METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF CHROMIUM IN WATER BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

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CONTENTS

FIGURES

Figures 1-3 Graphs showing:

TABLES

TABLES--Continued

CONVERSION FACTORS AND ABBREVIATIONS

Multiply	*By*	*To obtain*
gram (g)	0.03527	ounce, avoirdupois
microgram (μg)	3.52×10^{-8}	ounce
microliter (μL)	2.64×10^{-7}	gallon
milliliter (mL)	2.64×10^{-4}	gallon
nanometer (nm)	3.93×10^{-8}	inch

Degree Celsius (^{o}C) may be converted to degree Fahrenheit (^{o}F) by using the following equation:

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

The following water-quality terms also are used in this report:

microgram per liter	(μg/L)
microsiemens per centimeter at 25 degrees Celsius	(μS/cm)
milligram per liter	(mg/L)

Other abbreviations are as follows:

AAS	atomic absorption spectrophotometry
a-s	absorbance-seconds
ASTM	American Society for Testing and Materials
DCP-AES	direct-current plasma atomic emission spectrometry
FEP	fluorinated ethylene propylene
GF-AAS	graphite furnace atomic absorption spectrophotometry
MDL	method detection limit
N	normality (equivalent weight per liter of solution)
NIST	National Institute of Standards and Technology
NWQL	National Water Quality Laboratory
ppm	parts per million
RSD	relative standard deviation
sp gr	specific gravity
SRWS	Standard Reference Water Sample
USGS	U.S. Geological Survey
w/v	weight per volume

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ABSTRACT

Graphite furnace atomic absorption spectrophotometry is a sensitive, precise, and accurate method for the determination of chromium in natural-water samples. The detection limit for this analytical method is 0.4 µg/L (microgram per liter) with a working linear limit of 25.0 µg/L. The precision at the detection limit ranges from 20 to 57 percent relative standard deviation (RSD) with an improvement to 4.6 percent RSD for concentrations greater than 3 µg/L.

Accuracy of this method was determined for a variety of reference standards that was representative of the analytical range. The results were found to be well within the established standard deviations. Samples were spiked with known concentrations of chromium with recoveries ranging from 84 to 122 percent. In addition, a comparison of chromium concentrations analyzed by graphite furnace atomic absorption spectrophotometry and direct-current plasma atomic emission spectrometry resulted in suitable agreement between the two methods, with an average deviation of ±2.0 µg/L throughout the analytical range.

INTRODUCTION

Chromium is naturally occurring in the earth's crust, ranging in concentrations from 100 to 300 ppm (Windholz, 1983, p. 317). There are two forms of chromium found in the environment: chromium (+3), the more abundant of the two that can be a by-product of mining operations; and the more toxic chromium (+6), which also is found in industrial waste associated with metal plating and steel manufacturing as described in Windholz (1983, p. 317).

The development of graphite furnace atomic absorption spectrophotometry (GF-AAS) began in the late 1950's. Original work indicated improvement over flame atomic absorption spectrophotometry (flame-AAS) for the refractory elements, and lower detection limits for trace metal analyses such as chromium.

In comparison with flame-AAS and direct-current plasma atomic emission spectrometry (DCP-AES), the GF-AAS is slow. The GF-AAS techniques rarely exceed 20 to 30 determinations an hour for a single element, while flame-AAS and DCP-AES can perform multielement determinations and produce substantially more determinations an hour. Detection limits typically are lower for GF-AAS than for flame-AAS or DCP-AES.

The operation of the GF-AAS is based on the same principle as flame-AAS. Ground state atoms are heated and introduced into the optical path of an elemental light source. The ground state atoms absorb light of a wavelength at the resonant frequency. An absorbance signal is produced which is directly proportional to the metal concentration of the sample. Instead of introducing an aqueous sample into a flame through nebulization, a small (20-µL) sample is introduced onto a platform inside the graphite tube. The tube is held between two graphite rings with quartz windows at each end, producing a partially closed environment for analysis. The graphite tube and platform are pyrolytically coated with a high-density carbon that reduces the formation of nonvolatile carbides and prevents adsorption of the sample onto the platform or the wall of the tube.

For chromium determinations, the sample is introduced directly onto a platform inside the tube, then heated to dryness through a controlled temperature program. The next step is pyrolysis, which breaks down the matrix components. In the atomization step, all of the sample is atomized and held in residence for an extended time (3-6 seconds) in a flow-restricted environment. With a longer residence time, the sensitivity is increased, and detection limits are improved approximately one order of magnitude over most flame-AAS or DCP-AES techniques. A high-temperature clean-out step at the end of each analysis provides a clean environment and removes any potential problems with carryover to the next sample.

When determining chromium by GF-AAS, a 20-µL sample is introduced onto a platform along with a 5-µL aliquot of a 1-percent solution of magnesium nitrate matrix modifier. The matrix modifier is a method of manipulating the chemical form of the analyte and increasing the volatility of the sample. The total sample volume is dried at 140°C for 40 seconds. The pyrolysis is performed at 1,400°C for 30 seconds. A preatomization cool-down to 25°C for 10 seconds prepares the tube for uniform, maximum-power heating to a 2,600°C atomization temperature, which is held and read for 4 seconds. The signal at the time of analysis is expressed in peak area (absorbance-seconds). The tube and platform are prepared for the next sample by a clean-out step at 2,650°C for 10 seconds followed by a second cool-down step. During the high-temperature atomization, chromium may form carbides that result in memory effects or carryover problems. A solution to the problem of memory effects may be solved first by maintaining a slight gas flow during atomization followed by two sequential clean-out and cool-down steps. This procedure was necessary when using a heated graphite analyzer GF-AAS but not necessary with the transverse heated graphite analyzer GF-AAS. The time, temperature, and function of the heated graphite analyzer is shown in figure 1. Times and temperatures of GF-AAS programs will vary slightly from instrument to instrument.

All determinations were performed on a graphite furnace with Zeeman effect background correction. With the Zeeman effect, atomic lines are split into three or more polarized components in a strong magnetic field. This background correction makes it possible to compensate for nonspecific absorption. See training manual for complete details regarding Zeeman background correction (Perkin-Elmer Corp., 1991, p. 2-12).

This report describes a method for determining chromium in natural-water samples developed by the U.S. Geological Survey (USGS) for use in the Survey's National Water Quality Laboratory (NWQL). The method incorporates a GF-AAS, which has proven to be an efficient and effective tool for low-level determination of chromium and other trace metals in natural-water samples. The low detection limit, small sample size, and minimal sample preparation substantially expand the determination of chromium in natural-water samples at the NWQL. The method supplements other methods of the USGS for determination of chromium in water and fluvial sediments that are described by Fishman and Friedman (1989). The method was implemented in the NWQL in 1993.

This report provides a detailed description of all aspects of the method from application and interferences to reagents and detection limits. Precision and accuracy data are presented in this document.

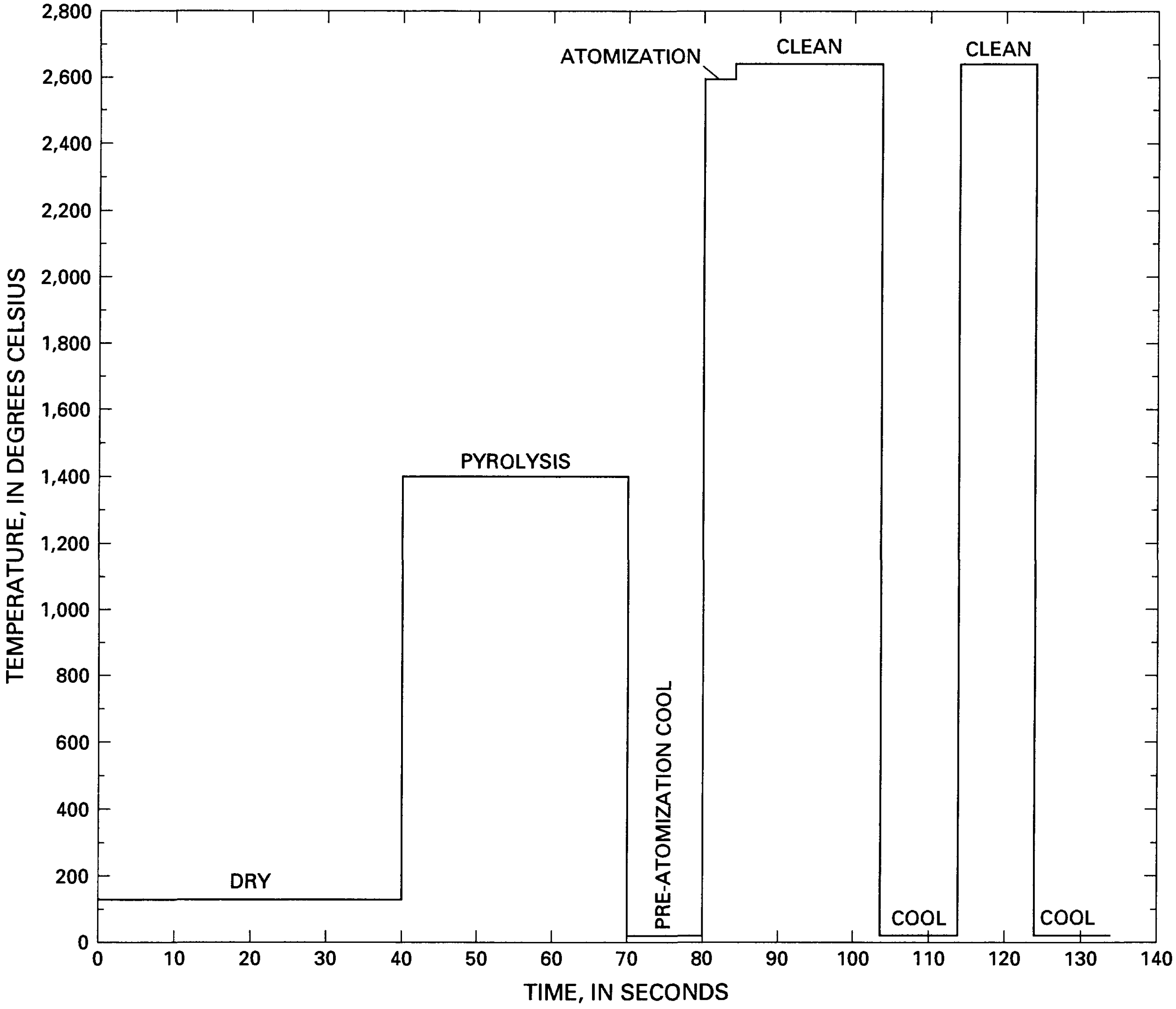

Figure 1.—Time, temperature, and function of the graphite furnace atomic absorption spectrophotometry program when using a heated graphite analyzer.

ANALYTICAL METHOD

Parameters and Codes:
Chromium, dissolved, I-1233-93 (µg/L as Cr): 01030
Chromium, whole water recoverable, I-3233-93 (µg/L as Cr): 01034

1. Application

This method is applicable in the range from 0.5 to 25.0 µg/L of chromium in water and water-suspended sediment. Sample solutions that contain chromium in concentrations greater than 25.0 µg/L or have a specific conductance greater than 10,000 µS/cm will need to be diluted prior to analysis or analyzed by an alternate method.

2. Summary of method

Chromium is determined by atomic absorption spectrophotometry in conjunction with a graphite furnace containing a pyrolytically coated tube and platform (Hinderberger and others, 1981). A sample is placed on the graphite platform, and a matrix modifier is added. The sample then is evaporated to dryness, pyrolized, and atomized using maximum-power heating. Maximum-power heating is a term associated with stabilized temperature platform furnace technology, which refers to a zero time ramp that allows for a 2,000°C per second heating rate of the tube and creates the longest temperature lag between the platform and the tube wall (Carnrick and Slavin, 1989). The absorption signal produced during atomization is recorded and compared with standards.

3. Interferences

Refractive elements such as chromium have the potential to form carbides. The use of pyrolytically coated tubes and platforms (Fishman and Friedman, 1989, p. 169) improves sensitivity and reduces carbide formation and memory effect.

The use of pyrolytically coated tubes and platforms in conjunction with a matrix modifier reduces the potential for interferences. Multiple natural-water samples and Standard Reference Water Samples were spiked with known concentrations of chromium with no indication of signal suppression or enhancement. These samples contained major cation concentrations as great as 300 mg/L sodium, 200 mg/L calcium, 111 mg/L magnesium, and 20 mg/L potassium; and major anion concentrations with 620 mg/L sulfate and 210 mg/L chloride.

4. Apparatus

4.1 *Atomic absorption spectrophotometer*, for use at 357.9 nm and equipped with a graphite furnace with temperature programmer, Zeeman background correction, digital integrator to quantitate peak areas, and automatic sample injector. The programmer must have maximum-power heating and controlled argon flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize operations and instrumental performance. The analytical ranges reported in section 1 are for a 20-µL sample.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize chromium (2,600-2,700°C). WARNING: Dial settings frequently are inaccurate and newly conditioned furnaces must be temperature-calibrated.

4.1.3 *Graphite tubes and platforms*, pyrolytically coated graphite tubes and platforms are recommended.

4.2 *Labware*. Many trace metals at low concentrations have been found to adsorb rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon[1] labware may be used. Polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reusable Teflon or FEP cups may be purchased.

4.3 *Argon*. Standard, welder's grade, commercially available. Nitrogen also may be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Chromium standard solution I*, 1.00 mL = 1,000 µg Cr: Use a commercially prepared and certified Cr calibration standard, 1,000 mg/L, 0.100 percent w/v, or dissolve 2.8290 g primary standard $K_2Cr_2O_7$, dried for 1 hour at 180°C, in Type I water. Add 4 mL ultrapure, concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with Type I water.

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[1] Use of brand, firm, or trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

5.2 *Chromium standard solution II*, 1.00 mL = 10.0 µg Cr: Dilute 10.0 mL chromium standard solution I to 1,000 mL (NOTE 1).

NOTE 1. Use acidified Type I water (paragraph 5.8) to make dilutions. All standards need to be stored in sealed Teflon or FEP containers. Standards stored for 6 months yielded values equal to freshly prepared standards.

5.3 *Chromium standard solution III*, 1.00 mL = 1.00 µg Cr: Dilute 100.0 mL chromium standard solution II to 1,000 mL.

5.4 *Chromium standard solution IV*, 1.00 mL = 0.025 µg Cr: Dilute 25.0 mL chromium standard solution III to 1,000 mL (calibration standard).

5.5 *Chromium standard solution V*, 1.00 mL = 0.010 µg Cr: Dilute 10.0 mL chromium standard solution III to 1,000 mL (calibration standard).

5.6 *Nitric acid, concentrated*, ultrapure (sp gr 1.41): J.T. Baker Ultrex HNO_3 is adequately pure; however, each lot needs be checked for contamination. Analyze acidified Type I water for chromium. Add 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-second.

5.7 *Magnesium nitrate solution,* 1 percent w/v. Weigh 1.0 g of magnesium nitrate, $Mg(NO_3)_2$ ultrapure quality reagent into a 100-mL volume of deionized water. Mix until salt is in solution.

5.8 *Water, acidified*: Add 4 mL ultrapure, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.9 *Water*: All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1983).

6. Procedure

6.1 The autosampler and the graphite furnace need to be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1 *N* HNO_3 solution and dry.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-µL aliquots of blank and a minimum of two standards plus 5 µL magnesium nitrate solution and analyze. Use duplicate injections of each. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear up to a peak-absorbance (peak-height) value of 0.40 absorbance unit. A typical calibration curve for the determination of chromium by GF-AAS is shown in figure 2.

6.5 Similarly, inject and analyze the samples. Every tenth sample cup must contain a sample blank, standard, or a reference material as a quality-control measure. If variances are greater than precision limits of this method, the instrument needs to be recalibrated and the samples reanalyzed.

7. Calculations

Obtain the concentration of each sample from the display screen or printer. Dilute and reanalyze those samples containing concentrations of chromium greater than 25.0 µg/L, then multiply the new concentration value by the proper dilution factor.

DISCUSSION OF RESULTS

The following is a description of the methods used and a discussion of the results verifying the precision and accuracy for the determination of chromium by GF-AAS.

Method Detection Limit

The method detection limit (MDL), using the procedure from the U.S. Environmental Protection Agency (1990, p. 537-539), 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. The theoretical detection limit was determined to be 0.5 µg/L, based on three times the standard deviation of multiple blank determinations. A chromium standard was prepared with a concentration of 1.0 µg/L (two times the theoretical detection limit). This

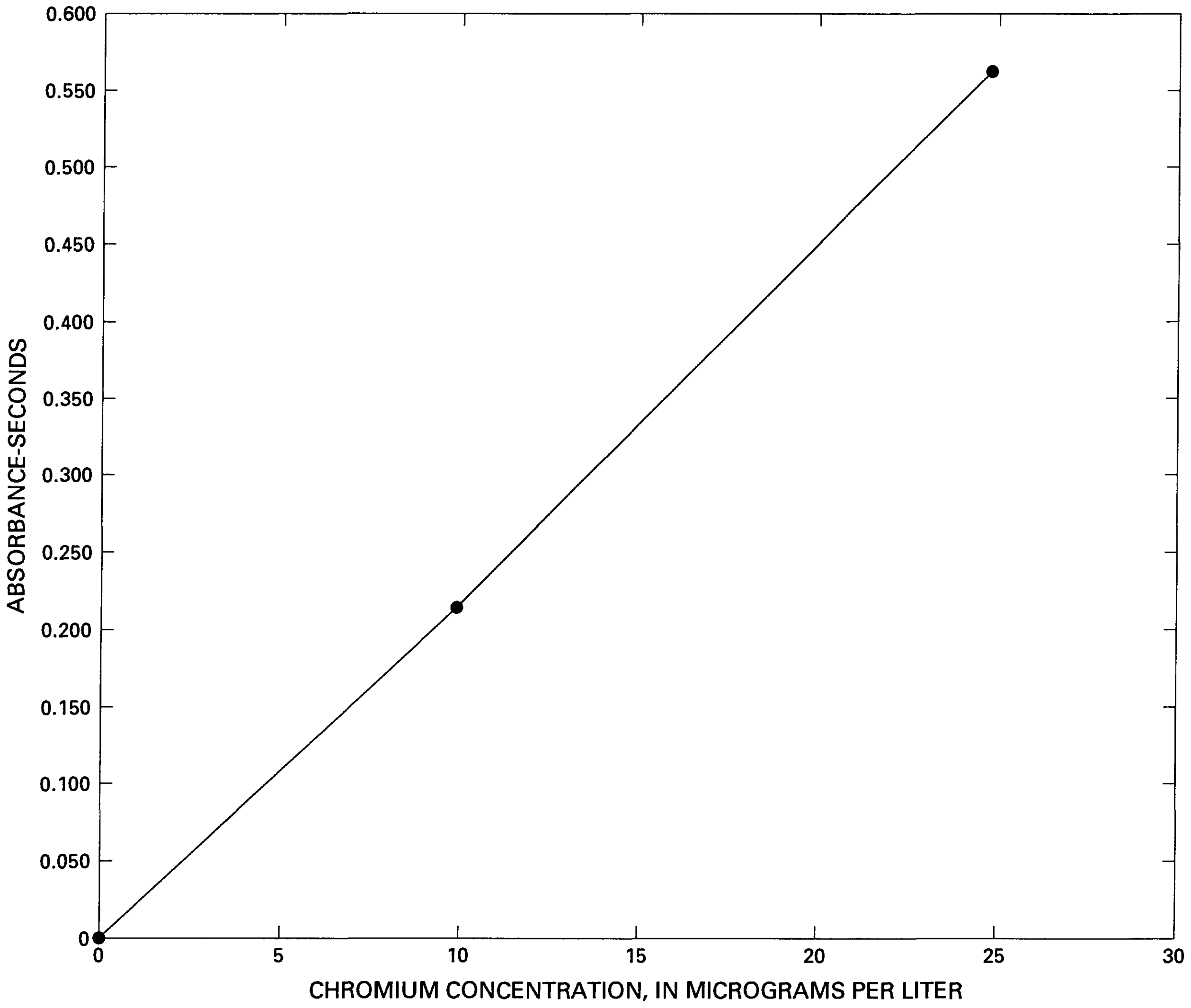

Figure 2.—Typical calibration curve for the determination of chromium by graphite furnace atomic absorption spectrophotometry.

standard then was analyzed ten times nonconsecutively. From these data, a mean and a standard deviation were calculated (table 1) to determine the MDL. The MDL was determined to be 0.4 μg/L with a reporting limit of 0.5 ±0.1 μg/L.

Table 1.--*Multiple analysis of a 1.0-μg/L chromium standard by graphite furnace atomic absorption spectrophotometry for the determination of method detection limit*

[μg/L, micrograms per liter]

Replicate number	Concentration (μg/L)
1	1.3
2	1.3
3	1.1
4	1.4
5	1.1
6	1.3
7	1.0
8	1.2
9	1.4
10	1.1

1.24 = Mean (μg/L)
0.13 = Standard deviation (μg/L)
10 = Number of points
9 = Degrees of freedom
2.821 = t value (99 percent confidence)
0.37 = Method detection limit

Precision

U.S. Geological Survey Standard Reference Water Samples (SRWS) were analyzed, along with a number of filtered and water-suspended sediment samples, to determine the precision of chromium by GF-AAS. The samples were analyzed for a period of 15 days. Precision data at the detection limit for the determination of chromium in water samples by GF-AAS has a mean relative standard deviation (RSD) of 15 to 57 percent and a mean RSD of 4 to 5 percent throughout the analytical range (see table 2).

Table 2.--*Precision data for the determination of chromium in water samples analyzed by graphite furnace atomic absorption spectrophotometry*

[µg/L, micrograms per liter; USGS, U.S. Geological Survey]

Mean (µg/L)	Standard deviation (µg/L)	Number of replicates	Relative standard deviation (percent)
Filtered, acidified samples and USGS Standard Reference Water Samples			
0.7	0.4	24	57
1.3	.2	24	15
1.8	.4	22	22
6.5	.4	22	6.1
9.8	.2	22	1.9
10.2	.4	24	3.9
13.8	.8	22	5.8
14.0	1.1	24	7.8
19.2	.7	24	3.6
25.0	1.9	22	7.6
35.4	1.6	24	4.5
57.8	2.9	22	5.0
Raw, acidified samples			
.5	.1	7	20
3.0	.2	7	6.7
7.1	.3	7	4.2
13.6	.4	7	2.9
23.5	.4	7	1.7
38.4	1.4	7	3.6
48.5	2.9	7	4.7

Accuracy

Accuracy for this method was demonstrated by determining chromium in Standard Reference Water Samples (SRWS) by GF-AAS. The results of these analyses were collected for a period of 15 days and are listed in table 3. The average chromium concentration determined for each SRWS is within the standard deviation of the most probable values.

Table 3.--*Accuracy for the determination of chromium performed by graphite furnace atomic absorption spectrophotometry using Standard Reference Water Samples*

[All values in micrograms per liter; No., number; SRWS, Standard Reference Water Samples; NIST, National Institute of Standards and Technology; SPEX, commercially prepared and certified standards; --, no data]

Graphite furnace value				Standard value	
Reference No.	Standard mean	Standard deviation	No. of replicates	Mean	Standard deviation
SRWS-93	9.8	0.2	24	9.8	2.6
SRWS-95	1.9	.5	10	3.9	2.1
SRWS-97	24.8	1.2	24	26.0	4.1
SRWS-99	14.8	1.4	24	16.3	3.2
SRWS-101	17.8	1.0	24	18.0	3.3
SRWS-103	6.2	.3	24	5.8	1.0
SRWS-105	20.6	1.0	24	20.0	3.5
SRWS-107	13.8	.8	24	13.0	2.9
SRWS-109	18.2	1.0	24	18.7	3.4
NIST-1643	18.7	.7	24	18.6	--
SPEX-20	20.3	.5	12	20.0	2.0
SPEX-25	25.0	1.9	19	25.0	2.5
SPEX-50	53.8	2.9	12	50.0	5.0

Spike recovery studies are an additional demonstration of accuracy for the determination of chromium by GF-AAS, as listed in table 4. Natural-water samples were spiked with known quantities of chromium, analyzed for a period of 15 days, and the percent recoveries calculated. The recoveries of chromium ranged from 84 to 122 percent.

Table 4.--*Spike-recovery data for graphite furnace atomic absorption spectrophotometry*

[µg/L, micrograms per liter]

Amount present (µg/L)	Amount added (µg/L)	Amount found (µg/L)	Recovery (percent)
1.9	10	11.5	96
6.2	5	11.3	102
6.2	10	15.6	94
10.3	5	14.7	88
10.3	10	18.7	84
14.7	5	19.4	94
14.7	10	23.6	89
18.4	5	24.5	122
20.3	5	25.0	94
20.3	10	29.7	94
29.4	5	34.3	98

A further demonstration of accuracy for the determination of chromium by GF-AAS is established by comparison to another method. Natural-water samples were analyzed for chromium for a 5-day period using the GF-AAS and DCP-AES. The results for chromium determination for both methods are listed in table 5. Samples with chromium concentrations greater than 25.0 µg/L were diluted prior to analysis. The comparison indicates agreement between GF-AAS and DCP-AES.

Figure 3 shows data from table 5 that demonstrate the accuracy for the determination of chromium by GF-AAS. The graph represents a correlation coefficient of 0.9958 for the data collected by DCP-AES and GF-AAS.

CONCLUSION

As can be seen from the data presented, GF-AAS is an excellent technique for the determination of chromium. The method has proved to be precise and accurate. In addition, GF-AAS is more sensitive and has lower detection limits than DCP-AES and flame-AAS. Although GF-AAS has a slower analytical rate than DCP-AES or flame-AAS, the small sample size and lack of sample preparation make it an attractive analytical tool. The method is suitable for determining chromium in various types of natural water.

Table 5.--*Analytical results of natural-water samples using graphite furnace atomic absorption spectrophotometry and direct-current plasma atomic emission spectrometry*

[No., number; GF-AAS, graphite furnace atomic absorption spectrophotometry; DCP-AES, direct-current plasma atomic emission spectrometry; µg/L, micrograms per liter; <, less than]

Sample No.	GF-AAS mean (µg/L)	DCP-AES value (µg/L)	Difference (µg/L)
Filtered, acidified samples			
1	0.3	<1	0
2	1.3	2	-.7
3	.7	1	-.3
4	.7	2	-1.3
5	10.2	10	+.2
6	14.0	16	+2.0
7	19.2	19	+.2
8	23.2	23	+.2
9	25.7	25	+.7
10	35.4	34	+1.4
11	43.1	39	+4.1
Water-suspended sediment, acidified samples			
12	3.0	2	+1.0
13	4.0	3	+1.0
14	.5	<1	0
15	.4	<1	0
16	7.1	8	-.9
17	16.0	16	0
18	18.4	20	-1.6
19	23.5	24	-.5
20	30.8	30	+.8
21	38.4	37	+1.4
22	42.2	40	+2.2
23	48.5	48	+.5

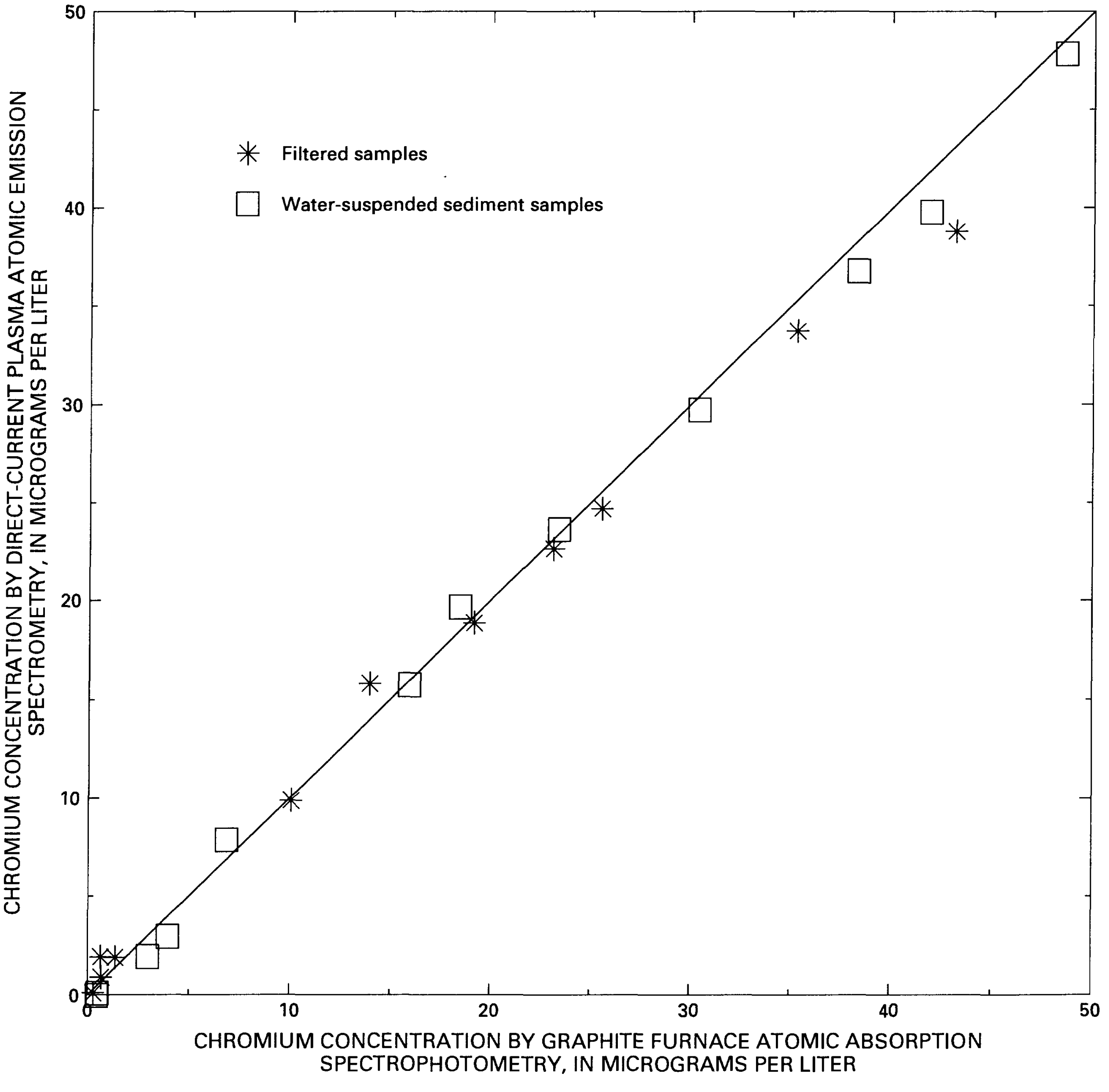

Figure 3.—Analytical results for the determination of chromium by direct-current plasma atomic emission spectrometry and graphite furnace atomic absorption spectrophotometry.

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