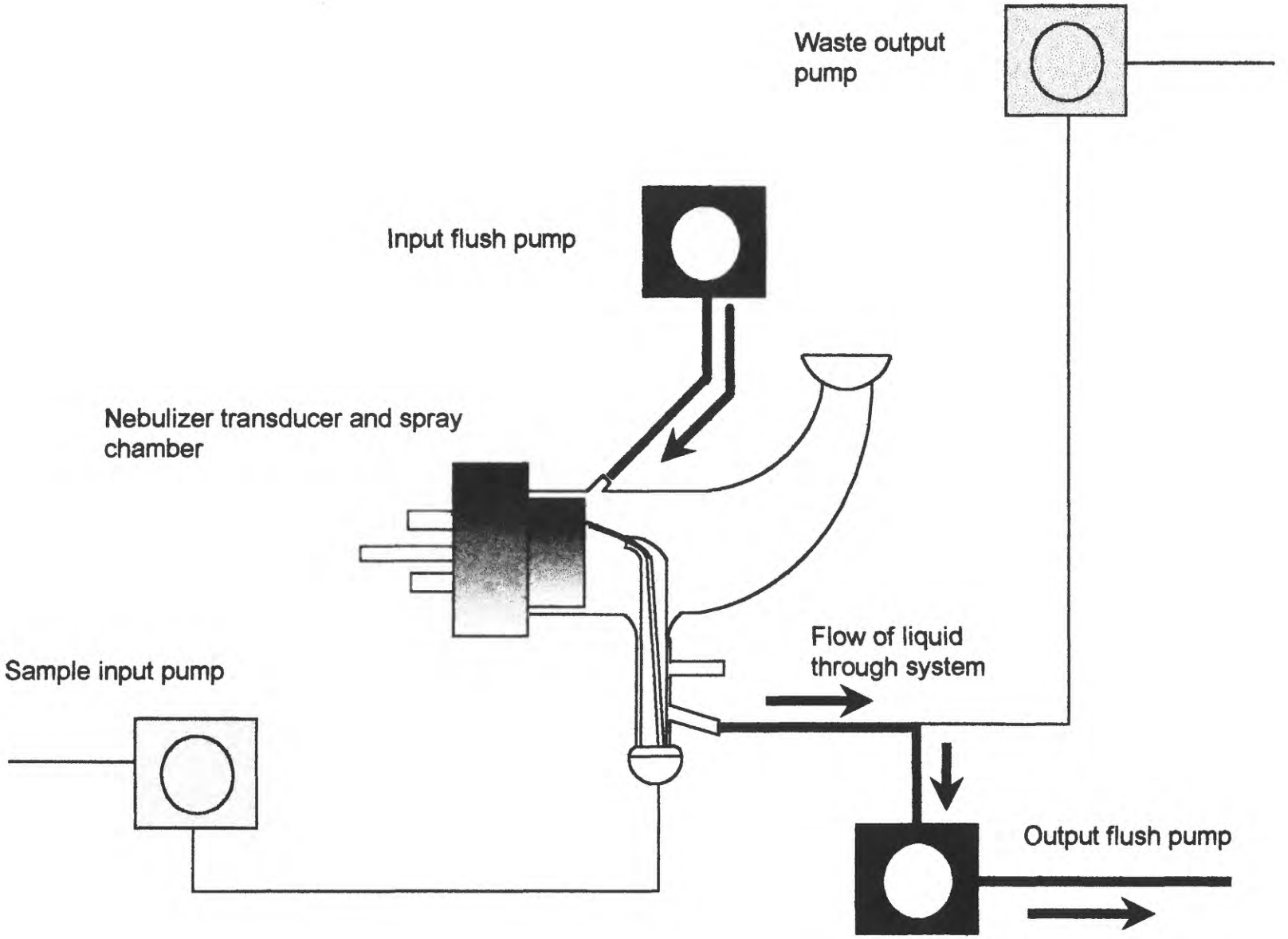

Figure 6.—Operation of the ultrasonic nebulizer's flush wash system.

Table 2.-- Single-element interference at 100 mg/L with background correction

[mg/L, milligram per liter; µg/L, microgram per liter; - -, indicates signal saturation]

100 mg/L	Ag µg/L	Al µg/L	B µg/L	Ba µg/L	Be µg/L	Ca mg/L	Ca_2 mg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Fe µg/L	K mg/L	Li µg/L	Mg mg/L	Mg_2 mg/L	Mn µg/L	Mo µg/L	Na mg/L	Na_2 mg/L
Ag	- -	4	57.9	0.89	1	0.01	0	0	4.5	1.7	2.9	55.9	0.04	0.01	0	0	0.76	5.9	0	0.65
Al	42.29	- -	43.7	0.34	0.59	0	0	0	3.1	0	0.45	1.89	0.09	0.03	0	0	0.16	3.76	0	1.06
B	53.16	19.61	- -	0.23	0.3	0	0	0	2.25	0.01	0	0.59	0.16	0.11	0	0	0	3.8	0	1.03
Ba	2.2	13.54	1,004	- -	0.38	0	0	0	2.9	0	1.29	2.57	0.08	0	0	0	0	4.87	0	1.02
Be	2.5	42.82	566	17.39	- -	0	0	0.97	5.56	5.57	2.45	50.03	0.03	0	0	0	10.2	3.15	0	0
Ca	54.51	11.75	413	2.67	13.89	- -	98.73	0	3.15	0.51	1.48	6.07	0	0	0	0	0	4.04	0	0.64
Ca_2	28	10.83	348	1.74	2.92	- -	95.23	0	3.37	0.46	1.67	5.9	0.06	0	0	0	0	4.98	0	0.64
Cd	16	2.09	309	0.89	1.9	0.01	0.01	- -	2.66	0	4.7	2.24	0	0	0	0	0	4.56	0	1.02
Co	11	4.39	299	0.71	1.45	0	0.29	15.56	- -	0.46	15.28	19.01	0.04	0	0	0	0.26	94.02	0	0.24
Cr	2.06	3.26	210	0.51	0.58	0	0	1.2	0	- -	0	1.44	0.03	0	0	0	0.14	0	0	0
Cu	11.7	0.1	239	0.47	1.09	0	0	0	8.6	21.85	- -	2.29	0	0	0	0	0	11.99	0	0.75
Fe	0	225.3	414	0.27	0.7	0	0	5.2	1,980	1.03	8.1	- -	0	0	0	0	0	5.59	0	0
K	1	2.66	256	0.2	0.61	0.01	0	0	5.62	0.14	4.25	9.01	- -	0	0	0	0	7	0	1.92
Li	5.1	2.76	158.6	0.44	1.02	0	0	0	3.82	1.69	2.96	6.17	0.19	- -	0	0	0	9.66	0	0.78
Mg	6.7	8.6	196	0.13	0.54	0	0	0	4.15	0.11	3.09	7.13	0.18	7.7	- -	98.81	3.4	6.16	0	1.37
Mg_2	4.9	8.09	186	0.06	0.45	0	0	0	3.25	0	1.87	5.25	0	1.65	- -	98.81	3.39	5.17	0	0.83
Mn	16.7	3.44	186	0	0.61	0.01	0	0	0.46	0	0.12	34.4	0	0	0	0	- -	19.22	0	1.35
Mo	17.57	14.89	156	0.2	0.42	0	0.1	0	0	24	37.6	53.8	0.15	5.43	0	0.19	0	- -	0	0.94
Na	0	0.39	127	0.06	0.35	0	0	0	3.67	0.94	3.8	3.24	0.12	1.15	0	0	3.36	38.56	0	102.6
Na_2	0	0.64	122	0	0.29	0	0	0	3.39	0.56	3.28	2.06	0.08	0.38	0	0	0.56	10.6	0	102.7

The 10-fold increase in spectraline intensity produced by the ultrasonic nebulizer causes interfering components to impact sample analyte signals at concentrations that are ten times less than those of a cross-flow nebulizer. Samples should not exceed a specific conductance of 100 µS/cm to minimize interference problems.

4. Instrumentation and apparatus

This method has been written explicitly for the following combination of instruments and modifications:

4.1 *Emission spectrometer*, Thermo-Jarrell Ash ICP–OES, Model ICAP 61E with nitrogen purge.

4.1.1 Autosampler, Thermo-Jarrell Ash, XYZ autosampler.

4.1.2 Ultrasonic nebulizer, Baird UDX, with a custom-built spray chamber.

4.1.3 Peristaltic pump, Gilson Mini Pulse II, with a 10-roller barrel Baird high-speed peristaltic pump.

4.1.4 Water pumps, National pump, high-speed graphite gear pumps.

4.1.5 Transformers, Variac, variable 120/140-volt autotransformers.

4.2 *Operating Conditions*

ICP–OES

Torch Gas	18 L/min
Auxillary Gas	1 L/min
Nebulizer Gas Pressure	30 lb/in^2 (21,092 kg/m^2)
Approximate radio frequency forward power	1,350 kW

Nebulizer

Heater Tube Temperature	120°C
Condenser Temperature	1°C
Sample Flow Rate	2.6 mL/min
Sample Flush Rate	680 mL/min

5. Reagents

Use glass, class "A", for all pipets and glassware. Wash all pipets first in 10 percent (v/v) nitric acid and then three times in ASTM Type I water. Soak all volumetric flasks in 10 percent nitric acid, and rinse three times in ultrapure water prior to use.

5.1 *Water*, all references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1994, p. 45–47).

5.2 *Ultrapure nitric acid*, J.T. Baker, Ultrex II, ultrapure reagent or equivalent.

5.3 *10 percent (v/v) nitric acid wash solution*: Pour 100 mL ultrapure nitric acid into a 1,000-mL volumetric flask, and fill to volume with reagent grade water.

5.4 *Calcium*, Standard Solution I, 1.00 mL = 100 mg Ca, T.J. Baker instra-analyzed atomic absorption standard solution or equivalent.

5.5 *Iron*, Standard Solution I, 1.00 mL = 100 mg Fe, T.J. Baker instra-analyzed atomic absorption standard solution or equivalent.

5.6 *Magnesium*, Standard Solution I, 1.00 mL = 100 mg Mg, T.J. Baker instra-analyzed atomic absorption standard solution or equivalent.

5.7 *Manganese*, Standard Solution I, 1.00 mL = 100 mg Mn, T.J. Baker instra-analyzed atomic absorption standard solution or equivalent.

5.8 *Silica*, Standard Solution I, 1.00 mL = 100 mg SiO_2, T.J. Baker instra-analyzed atomic absorption standard solution or equivalent.

5.9 *Sodium*, Standard Solution I, 1.00 mL = 100 mg Na, T.J. Baker instra-analyzed atomic absorption standard solution or equivalent.

6. Calibrants

6.1 *Summary of procedure*

Make all mixed working standard solutions from single-element stocks that are manufactured certified commercial standards. Working standard solutions are prepared by diluting 25 mL of a single-element stock standard into a 250-mL plastic polyethylene volumetric flask. This procedure will produce two mixed calibration standards (Mix 1 and Mix 2) and a synthetic mixed calibration check standard (Mixall).

6.2 *Stock I calibration standard solutions*

All stock I calibration standard solutions have a concentration of 1,000 mg/L or 1 mg/mL of constituent (table 3). The standard solutions can be manufactured in-house or purchased as a certified standard.

Table 3.--Preparation of stock I calibration standard solutions
[mg/L, milligram per liter]

Major ion, trace metal, or constituent	Stock I concentration (mg/L)
Calcium	1,000
Iron	1,000
Magnesium	1,000
Manganese	1,000
Silica	1,000
Sodium	1,000

6.3 *Stock II calibration standard solutions*

Prepare stock II calibration standard solutions by diluting a fixed amount of all six stock I calibration standard solutions into 1 L of ASTM Type I reagent water (table 4).

Table 4.--Preparation of stock II calibration standard solutions
[mL, milliliter; mg/L, milligram per liter]

Major ion, trace metal, or constituent	Amount of stock I (mL)	Final volume (mL)	Final concentration (mg/L
Calcium	100	1,000	100
Iron	5	1,000	5
Magnesium	50	1,000	50
Manganese	5	1,000	5
Silicas	50	1,000	50
Sodium	1,000	1,000	100

6.4 *Working calibration standard solutions*

All working calibration standard solutions are prepared by pipeting 25 mL of the stock II calibration standard solutions into 250-mL plastic polyethylene volumetric flasks and filling the flasks to volume with ASTM Type I reagent water (table 4). There are two mixed calibration standards because the silica component is made from sodium silicate that will interfere with the sodium component. The six components are split into two mixes to simplify manufacture of the calibration standard solutions (table 5).

Table 5.--Preparation of working calibration standard solutions
[mL, milliliter; µg/L, microgram per liter; mg/L, milligram per liter]

Major ion, trace metal, or constituent	Amount of stock II (mL)	Final volume (mL)	Final concentration
	Mix 1		
Iron	25	250	500 µg/L
Magnesium	25	250	5 mg/L
Silica	25	250	5 mg/L
	Mix 2		
Calcium	25	250	10 mg/L
Manganese	25	250	500 µg/L
Sodium	25	250	10 mg/L

Synthetic mixed calibration check standard solutions are listed in table 6.

7. Calibration

Calibrate the instrument by scanning an ASTM Type I reagent water blank and the two calibrants, Mix 1 and Mix 2, in succession. The ThermoSpec software of the spectrometer will construct a calibration curve from the spectral intensities of the blank and calibrants. Check the accuracy of the calibration curve by analyzing the Mixall, NIST (National Institute of Standards and Technology), and SRWS (Standard Reference Water Sample) check

Table 6.--Preparation of Mixall calibration check standard solutions
[mL, milliliter; µg/L, microgram per liter; mg/L, milligram per liter]

Major ion, trace metal, or constituent	Amount of stock II (mL)	Final volume (mL)	Final concentration
Calcium	25	500	5 mg/L
Iron	25	500	250 µg/L
Magnesium	25	500	2.5 mg/L
Manganese	25	500	250 µg/L
Silica	25	500	2.5 mg/L
Sodium	25	500	5 mg/L

standards and comparing quantities detected with certified quantities listed for each standard. The quantities determined must agree to published values to within 1.5 standard deviations from the most probable value. If values fail to meet acceptance limits, abort the calibration and investigate a probable cause for the failure to meet quality-control limits.

8. Procedure

Start the instruments and purge the system with argon. Fill the UDX wash pump lines with water before igniting the torch. Ignite the torch and wait until the heater tube and the cooling water of the UDX have reached 120° and 1°C, respectively. Turn on the autosampler and waste pumps. The next step is to energize the transducer and allow the aerosol to flow through the system for 15 minutes before calibrating the instrument.

9. Calculations and data evaluation

Before the calibration function can be estimated, program interelement interferences and background correction offset parameters into the computer software of the ICP. Determine the interelement interferences by scanning a 100-mg/L standard of a particular element, and chart its effect on the blank signals of the 26 lines available on the ICP. Interference correction factors were needed for aluminum, iron, and cobalt. Determine background correction offset values by scanning a mixed standard containing a suite of all 23 major ions, trace metals, and constituents that the ICP determines and setting the background correction points by inspecting the peak profiles. Predominantly, this factor has been set at +15 for all ions, metals, and constituents except sodium, which is not corrected because of the need for increased sensitivity of this spectral line. All baselines were measured on the high wavelength side of each peak. Program all other calculations, which are applied automatically as needed, such as reporting limits, significant figures, concentration units, and offscale concentrations, into the ThermoSpec software.

10. Reporting of results

Report concentrations of iron and manganese of 10 µg/L or less to one decimal place; greater than 10 µg/L, two decimal places. Report calcium, silica, and sodium of 1 mg/L or less to one

decimal place; greater than 1 mg/L, two decimal places. Report magnesium of 0.1 mg/L or less to two decimal places; greater than 0.1 mg/L, three decimal places.

11. Precision and bias

11.1 Precision was measured for the method using a combination of Standard Reference Water Samples (SRWS), natural-water samples, and National Institute for Standards and Technology (NIST) check standards. Precision data for each analyte are listed in table 7.

Table 7.--Precision data
[µg/L, microgram per liter; mg/L, milligram per liter]

Analyte	Number of replicates	Average concentration	Standard deviation (percent)	Relative standard deviation (percent)
Calcium	4	1.90 mg/L	0.14	7.7
	10	5.35 mg/L	.04	.9
	8	8.97 mg/L	.09	1.1
Iron	4	98.1 µg/L	5.6	6.7
	8	205.1 µg/L	8.9	4.3
Magnesium	4	0.64 mg/L	.06	8.5
	10	1.39 mg/L	.03	2.0
	8	2.69 mg/L	.10	3.8
	8	3.99 mg/L	.08	1.9
Manganese	4	98.8 µg/L	7.4	7.5
	8	203.6 µg/L	10.4	5.1
Silica	4	0.74 mg/L	.01	2.0
	10	1.54 mg/L	.04	2.9
	8	1.63 mg/L	.004	0.7
	8	15.03 mg/L	.58	3.9
Sodium	4	1.55 mg/L	.13	8.3
	10	3.26 mg/L	.13	4.0
	8	5.66 mg/L	.26	4.5
	8	13.19 mg/L	.15	1.1

11.2 Bias was calculated by comparing the mean of the paired differences of 80 NIST and SRW samples to that of the cross-flow method. The overall bias is listed in table 8.

Table 8.--Method bias of ultrasonic nebulizer
[mg/L, milligram per liter; (µg/L, microgram per liter]

Major ion, trace metal, or constituent	Bias using ultrasonic method
Calcium	–0.008 mg/L
Iron	0.18 µg/L
Magnesium	–0.03 mg/L
Namgnese	–0.09 µg/L
Silica	–0.001 mg/L
Sodium	–0.03 mg/L

DISCUSSION OF RESULTS

The nebulizer was tested to find the best forward power, sample uptake rates, and condenser temperatures, as well as optimum carrier gas-flow rates and observation heights for the spectrometer. A comparison of forward power in relation to intensity for cross-flow and UDX nebulizers showed that the UDX produced signal intensities 8 to 16 times more intense than those obtainable by pneumatic cross-flow nebulizers (fig. 7). The best instrument operating conditions are listed in Section 4.2 and are similar to those of other systems developed by Fassel and Bear (1986), Nygaard and Bulman (1990), and Petrucci and Van Loon (1990). A method detection limit (MDL) was calculated using the procedure outlined by the U.S. Environmental Protection Agency (1992, p. 537–539). The estimated MDL was unknown. Other authors cited detection limits 5 to 50 times less than those obtainable with pneumatic nebulizers. Using these reported MDLs as a guideline, synthetic detection limit standard solutions were mixed with concentrations equal to the reporting limits of the conventional cross-flow ICPs used elsewhere in the laboratory. All standard solutions were analyzed nonconsecutively for two weeks. The concentrations for synthetic standards of iron, manganese, and magnesium were less than expected. This could be a result of inaccurate calibrants or a compromised torch position creating a small bias. Other authors such as Taylor and Floyd (1981) have noted that the optimal torch position varies between the two different nebulizers. Torch position refers to the height of the plasma tongue above the load coil. The position of the plasma tongue dictates which part of the plasma cross section is being viewed by the instrument optics. Optimal placement of the plasma tongue is essential to achieve optimal sensitivity from the instrument. A fixed torch height was selected as a compromise between the two different nebulizers because the same ICP was used to analyze regular production samples. This compromise made installing and reinstalling the nebulizers easier and less time consuming. Initial results showed that a lower set of detection-limit standards should have been made and the samples reanalyzed to obtain more accurate results. The project was terminated before additional tests could be made. However, the concentrations measured are still useful in determining the MDL for this method. Results were obtained by multiplying the standard deviation of N-1 trials by the Student's *t*-value at the 99 percent confidence level. The results are listed in table 9.

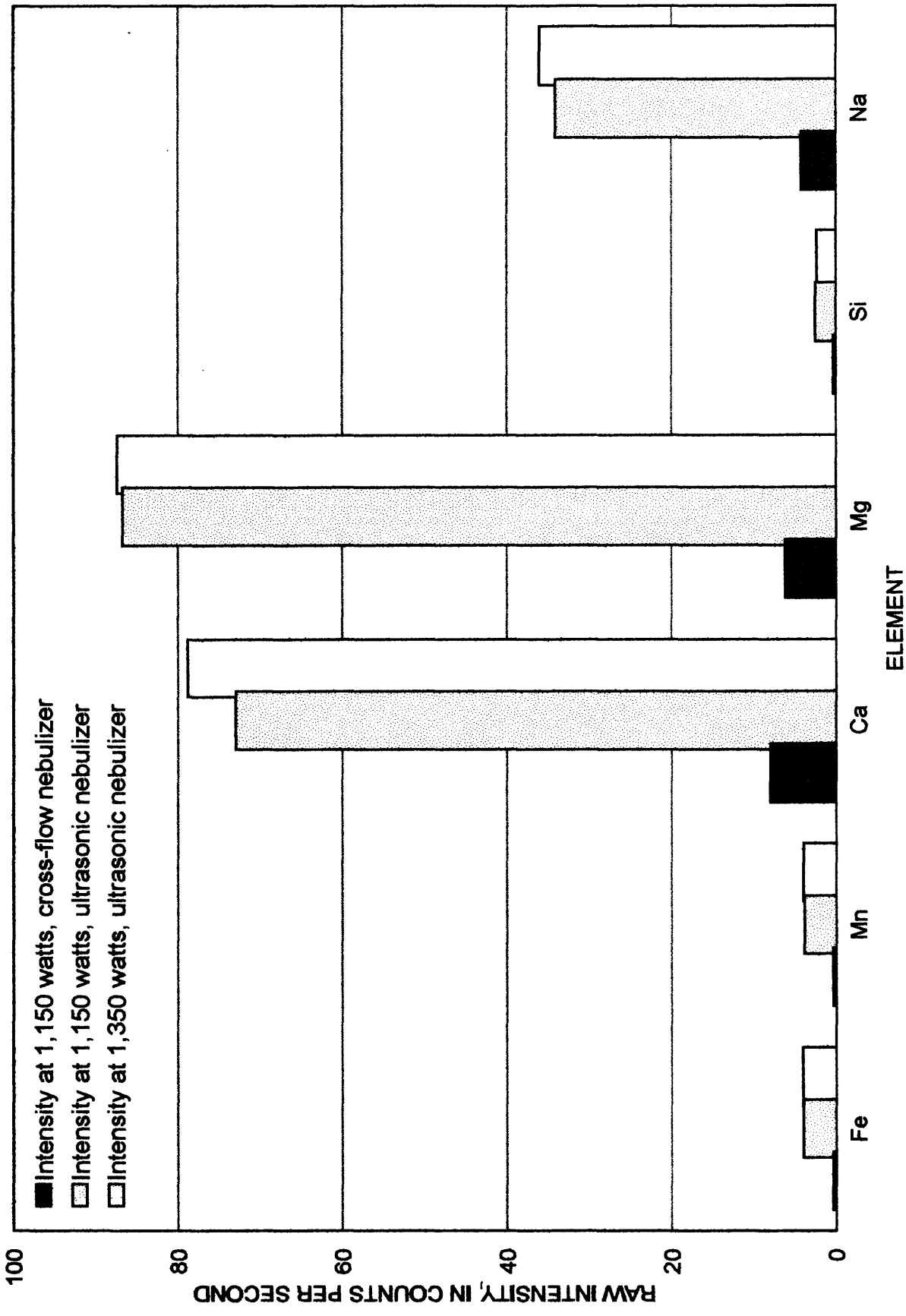

Figure 7.--Spectral intensity of cross-flow and ultrasonic nebulizers.

Table 9.--Results of method detection limit calculations
[µg/L, microgram per liter; mg/L, milligram per liter]

Major ion, trace metal, or constituent	Expected concentration	Concentration measured										Average concentration	Standard deviation	Method detection limit
		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10			
Calcium (mg/L)	0.1	0.106	0.106	0.101	0.105	0.104	0.103	0.102	0.104	0.104	0.102	0.104	0.0017	0.005
Iron (µg/L)	3	1.7	1.9	2.0	1.9	1.9	1.9	1.9	1.6	1.8	1.8	1.84	.117	.33
Magnesium (mg/L)	.01	.008	.009	.008	.009	.008	.009	.009	.008	.009	.008	.0085	.0005	.0014
Manganese (µg/L)	1	.8	.8	.8	.8	.7	.7	.7	.7	.8	.7	.75	.0527	.14
Silica (mg/L)	.02	.02	.019	.011	.021	.025	.023	.023	.016	.019	.021	.018	.0069	.019
Sodium (mg/L)	.2	.19	.19	.19	.19	.19	.19	.19	.20	.20	.19	.192	.0047	.011

The UDX produces improved detection limits compared to those obtained by conventional cross-flow nebulizers. A comparison of UDX and cross-flow nebulizer detection limits shows an average improvement of eight times greater than the cross-flow system (table 10). Cross-flow data were compiled by M.R. Hill (U.S. Geological Survey, written commun., 1992) and E.J. Zayhowski (U.S. Geological Survey, written commun., 1992). The ultrasonic nebulizer is a low-cost alternative, considering that other methods to reach detection limits equaling or exceeding this nebulizer, such as ICP–MS, IC, or ICP–OES, are expensive to purchase and operate. With a mass spectrometer priced up to $200,000, the nebulizer costs $13,000 with modifications. It is portable and only takes up the space of a personal computer, unlike a mass spectrometer, which usually requires its own room and special environmental controls to keep it operating.

Table 10.--Ultrasonic and cross-flow nebulizer detection limits
[mg/L, milligram per liter; µg/L, microgram per liter; UDS, ultrasonic nebulizer; X, times]

Major ion, trace metal or constituent	Detection Limit		Improvement over cross-flow
	UDX	Cross-flow	
Calcium	0.005 mg/L	0.02 mg/L	4X
Iron	.33 µg/L	3 µg/L	10X
Magnesium	.0014 mg/L	.01 mg/L	7X
Manganese	.14 mg/L	1 µg/L	7X
Silica	.019 mg/L	.02 mg/L	None
Sodium	.011 mg/L	.2 mg/L	18X

Some samples were spiked with two concentrations of the six metals. The results indicate no negative interferences for natural-water samples whose specific conductances are 100 µS/cm or less. The data are listed in table 11. Spikes were produced by measuring the proper quantity of sample and spike gravimetrically into a disposable beaker cup. Percent recoveries for Ca, Mg, Na, and SiO_2 at the spike concentration levels indicated should have been within ± 10 percent. High and low recoveries outside this range indicate problems in spike preparation or instrument performance.

To find the maximum concentrations of major cations determinable with the UDX, synthetic samples were prepared containing calcium, magnesium, silica, and sodium. Iron and manganese concentrations initially were not investigated because in the first phase of the project the low ionic-strength samples usually analyzed do not contain high concentrations of these metals. The samples were prepared in increasing concentrations from 5 to 500 mg/L for each component. They were analyzed against the standard calibration curve, and the concentrations are listed in table 12. Concentrations for the ultrasonic and conventional cross-flow nebulizers are shown in figure 8.

Comparison of the linearity or maximum concentrations obtainable by the spectrometer between the two different nebulizers indicates that the UDX has a much lower maximum.

Table 11.--Results of spiked samples

[mg/L, milligram per liter; µg/L, microgram per liter; DI, deionized; NIST, National Institute of Standards and Technology; SRW, Standard Reference Water]

Calcium

Sample	Unspiked concentration (mg/L)	Concentration of spike (mg/L)	Concentration measured										Average spiked sample concentration (mg/L)	Average recovery (percent)
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10		
DI blank	0.002	2	1.82	1.90	1.79	2.16							1.91	93.29
DI blank	.002	4	4.32	4.35	4.07	4.08	3.86	3.98	4.08	3.89			4.08	101.96
NIST1643B	3.492	2	5.28	5.36	5.39	5.34	5.42	5.45	5.32	5.33	5.35	5.28	5.35	92.9
NIST1643B	3.492	4	7.37	7.26	7.32	7.21	7.15	7.32					7.27	94.62
SRW T103	5.562	2	7.32	7.56	7.50	7.42	7.52	7.32	7.38				7.43	93.66
SRW T103	5.562	4	9.04	8.94	9.04	8.93	9.07	8.76	9.00	8.86	9.09	9.01	8.97	85.38
3490108	4.78	2	6.37	7.35	7.33	6.91	7.72	7.18	7.41	7.60			7.32	122.93
3490108	4.78	4	9.27	9.13	9.31	8.55	10.00	9.31	9.43	9.62			9.33	113.80
3490109	4.14	2	7.44	6.4	6.8	6.30	7.25	6.63	6.82	6.81			6.80	133.45
3490109	4.14	4	8.45	8.80	8.83	7.98	9.36	8.78	8.93	9.15			8.78	116.24
3490110	4.875	2	6.38	7.32	7.68	6.97	7.97	7.56	7.62	7.66			7.39	126.2
3490110	4.875	4	9.22	9.37	9.58	8.86	10.22	9.47	9.75	9.86			9.54	116.73
												Overall average recovery		**107.84**

Iron

Sample	Unspiked concentration (µg/L)	Concentration of spike (µg/L)	Concentration measured										Average spiked sample concentration (µg/L)	Average recovery (percent)
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10		
DI blank	1.416	100	108.3	98.89	94.82	90.47							98.1	96.7
DI blank	1.567	200	205.4	204.9	218.9	216.8	199.8	194.4	195.8				205.1	101.7
NIST1643B	12.05	100	114.1	111.4	111.1	112.0	110.3	111.2	110.5	111.8	103.5	108.3	110.4	98.3
NIST1643B	12.22	200	204.7	203	207.6	207.6	205.0	206.6					205.7	96.7
SRW T103	4.006	100	111	100.9	115	114.0	113.0	114.5					111.4	107.3
SRW T103	4.56	200	196.2	193.8	195.5	192.9	204.7	198.8	209.4	197.3	191.1	198.9	197.8	96.6
3490108	11.75	100	125.3	141.1	120.5	125.6	113.7	125.3	116.1	105.2			123.9	112.1
3490108	11.75	200	211.1	218.9	217.2	233.6	212.8	229.5	205.2	202.4			218.3	103.2
3490109	34.46	100	142.2	153.3	137.6	155.9	147.7	134.6	134.5				143.6	109.2
3490109	34.46	200	230.4	258.2	240.3	262.7	247.6	238.9	248.2				246.6	106.0
3490110	14.98	100	120.4	125.5	126.9	129.8	121.6	127.5	118				124.2	109.2
3490110	14.98	200	218.1	220.4	225.5	241.6	217.7	236.2	218.7				225.4	105.2
												Overall average recovery		**103.5**

Table 11.--Results of spiked samples—Continued

Magnesium

Sample	Unspiked concentration (µg/L)	Concentration of spike (µg/L)	Concentration measured										Average spiked sample concentration (µg/L)	Average recovery (percent)
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10		
DI blank	0.001	0.75	0.598	0.635	0.608	0.736							0.64	85.81
DI blank	.001	1.5	1.339	1.5	1.512	1.414	1.42	1.36	1.337	1.478			1.42	94.59
NIST1643B	.783	.75	1.383	1.374	1.374	1.416	1.418	1.426	1.416	1.431	1.338	1.386	1.39	81.66
NIST1643B	.783	1.5	2.053	2.006	2.029	2.119	2.087	2.108					2.06	85.55
SRW T103	2.913	.75	3.578	3.546	3.509	3.563	3.362	3.461					3.50	78.68
SRW T103	2.913	1.5	3.975	3.999	3.959	4.002	3.963	3.907	3.868	4.114	4.063	4.108	3.99	72.18
39108	1.164	.75	1.911	1.559	1.923	1.913	2.043	1.803	1.999	2			1.89	97.31
3490108	1.164	1.5	2.524	2.633	2.617	2.521	2.812	2.516	2.73	2.729			2.63	98.08
3490109	.8511	.75	1.5	1.992	1.629	1.592	1.736	1.514	1.677	1.641			1.66	107.8
3490109	.8511	1.5	2.315	2.268	2.34	2.214	2.484	2.235	2.492	2.443			2.34	99.85
3490110	1.19	.75	1.885	1.543	2.006	1.93	2.082	1.9	2.037	2.019			1.92	98.03
3490110	1.19	1.5	2.588	2.622	2.696	2.636	2.853	2.562	2.816	2.79			2.69	100.35
													Overall average recovery	**91.66**

Manganese

Sample	Unspiked concentration (µg/L)	Concentration of spike (µg/L)	Concentration measured										Average spiked sample concentration (µg/L)	Average recovery (percent)
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10		
DI blank	0.163	100	109.2	95.9	88.9	100.9							98.7	98.5
DI blank	.273	200	199.8	194.4	186.6	204.1	206.3	217.9	216.4				203.6	101.6
NIST1643B	3.305	100	102.1	102.7	102.2	103.3	96.8	101.3	107.8	104.9	105	105.6	101.4	98.0
NIST1643B	3.087	200	199.8	197	198.8	199.5	197.5	201.7					199.0	97.9
SRW T103	.573	100	105	108.5	99.3	110.9	110.2	109.1	110.5				107.6	107.0
SRW T103	.546	200	191.9	199.1	188.1	197	190	198.9	193.1	192.5	190.2	192.2	193.3	96.3
3490108	.792	100	117	108.9	103.3	92.5	108.5	99.58	104.7	105.2			104.9	104.1
3490108	.792	200	204.7	210.5	195.5	172.3	212.8	197.4	200.1	202.4			199.4	99.3
3490109	1.393	100	105	106.8	101	113	105.9	122.7	103.2	94.2			106.4	105.0
3490109	1.393	200	210.1	205.3	201.6	217.2	201.9	208.2	219.6	173.2			204.6	101.6
3490110	1.12	100	106.3	105.1	109.5	92.2	110.3	105.6	104.6	106.6			105.0	103.9
3490110	1.12	200	201.5	210	210	181.5	216.9	199.9	206.7	205.4			203.9	101.4
													Overall average recovery	**101.2**

Table 11.--Results of spiked samples—Continued

Silica

Sample	Unspiked concentration (mg/L)	Concentration of spike (mg/L)	Concentration measured										Average spiked sample concentration (mg/L)	Average recovery (percent)
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10		
DI blank	0	0.75	0.72	0.76	0.73	0.73							0.74	98.78
DI blank	0	1.5	1.59	1.58	1.70	1.68	1.59	1.47	1.55	1.62			1.60	106.70
NIST1643B	0	.75	.77	.76	.76	.77	.80	.79	.79	.82	0.77	0.72	.77	103.82
NIST1643B	0	1.5	1.50	1.5	1.51	1.75	1.53	1.55	1.64				1.54	103.07
SRW T103	.864	.75	1.63	1.61	1.63	1.64							1.63	102.48
SRW T103	.864	1.5	2.26	2.23	2.26	2.31	2.35	2.27	2.32	2.24	2.34	2.29	2.29	95.15
39108	13.36	.75	14.08	14.12	14.34	13.77	15.60	14.20	14.49	14.75			14.41	141.16
3490108	13.36	1.5	14.67	15.16	14.98	14.00	16.24	14.97	14.99	15.30			15.03	111.91
3490109	13.48	.75	14.42	14.33	14.40	13.85	15.97	14.51	14.63	14.69			14.60	149.33
3490109	13.48	1.5	14.99	15.04	15.33	14.32	16.36	15.31	15.32	15.60			15.28	120.25
3490110	13.54	.75	14.57	14.38	14.57	13.77	15.76	14.73	14.72	14.70			14.65	148.00
3490110	13.54	1.5	14.96	14.99	15.29	14.29	16.41	15.22	15.37	15.57			15.26	114.83
												Overall average recovery		**116.29**

Sodium

Sample	Unspiked concentration (mg/L)	Concentration of spike (mg/L)	Concentration measured										Average spiked sample concentration (mg/L)	Average recovery (percent)
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10		
DI blank	0	1.5	1.77	1.46	1.52	1.46							1.55	103.83
DI blank	0	3	3.09	3.15	3.45	3.46	3.23	3.25	3.23				3.26	108.96
NIST1643B	.840	1.5	2.36	2.35	2.48	2.41	2.41	2.42	2.40	2.40	2.37	2.40	2.40	104.36
NIST1643B	.840	3	3.91	3.86	3.95	3.97	3.91	3.92					3.92	102.88
SRW T103	10.81	1.5	12.18	12.22	12.46	12.32	12.16						12.26	97.20
SRW T103	10.81	3	13.17	13.25	12.91	13.11	13.02	13.27	13.2	13.43	13.25	13.37	13.19	79.60
3490108	2.149	1.5	3.92	4.15	4.10	4.02	1.21	3.72	4.12	4.24			4.06	127.56
3490108	2.149	3	5.68	5.60	5.68	5.64	6.02	5.07	5.74	5.85			5.66	117.17
3490109	2.152	1.5	4.41	3.89	4.14	4.00	4.37	3.73	4.15	4.18			4.11	130.84
3490109	2.152	3	5.54	5.79	5.81	5.69	6.07	5.06	5.86	5.99			5.73	119.35
3490110	2.183	1.5	3.93	4.08	4.30	4.15	4.35	3.75	4.20	4.26			4.13	129.90
3490110	2.183	3	5.62	5.73	5.86	5.68	6.17	5.25	5.92	5.99			5.78	120.00
												Overall average recovery		**111.80**

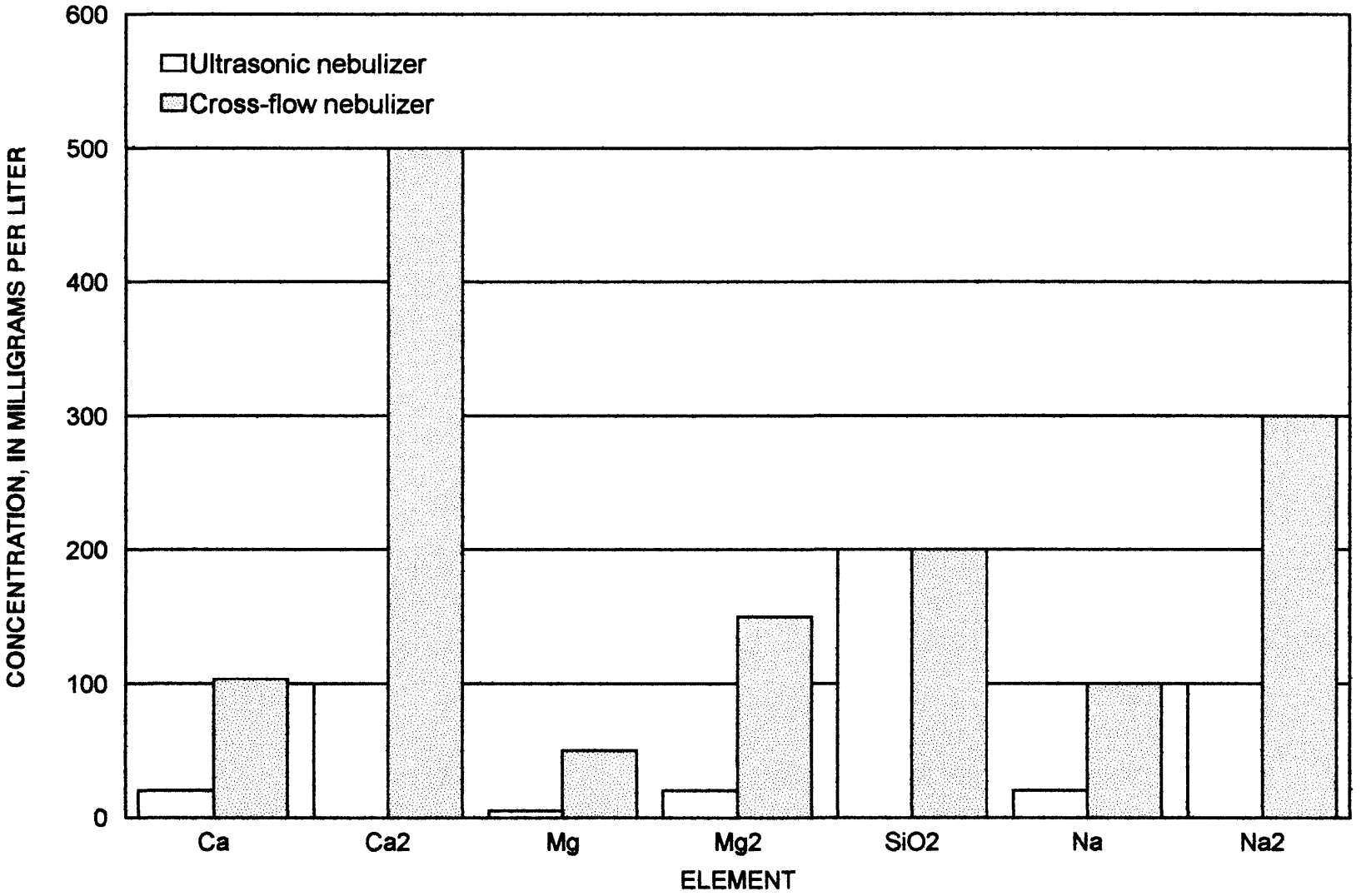

Figure 8.–Maximum concentration before nonlinearity or saturation of signal is reached for ultrasonic and cross-flow nebulizers.

Table 12.--Linearity of increasing concentrations of constituents for ultrasonic nebulizer
[nm, nanometer; --, concentration not analyzed; xxx, signal saturated. All concentrations in milligrams per liter]

Selected concentrations	Calcium (396.84 nm)	Magnesium (279.55 nm)	Sodium (588.00 nm)	Silica (288.1 nm)
5	4.368	4.784	5.66	4.009
10	9.406	--	9.46	9.392
20	17.96	--	17.58	18.27
50	21.48	xxx	21.10	22.42
100	xxx	xxx	--	45.27
150	xxx	xxx	xxx	103.0
200	xxx	xxx	xxx	199.5
250	xxx	xxx	xxx	xxx
500	xxx	xxx	xxx	xxx

Since the UDX enhances the signal for most elements by 8 to 16 times that of a conventional nebulizer, it follows that the saturated signal intensities will be reached 8 to 16 times sooner by the UDX. This enhanced signal will limit the ranges of the maximum amounts of each element that can be determined. Take care to ensure that samples contain elemental concentrations low enough not to saturate the detectors of the spectrometer. The only exception was silica; it did not show a difference from a cross-flow system. Silica did not show a marked increase or decrease in maximum signal intensities because the entire instrument and delivery system is made of borosilicate glass and quartz. This composition produces enough background silica to prevent the nebulizer from producing higher detection limits than for conventional cross-flow nebulizers.

For comparison, identical natural-water samples were analyzed on both systems to determine bias between the UDX and cross-flow methods. Review of box plots of the data indicated that the sample groups were not normal in their distribution. A paired sign test of the two sample groups at $\alpha = 0.05$ was performed and the results are listed in table 13.

Table 13.--Results of paired sign test of cross-flow and ultrasonic nebulizers
[mg/L, milligram per liter; µg/L, microgram per liter]

Trace metal or constituent	Concentration range	Total observations	Positive observations	Significance level *p*-value	Reject null hypothesis
Calcium	0–6.00 mg/L	73	45	0.0604	no
Iron	0–250 µg/L	73	36	1.000	no
Magnesium	0–5.00 mg/L	73	42	0.1006	no
Manganese	0–250 µg/L	68	58	0.00001	yes
Silica	0–7.00 mg/L	73	35	0.8151	no
Sodium	0–10 mg/L	73	32	0.4828	no

The data set of 80 samples included natural-water samples, SRWS, and NIST standards. Graphs of each of the six elements and the correlation coefficients associated with each plot are included. (See figs. 9 through 14.) In these figures, the concentrations of each constituent obtained from the cross-flow nebulizer were plotted against the concentrations of each constituent obtained from the ultrasonic nebulizer. If the two methods are equivalent, then the slope of the line connecting each sample pair will be 1. Using the cross-flow nebulizer as the standard, a slope greater than 1 indicates positive bias in the ultrasonic nebulizer, and a slope of less than 1 indicates negative bias in the nebulizer data. A *y*-intercept significantly offset from zero indicates background problems in one of the methods.

As stated earlier, this technology was to be expanded for use with other methods, including samples that have high (>100 µS/cm) specific conductances and problematic matrices. The high-speed rinse system was specifically built into the design of the spray chamber to address these potential problems. Under normal operating conditions, cross-flow nebulizers are sensitive to samples with high salt matrices such as brine or sea water. They commonly clog when concentrations reach 1 to 4 percent salt by volume (Fassel and Bear, 1986). However, the ultrasonic nebulizer has no limiting orifices to clog. The cross-flow nebulizers used at the NWQL contain stainless steel ventri which can be attacked by strongly acid or basic samples such as acid mine drainage or storm runoff from industrial parks. The ultrasonics quartz end plate is extremely resistant to caustic samples and is not significantly affected by samples with nitric acid matrices of 4 percent or more (Fassel and Bear, 1986).

Samples analyzed by the NWQL are processed by each analyst as "unknowns." Commonly, the operator has no prior knowledge as to the specific makeup of each sample. This means that complex matrix or samples with high salt content are analyzed along with drinking-water samples or other water-sample types that do not contain problematic matrices. This process can cause substantial carry-over problems that bias the result of samples analyzed immediately after a "dirty" sample has passed through the instrument. Acid mine water and sea-water samples were selected to test the ultrasonic nebulizers washability and overall performance. As stated earlier, cross-flow nebulizers performed poorly when used for these types of samples. It is standard NWQL protocol to dilute water samples with specific conductances greater than 2,000 µS/cm prior to analysis on cross-flow equipped ICP–OES systems. These acid mine water and sea-water samples had conductances greater than 50,000 µS/cm. They were analyzed directly through the ultrasonic nebulizer without dilution by simulating a worst-case scenario that would commonly cause a cross-flow equipped system to fail. The actual chemical concentrations of the analytes in the acid mine water or sea-water samples were not determined. The total sample and wash cycle of the ultrasonic nebulizer is only 10 seconds slower than that of the cross-flow system (that is, 3 minutes and 25 seconds as opposed to 3 minutes and 15 seconds). The nebulizer was tested by analyzing the "unknown" problem sample followed by three deionized water blanks without the wash system. Then the process was repeated with the wash system in operation.

Dilution of such problematic samples would certainly reduce carry-over effects and complement the high-speed wash circuit. The project was terminated before the high-speed wash could be investigated with whole water samples. However, the ultrasonic nebulizer is clearly superior in performance if such difficult sample matrices are to be analyzed. This

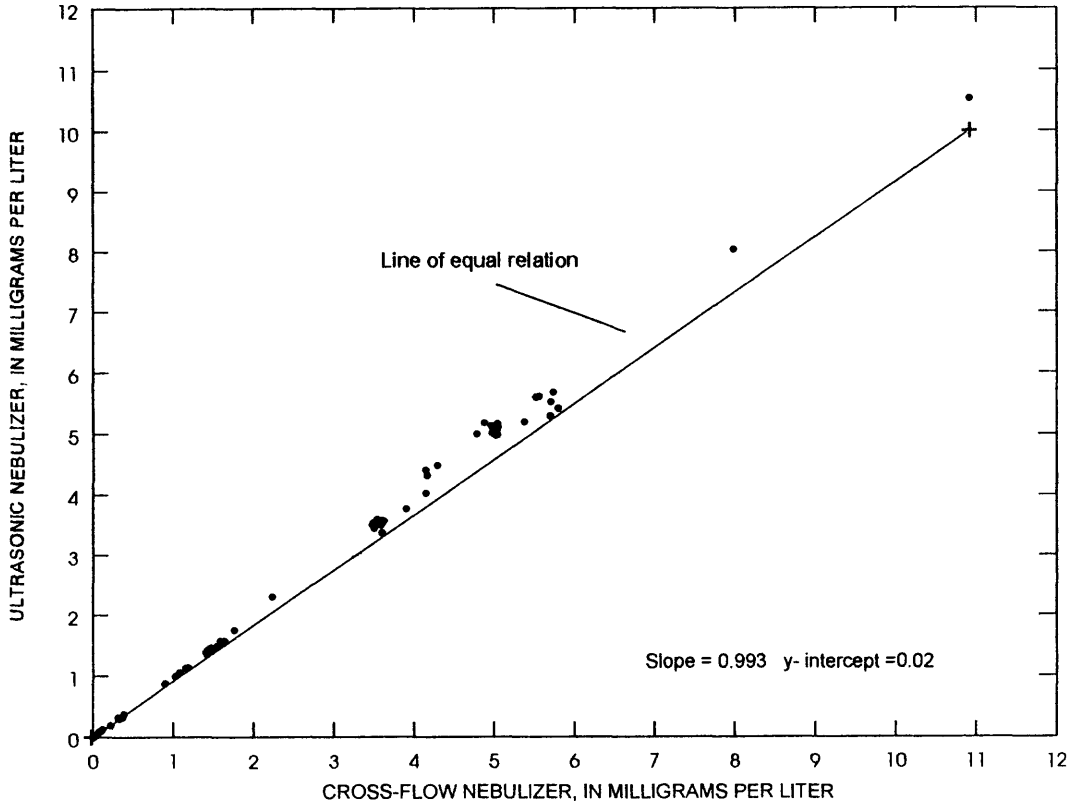

Figure 9.--Calcium sample concentrations for ultrasonic and cross-flow nebulizers.

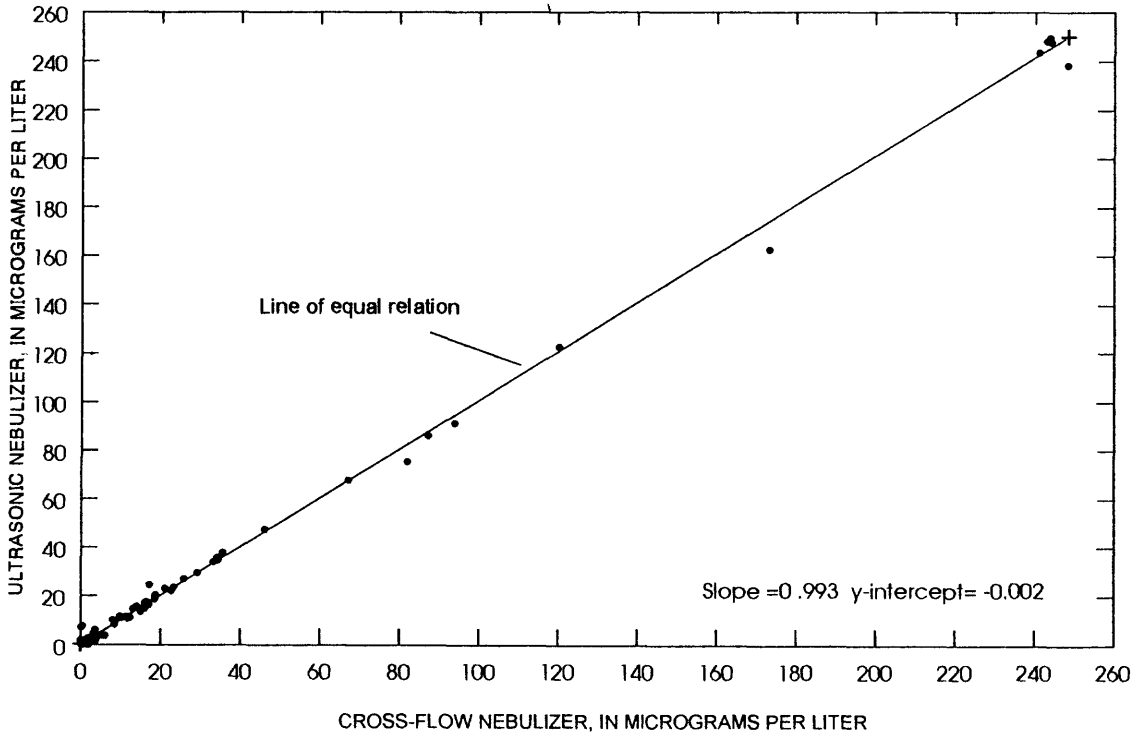

Figure 10.--Iron sample concentrations for ultrasonic and cross-flow nebulizers.

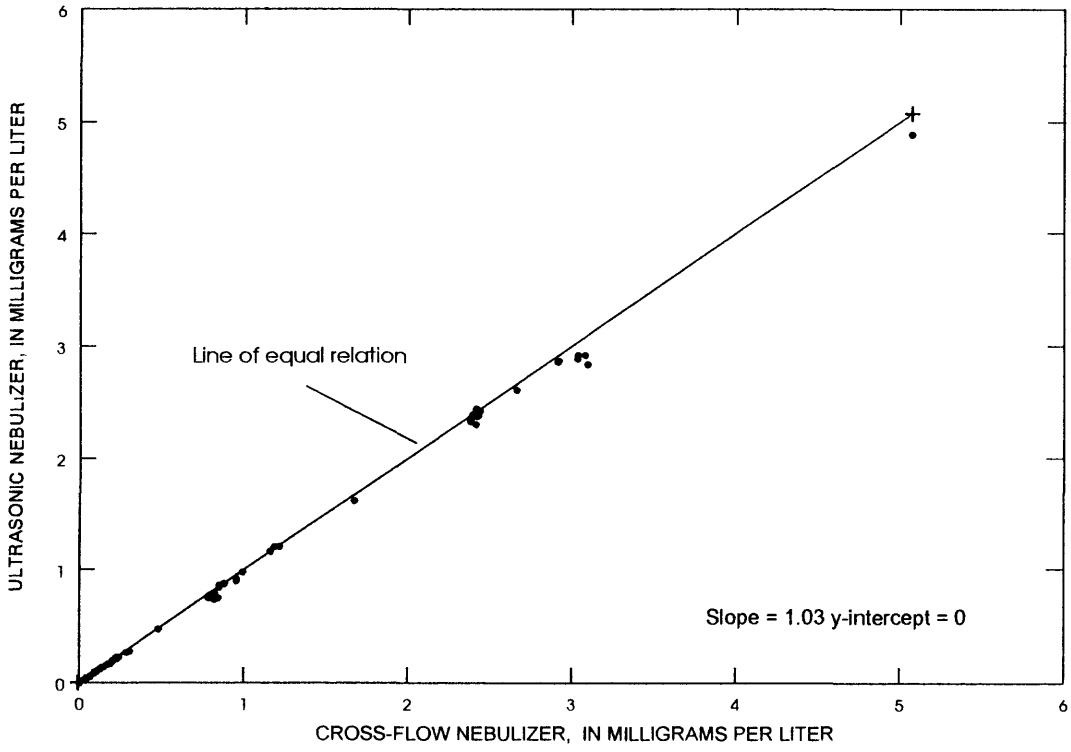

Figure 11.--Magnesium sample concentrations for ultrasonic and cross-flow nebulizers.

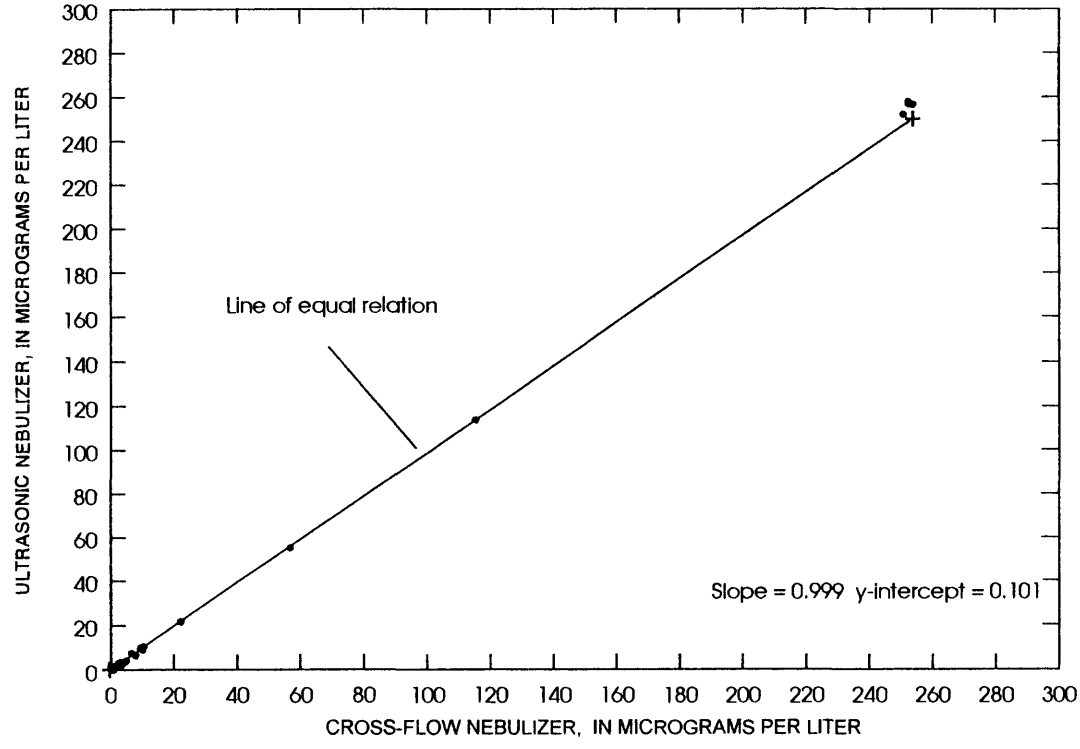

Figure 12.--Manganese sample concentrations for ultrasonic and cross-flow nebulizers.

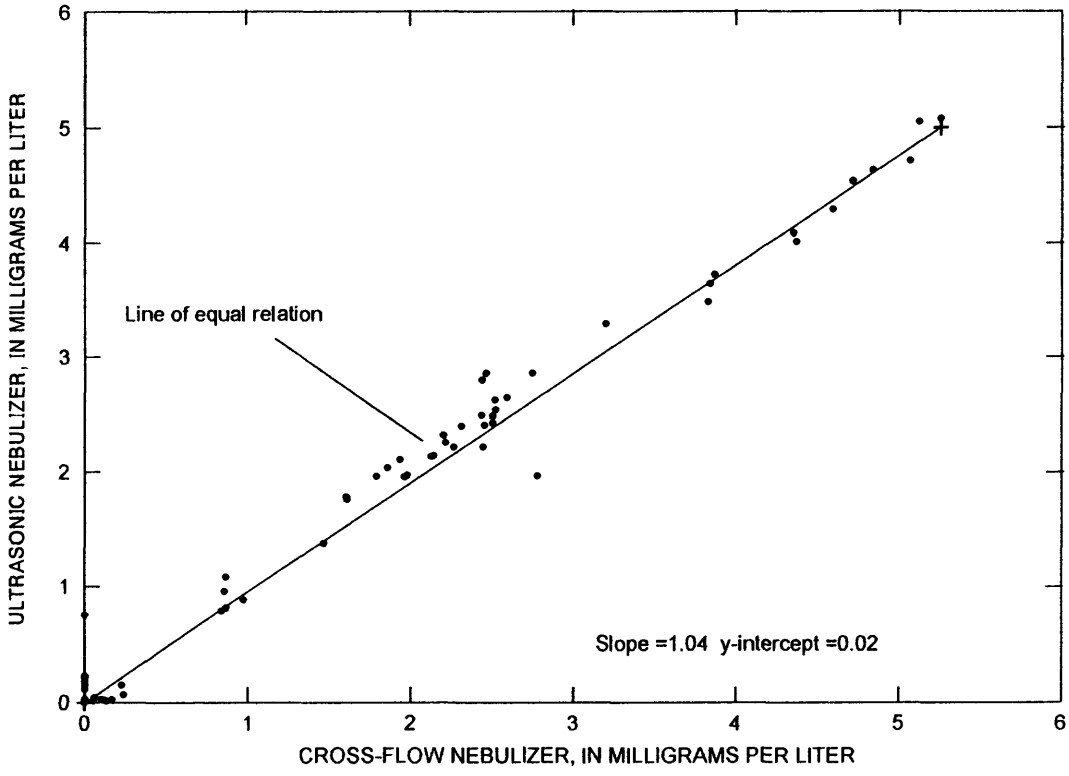

Figure 13.--Silica sample concentrations for ultrasonic and cross-flow nebulizers.

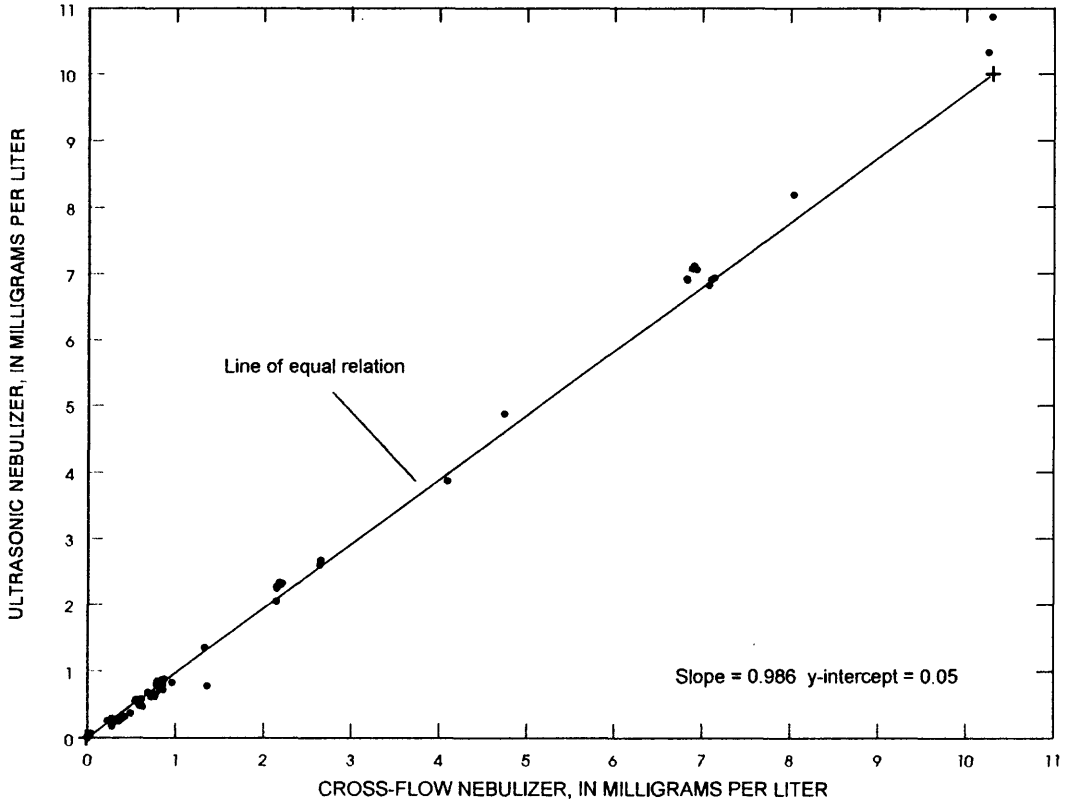

Figure 14.--Sodium sample concentrations for ultrasonic and cross-flow nebulizers.

advantage could be helpful to technicians and researchers because of the nebulizer's resistance to clogging or chemical attack. Efforts could then be focused on how to quantify the actual concentration of analyte in these difficult samples rather than how to prepare the sample so it does not cause nebulizer failure.

Graphs of both rinse modes show that the sample immediately following an "offscale" sample was less affected by carryover with the high-speed wash than if no wash was performed. (See figs. 15 through 20.) However, this decrease in carryover is not as great as first anticipated, with the reduction in carryover ranging from 12 to 80 percent, depending on the element. Overall, the reduction in carryover averages about 45 percent. Calculations were based on the concentration of the blank immediately following the offscale sample for both rinsed and unrinsed blanks. Considering the simplicity of the high-speed rinse circuit, it is a useful addition to the nebulizer.

With the addition of the high-speed rinse and optimizing path length to the torch, the analysis time required to perform one determination is 3 minutes 25 seconds compared with the cross-flow nebulizer-equipped ICPs used elsewhere in the laboratory that average 3 minutes 15 seconds per analysis (Mark Hill, U.S. Geological Survey, written commun., 1992).

CONCLUSION

This modified ultrasonic nebulizer produces detection limits for those analytes investigated that are lower than the cross-flow nebulizer equipped with ICP–OES systems used elsewhere in the laboratory. Detection limits for the ultrasonic nebulizer commonly are 4 to 18 times less than for a cross-flow system. The ultrasonic nebulizer is resistant to acidic solutions such as nitric acid, which is commonly used to digest samples for metals. Unlike a cross-flow nebulizer, the ultrasonic nebulizer does not have an orifice that will clog when high-salt samples are analyzed. The high-speed rinse reduces the carryover effects from offscale samples or those with interfering matrices. The ultrasonic nebulizer is a low-cost alternative compared to other methods with comparable detection limits such as inductively coupled mass spectrometry or ion chromatography/ICP–OES. A mass spectrometer costs $200,000; the nebulizer costs $13,000 with modifications. It is portable and only takes up the space of a personal computer, unlike a mass spectrometer which usually requires its own room and special environmental controls to keep it operating. Customers seek lower detection limits but may not afford the high cost of a mass spectrometer or equivalent method. An ultrasonic nebulizer equipped with ICP–OES could offer a low-cost alternative that fills the gap between the conventional ICP–OES methods and the ultratrace capabilities of mass spectrometer methods offered by the laboratory.

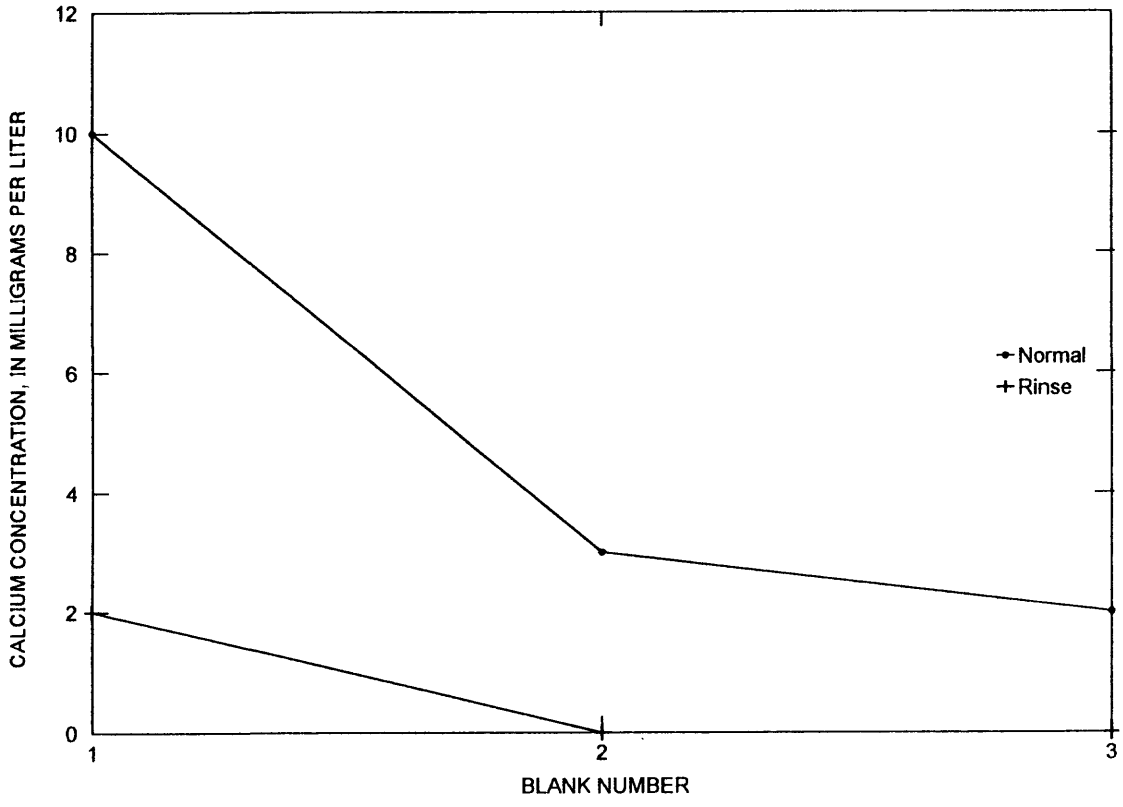

Figure 15.--Normal and rinse wash carryover of high-concentration calcium sample.

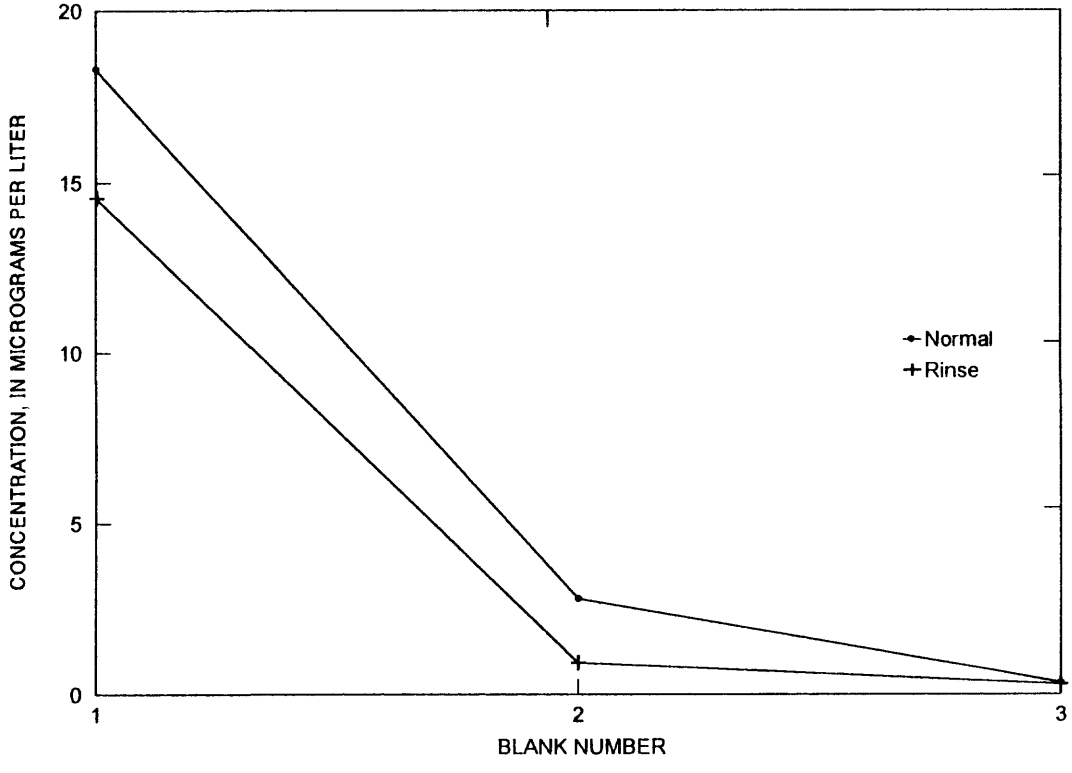

Figure 16.--Normal and rinse wash carryover of high-concentration iron sample

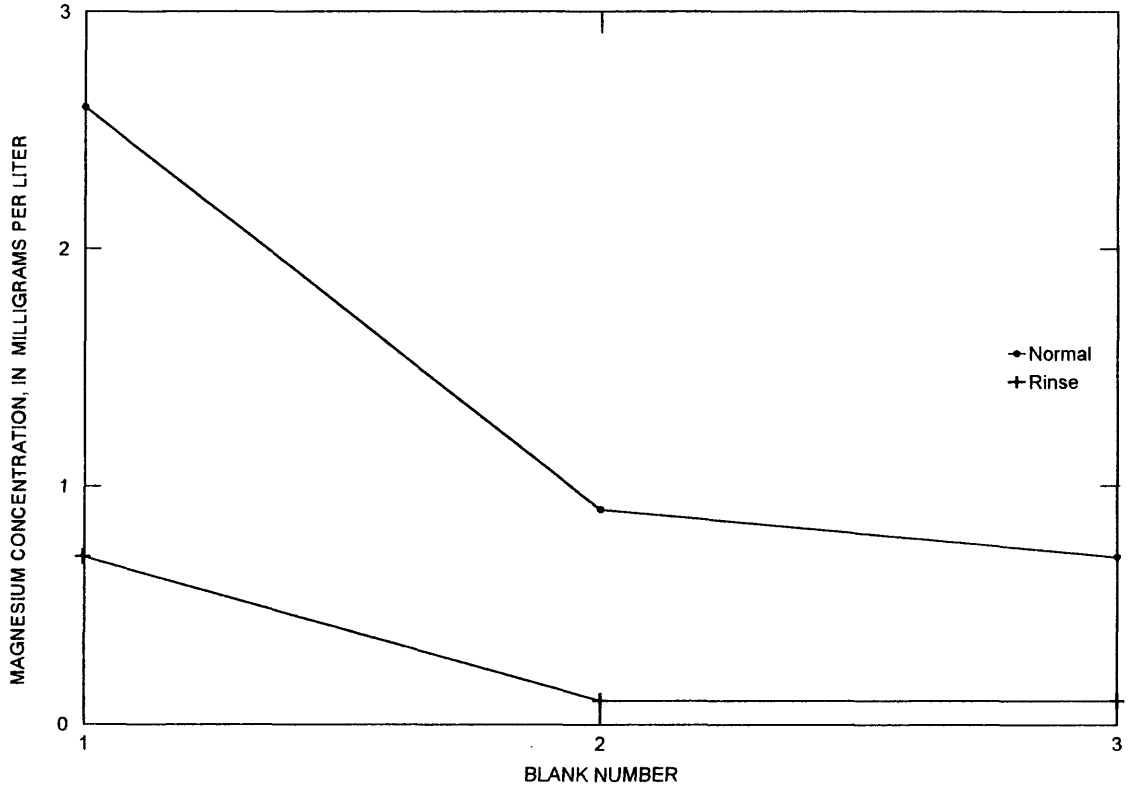

Figure 17.--Normal and rinse wash carryover of high-concentration magnesium sample.

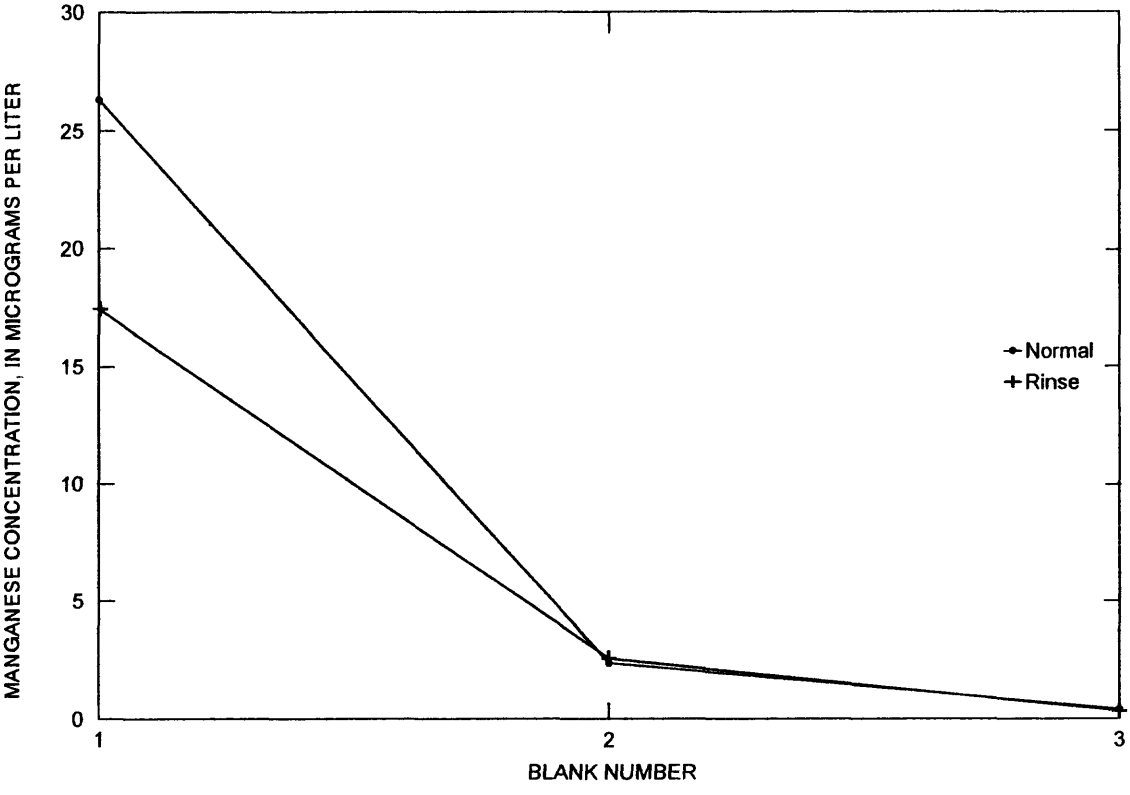

Figure 18.--Normal and rinse wash carryover of high-concentration manganese sample.

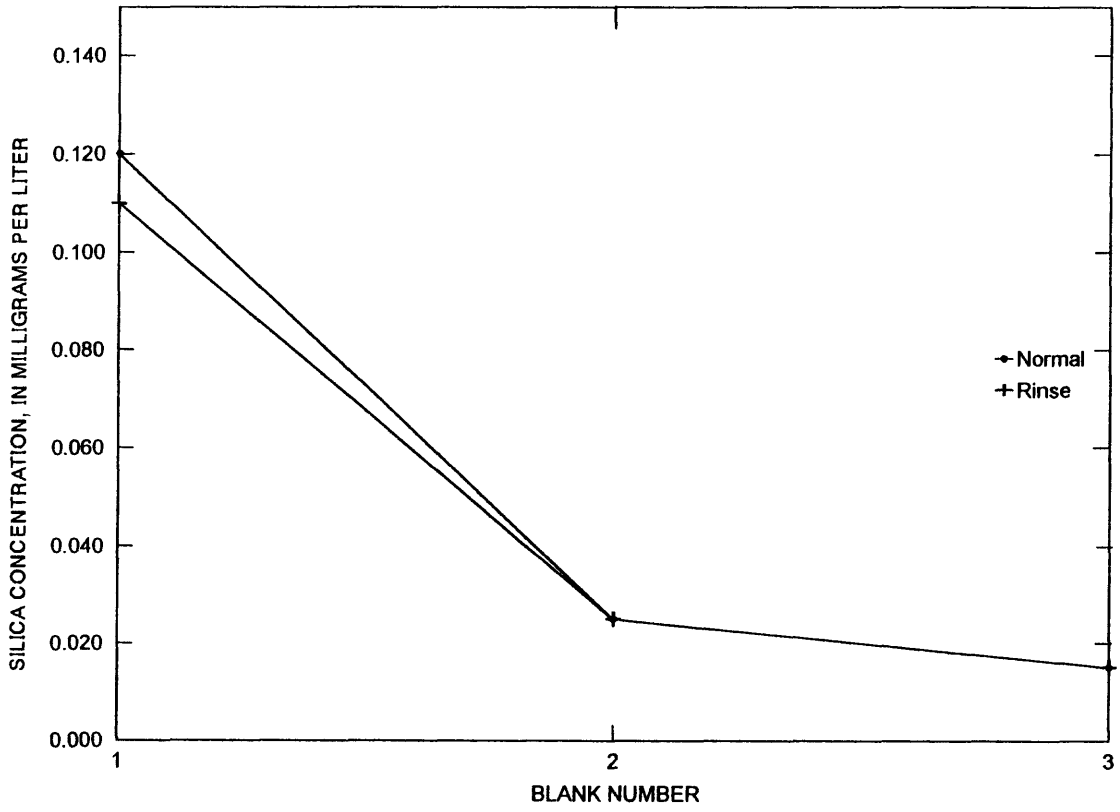

Figure 19.--Normal and rinse wash carryover of high-concentration silica sample.

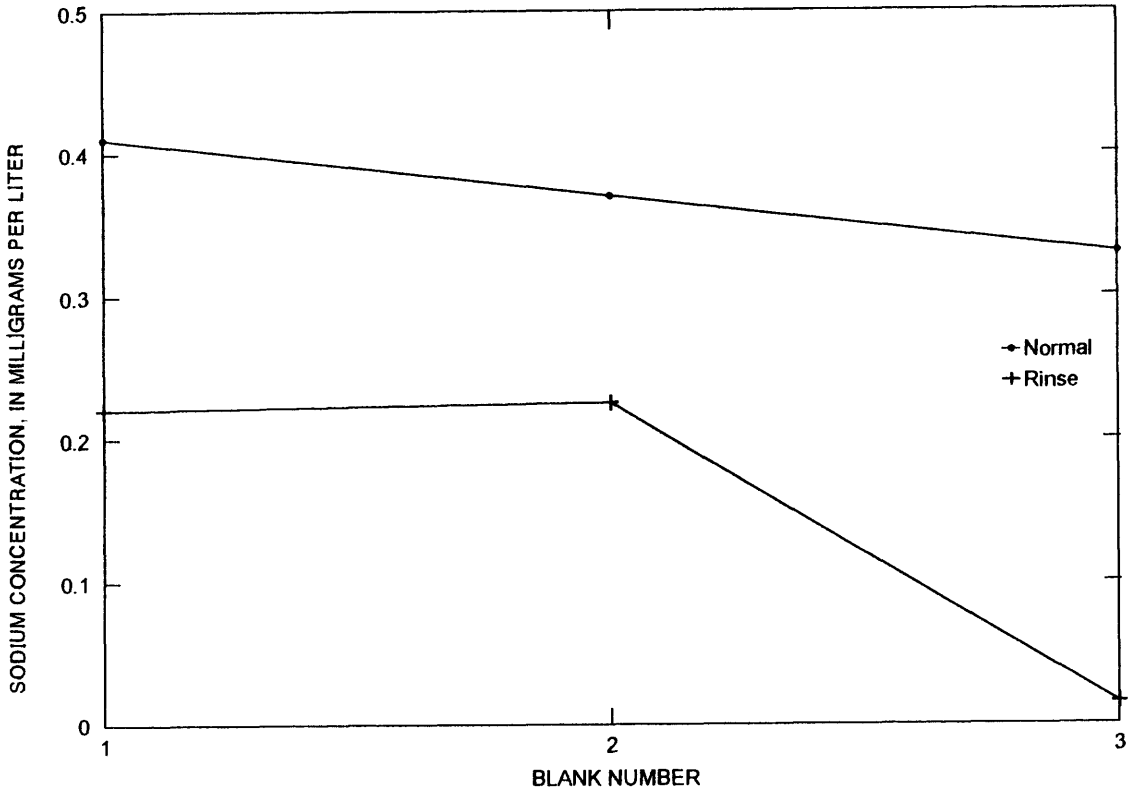

Figure 20.--Normal and rinse wash carryover of high-concentration sodium sample.

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