GEOHERMAL WATER AND GAS --
Collected Methods for Sampling and Analysis
Comment Issue

by

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INTRODUCTION

Recent emphasis on broadening the base of energy resources in the United States has rapidly expanded our interest and activity in exploration, development, and utilization of geothermal energy. Any gathering of participants in these efforts arrives at a consensus that geothermal sampling and analysis is filled with "pitfalls for the unwary." The Energy Research and Development Administration has undertaken a program to focus on this problem with the eventual goal of publishing a manual for sampling and analysis of geothermal fluids and gases. The plan is to organize a small working group to assess the state-of-the-art, select candidate methods, verify accuracy and reliability through round-robin testing, and assess chemical interferences through systematic study of the methods. To initiate the program Battelle-Northwest has assembled this collection of methods. It is admittedly a one-sided look at the state-of-the-art. Its purpose is to catalyze other viewpoints, identify omissions, and aid in planning further tests. If recipients take issue with its content and make this fact or other suggestions known to the authors our collective goal will be served.

We emphasize here and again in the text that analytic methods included in this coverage should not be taken as recommendations since in many instances applicability to geothermal brines has not been evaluated. It appears however, that emphasis in subsequent stages of this program should be placed on verifying the applicability and in some cases modifying established standard analytic methods rather than developing new methods. Sampling practices, on the other hand, are not standardized and methods development is needed.

SURVEY OF CONSTITUENTS

The analyst often finds it desirable to have some idea of the concentration level he may expect to encounter, particularly in samples from an unfamiliar source. In response to this need, a survey of analyses reported for fourteen different geothermal fluid sources is condensed graphically in Figure 1. Included are data from brines sampled at well-known geothermal areas throughout the world and from areas in the U.S. in varying stages of development for which fairly complete analyses are available. Sources and literature references are given on pages following Figure 1.

The results emphasize that geothermal brines or waters encompass very broad ranges of concentration and that only when consideration is restricted to given wells or at most reservoirs, can characteristic levels of concentration be defined.

CONCENTRATION RANGES FOR ELEMENTS IN GEOTHERMAL WATERS

FIGURE 1

BRINE SOURCES FOR SURVEY OF GEOTHERMAL ANALYSES

<u>Source</u>	<u>Reference</u>	<u>Source</u>	<u>Reference</u>
Marysville, Montana - Battelle Northwest analysis Hot-dry rock deep exploration well, fluid from 6350', gases 5750'	1	Steamboat, Nevada Spring #8	6
Marysville, Montana - USGS analysis Fluid from 5750'	1	Broadlands, New Zealand Drillhole #2, 1030 m	5
Imperial Valley, East Mesa 6-1 Sampled at 7900', well flowing	2	Wairakei, New Zealand Well 5	6
Imperial Valley, DWR Dunes No. 1 Sample from 259-271 meters perforation	3	Rotorua, New Zealand Hole 219	7
Imperial Valley, Sinclair No. 4 Liquid phase, well head samples 6BHS and 3BHS	4	Italy Carboli A	6
Salton Sea California, Hole 1 I.I.D. Deep aquifer, 1600 m	5	Matsukawa, Japan Hole 1, 945 m	5
Salton Sea California, Drillholes Steam, 1500-1800 meters	5	Hveragerdi, Iceland Hole G-3, 650 m	5
Mexicali, Mexico, Hole 5 Water and steam, 1285 m	5		
The Geysers, California Devils Kitchen, water associated with vapor dominated system	6		

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MATRIX OF GEOTHERMAL TASKS AND RELATED CHEMICAL ANALYSES

The complexities of geothermal sources, the phases included in samples, and the varying applications for analytic results in exploration, development, and utilization all influence the scope of an analytic program. The interrelationships of these variables are presented here in matrix form as an aid to defining the scope and capabilities of an analytic program. References cited are the basis for the matrix in its present form and typically place greater emphasis on the evaluation and application of analytic results than on the methods used to obtain data.

Originally the matrix was based on a list of constituents compiled during preparation of the survey of constituents. The same list was used in surveying analytic techniques and standard methods. Subsequent review of the literature revealed additional entries included in the present matrix that are not covered in the surveys of techniques and standard methods.

Constituents added during matrix preparation include the following: Antimony, Beryllium, Gold, Lithium, Nickel, Radium, Rubidium, Thallium, Tin, Titanium, Radon.

It should also be noted that several constituents included in reported analyses did not appear again in searching for specific applications of analytic results. This category includes: Manganese, Nitrate, Nitrite, Carbon Monoxide, Nitrous Oxide.

Because the matrix emphasizes chemical aspects, it obviously cannot be regarded as a basis for complete sample characterization. Obvious omissions essential to full characterization include: Temperature, Pressure, Flow rate at time of sample, Flow history, Documentation of sampling and storage methods.

MATRIX OF GEOTHERMAL TASKS AND RELATED CHEMICAL ANALYSES

[illegible]

LEGEND

1 SAMPLE FORM

S - SOLID
L - LIQUID
G - GAS

2 SAMPLING PROCEDURE (S)

E - ESTABLISHED
D - DEVELOPED BUT NOT UNIVERSALLY APPLIED
U - UNDER DEVELOPMENT
N - NONE DISCOVERED BY AUTHORS. GEOPHYSICAL OR
OTHER ANALYTIC METHODS MAY SATISFY REQUIREMENTS

3 PROPERTY OF INTEREST

F - FIELD ANALYSIS
L - LABORATORY ANALYSIS

4 DISSOLVED SOLIDS, 5 GASES

F - FIELD ANALYSIS
L - LAB ANALYSIS
R - RATIO WITH OTHER CONSTITUENT
M - CONSTITUENT MODIFIES INTERPRETATION
 OF OTHER RESULTS
δ - ISOTOPIC COMPOSITION

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SAMPLE COLLECTION, STORAGE, PRESERVATION, AND ANALYSIS

The major problems encountered in procuring representative samples of the heterogeneous gas-liquid discharge from a geothermal well head discharge include:

1. maintaining the temperature and pressure regime present in the well during the vapor-liquid collection process;
2. designing and installing the necessary hardware to separate the vapor and liquid prior to collection;
3. finding compatible (chemically inert and structurally strong) materials to separate and collect the samples; and
4. preserving the vapor and liquid samples prior to analysis.

Before classification and intercomparisons of geothermal discharges can be performed, standard collection, storage and preservation techniques as well as analytical methods need to be adopted. Standard collection techniques should address and minimize the above problems.

The procurement of representative *in situ* samples at various subterranean levels from one bore hole presents further problems. At present, *in situ* sampling appears to be of the total mixed discharge with separation of vapor and liquid not performed until after flow to the surface. The dilution and phase changes caused by cooling and potential pressure drops have not been adequately investigated. Therefore, estimates of the accuracy of *in situ* sampling cannot be made. The grab sample approach also is usually restricted in volume because the sampler must fit freely into the well bore or casing. The necessity of *in situ* sampling versus well head discharge sampling must be clearly demonstrated before the added complexity and expense should be allocated.

Generalized Sampling Procedures for Geothermal Wells

For this discussion it is assumed that sampling will be performed at well head discharges and that only sampling fundamentals will be addressed. Several investigators (Mahon, 1961; Ellis, Mahon and Ritchie, 1968; Truesdell and Pering, 1974; Giggenbach, 1974; McSpadden, Woodruff and Shannon, 1975; and Hill and Morris, 1975) discuss in detail various sampling devices and techniques used to obtain vapor and liquid samples from various geothermal discharges.

To obtain representative samples, most investigators recommend that separate vapor and liquid samples be procured. In order to minimize phase changes which can significantly affect chemical characteristics, samplers should be inert to corrosion over short time spans. Corrosion can render the collection devices structurally useless besides causing serious H_2S , sulfide and redox potential interference and heavy metal impurities. Teflon coated stainless steel gas collectors show a short lifetime under the high temperature-pressure

environment (Hill and Morris, 1975). Titanium metal appears to resist corrosion and might be a suitable substitute (Giggenbach, 1974). Glass lined metal or externally padded heavy duty glass flasks also should be acceptable especially for low pressure systems.

Water

Water samples taken from well insulated separators usually require minimal corrections for condensate dilution or liquid concentration from evaporation (Ellis, Mahon and Ritchie, 1968).

The separated water is usually cooled before being placed in sampling containers or further manipulated such as by filtration. Upon cooling high silica containing and sulfide laden waters often form precipitates. Immediate dilution of a subsample with silica free distilled water is recommended for the silica sample. Acidification of a subsample should keep heavy metal sulfide precipitates from forming. Whatever preservation technique is chosen for the water sample, any precipitate which forms should be analyzed and corrections made to obtain the water concentrations. If the discharge is predominantly steam, steam condensation during sampling may significantly dilute the water sample. To minimize this occurrence pressure and temperature drops must be kept at a minimum. Preservation techniques, storage containers and analytical procedures for chemical constituents are included in Table I. In general, storage in plastic is recommended for metals and plastic or glass for anions. Dissolved gases can permeate plastic containers. Therefore, if prolonged storage is required, air tight glass containers are recommended for dissolved oxygen, hydrogen sulfide, pH and bicarbonate-carbonates.

Preservation techniques can arrest chemical changes for up to six months for many constituents but for others such as pH, bicarbonate, ammonia, hydrogen sulfide, sulfide, silica and possibly the nutrients, nitrogen and phosphorous rapid measurement is recommended.

Table I lists most of the constituents of importance in the liquid phase of geothermal discharges, storage and preservation techniques, typical concentrations in geothermal waters, various analytical procedures, instrument requirements, sample requirements, approximate cost per sample, accuracy and precision and limitations of each procedure.

Vapor

Vapor samples are usually obtained from a separator and water cooled to remove steam. At high pressure the enthalpy of the drill hole discharge must be measured accurately in order to calculate the gas contents of the discharge (Mahon, 1961). Several gas collection

bottles are described in the literature previously cited. Again, container strength and chemical inertness are important. Stainless steel may be used for non-corrosive discharges when storage times can be kept short. Pyrex glass-lined or reinforced glass collection bottles are also acceptable.

Prior to collection, the bottles are usually evacuated to create a driving force for gas collection. Upon collection, the bottles are water cooled to condense steam. The quantity of condensible vapors is determined by weight measurements. Oftentimes gases such as hydrogen sulfide and carbon dioxide are absorbed in alkaline solutions or other absorbing solutions during the collection process. The absorbing solutions are then analyzed by procedures discussed in Table 2. In other instances, gas collection bottles are returned to the lab where absorbing solutions are added to remove carbon dioxide, hydrogen sulfide and other acid gases. The residual gases present are finally pumped off for conventional, gas chromatographic and or mass spectroscopic analysis. Results are typically presented in mole % of the total gases in the vapor. These units are directly compatible with thermodynamic calculations. Sample container, preservation and analytical procedures for gases in the vapor samples are discussed in Table 2. In general, it is advantageous to analyze the gas composition as rapidly as possible. To check for entrained liquid and incomplete phase separations, one can measure the sodium or chloride content of the condensed phase and calculate corrections. In most geothermal discharges aside from the water vapor, about 95 to 97% of the gases emitted consist of carbon dioxide, sulfur gases (H_2S , SO_4 , SO_2), nitrogen and oxygen. In a few instances H_2 and CH_4 have been reported to contribute considerably to the total gas content.

SURVEY OF ANALYTIC OPTION

Tables 1 and 2 review analytic options for constituents in water and gases respectively. Notes preceding each table explain the basis for entries included and give a list of references used in the compilation.

Notes for Table 1, WATER

1. The constituents listed represent a comprehensive but not all inclusive list of chemicals which have been measured in geothermal waters.
2. The list of reasons for measuring each constituent is incomplete and often considers only environmental concerns.
3. The storage times quoted are not the maximum length of time samples can be stored before significant changes occur. The storage times represent safe periods of time for which very little changes are found for most water samples provided suitable preservation procedures have been followed.
4. The range in geothermal waters represents the extreme values reported in numerous articles available to the authors and should not be considered comprehensive.
5. The analytical procedures listed for each chemical constituent are not all inclusive but do represent those procedures most commonly used. Several new procedures utilizing specific ion electrodes, plasma emission spectroscopy, spark source mass spectrometry and anodic stripping voltametry are presently being used to determine certain constituents. As more work is performed and more researchers become familiar with these procedures, new and improved analytical techniques for some of the chemical constituents may be forthcoming.
6. Per sample costs are based on the assumption that a sufficient number of samples are being analyzed so that startup and calibration costs are relatively small. For most chemical analyses, a sample size of 10 to 50 ml would meet this requirement. If smaller sample sizes are used and the laboratory is not presently equipped to run the chemical analysis on a routine basis, per sample cost could easily double.
7. Several of the techniques such as X-ray fluorescence (XRF) and instrumental neutron activation (NAA) are multielement techniques in which values of several chemical constituents are obtained at the same time at no additional costs. This fact is noted in the table by placing the word multielement by the per sample costs.

8. The numbers quoted for accuracy represent bias from the true results and can be calculated as the absolute value of the difference between the actual value and observed value divided by the actual value. This number is multiplied by 100 to convert to percent.

$$\left| \frac{\text{Actual}-\text{Observed}}{\text{Actual}} \right| \times 100 = \% \text{ Bias} = \text{Accuracy}$$

The precision values represent $\pm$ one standard deviation.

9. The terms mg/l and ppm have been used interchangeably in this table but to be correct, especially for brines, the specific density of the thermal water would have to be used to convert from one set of units to the other.

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TABLE 1
CONSTITUENTS IN GEOTHERMAL WATERS

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
pH	Hydrogen Ion important to water chemistry corrosion	Plastic, glass cool 4°C determine <6 hrs	4-10	Electrometric (1,2,3)	Meter \$200-1000 Simple Procedure	25 ml	\$1-5	1% Bias ±0.1 pH Unit	Oils and grease coat electrode Temp. dependent
REDOX Potential	Important to water chemistry	Plastic, glass determine rapidly keep out of atmos.	-400 mv to +500 mv	Electrometric (1)	Meter \$200-1000 Simple	100 ml	\$1-5	Not available ±5-10 mv	Reproducible redox determinations difficult, temperature dependent
Conductivity	Estimates total dissolved salts	Plastic, glass determine rapidly <24 hrs	500-50,000 µmho/cm	Conductivity Meter (1,2,3,4)	Meter \$250-400 Simple	100 ml	\$1-5	±5% Bias ±5-10% Precision	Temp. dependent
Alkalinity	Ability of water to absorb acid	Plastic, glass cool 4°C determine <24 hrs	50-1000 ppm as CaCO ₃	Titration (Electrometric) (1,2,3,4)	Buret \$40 pH Meter \$200-1000 Simple	100 ml	\$5-10	5-20% 3%	Oily matter, soaps, suspended solids and salts of weak acids if present in large amounts may interfere with pH measurements
Hardness	In general measure of Ca + Mg	Plastic, glass pH to 2 HNO ₃ cool to 4°C OK 7 days	5-20,000 ppm as CaCO ₃	EDTA Titration (1,2,3,4)	Buret \$40 Simple	100 ml	\$5-10	1-3% ±1-3%	Highly colored and strong brines interfere (AL >20 ppm, CO ₃ >1000 ppm, Cl >10,000 ppm, SO ₄ >10,000 ppm, Fe >30 ppm)
Suspended solids	Measure of particulates which may clog equipment	Plastic, glass cool to 4°C 7 days storage		Filtration (1,2,3)	Filtration Equip. \$50 Drying Oven \$300 Balance \$1000 Simple	100 ml	\$5-10	Not available Not available	
Dissolved solids	Measure of material in solution can affect scaling	Plastic, glass cool to 4°C 7 days storage	60-325,000 mg/l	Evaporation (1,2,3)	Drying Oven \$300 Balance \$1000 Simple	100 ml	\$5-10	Not available Not available	Highly mineralized waters leave hygroscopic salts which require prolonged drying and entrap water
Turbidity	Estimates suspended solids	Plastic, glass cool to 4°C 7 days storage	0-2000 JTU	Turbidimetric (1,2,3)	Turbidimeter \$300 or Nephelometer \$500 EPA suggests HACH Model 2100 or 2100A	100 ml	\$5-10	Not available 2-5%	Turbidity is an optical property and not correlatable to suspended solids; colored dissolved solids effect results; air bubbles interfere
Aluminum	Important in hydrogeochemical calculations	Plastic filter on site acidity pH 2 HNO ₃ storage to 6 mos	0-100 mg/l	a) Fluorometric (1)	Fluorometer \$1000-4000	100 ml	\$5-10	±1-7%	(A) Good for low Al 0-5 µg/l in rather high purity water; heavy metals >20 µg/l, Ca >1 mg/l interfere
				b) Colorimetric 8-quinolinol (1,14)	Spectrophotometer many steps \$500-5000	100 ml	\$10-20		(B) Good for 0-0.5 mg/l Al; copper, iron >1 mg/l, Ca >32 mg/l, Mg, PO ₄ >5 mg/l, Mn >1 mg/l
				c) Colorimetric ferron (1,2,3,4)	Spectrophotometer Fe correction necessary \$500-5000	25 ml	\$5-10	±10% ±10%	(C) Sample must be relatively free of interfering substances; iron interference is corrected; Mn, F >5 mg/l interfere; 0.05-2 mg/l Al working curve.
				d) Aluminon (2,3,15)	Spectrophotometer \$500-5000	100 ml	\$10-15	±10-25% ±5%	(D) F 7.5 mg/l interferes but can be removed; 0.02-1.0 mg/l Al working range; exact temperature control needed
				e) Atomic absorption (2,3)	Atomic absorption N ₂ O flame \$10,000-\$15,000	10 ml	\$5-10	±1-10% 10-25%	(E) High Fe, PO ₄ , Cl may interfere; 0.3-20 mg/l Al working range, nitrous oxide flame
				f) X-ray fluorescence (10)	X-ray fluorescence counting equipment \$50,000	100 ml	\$50 Multielement	0-15% 15-20%	(F) Sample matrix thin solid wafer; therefore sample must be evaporated
				g) Neutron activation (9)	Reactor counting equipment \$50,000	100 ml	\$100-200 Multielement	0-10% 0-10%	(G) 10 ppm detection limit must have access to reactor

TABLE 1b

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Ammonia	Presence signifies reducing conditions	Plastic glass Acidify pH2 H ₂ SO ₄ Cool to 4°C storage 1 day plastic acidify freeze storage 30 days	0-100 mg/l	a) Distillation method (1,2,3,15)	Distillation apparatus \$100 Spectrophotometer \$500-5K	500 ml	\$10-15	3-6%	(A) Applicable to most waters; 0.02-2 ppm NH ₄ working range; C ₄ >250 mg/l should be treated
				b) Direct nesslerization (1,2,3)	Spectrophotometer \$500-5K	500 ml	\$5-10	5-25% +5-10%	(B) Rapid, good for relatively clean waters; 0.02-2 ppm NH ₄ working range
				c) Selective ion electrode (2)	Probe meter \$1500	25 ml	\$5	5-10% 3-5%	(C) 0.05-1700 mg/l NH ₃ working range
				d) Automated phenate (2,6)	Spectrophotometer \$500-5K Technician Analyzer \$10K	100 ml	\$5-10	1-10% 1-5%	(D) Without automated control results variable unless strict control; 0.01-2 mg/l NH ₃ working range; high salts Ca, Mg need EDTA treatment
				e) Nitrite oxidation (5,7)	Spectrophotometer \$500-5K	50 ml	\$10-15	Not available 10%	(E) Used for sea water; also determines amino acids; 1.7-170 µg/l NH ₃ working range
Arsenic	Health hazard volatile	High density plastic acidify pH<2 H ₂ SO ₄ only 6 mos storage	0-10 mg/l	a) Arsine formation spectrophotometric (1,2,3,4,15)	Arsine generator \$100 Spectrophotometer \$500-5K	100 ml	\$10-15	0-10% +10-50%	(A) 0.020-10 µg/l as working range; Co, Ni, Hg, Ag, Pt, Cu, Cr, Mo, Sb interfere but usually not a problem for natural waters; large amounts of H ₂ S cause + interference
				b) AA Hydride formation (2)	Arsine generator \$100 AA \$10K	100 ml	\$10-15	0-15% +3-6%	(B) 0.002-0.020 mg/l working range
				c) Flameless AA (11)	AA \$10-15K Graphite Furnace \$5K	100 µl	\$10-15	Not available Not available	(C) 0.01-1 mg/l working range
				d) Neutron Activation (3)	Reactor Counting \$50-100K	100 ml	\$100-200 Multielement	+5-10% +10-25%	(D) Wet chemical separations after irradiation probably required detection limit pptillion
				e) XRF (10)	Inst. costs \$50-100K	100 ml	\$50-100 Multielement	5-10% +5-15%	(E) Detection limit 1-5 ppm; sample must be thin solid therefore evaporation or ion exchange necessary
Bicarbonate carbonate	Major buffering capacity important for corrosion and scaling	plastic or glass cool to 4°C storage 24 hrs	20-1000 mg/l	a) Titration (1, 2, 3, 4)	Buret \$40 pH meter \$200-1000	100 ml	\$5-10	5-20% +3%	(A) Oils or grease can cause erroneous pH readings
Barium	Human death at doses above 550 mg	Plastic acidify pH<2 6 mo storage	0-250 mg/l	a) AA (2,3)	AA \$10K	10-100 ml	\$5-10	1-10% +3-10%	(A) 0.5-25 mg/l working curve; nitrous oxide flame; use large spike of alkali salts to minimize ionization problems
				b) XRF (10)	Inst. costs \$50-100K	10-100 ml	\$50-100	5-25% 10-25%	(B) Detection limit 10-50 mg/l; need thin solid sample
Boron	Deleterious to plants 71mg/l	Plastic	0-1200 mg/l	a) Carmine method (1,2,3)	Steam generator Spectrophotometer \$500-5K	5 ml	\$5-10	+10%	(A) Good in all waters providing F, SiO ₂ , PO ₄ interferences are not too great; 0.2-5 mg/l working range; use plastic or B free glass
				b) Curcumin (2,3)	Spectrophotometer \$500-5K	1 ml	\$5-15	0-10% +10-25%	(B) Nitrate >80 ppm invalidates Ca+Mg >100 ppm causes high results unless removed, procedure requires careful T° and time control; 0.1-1.0 mg/l working range

TABLE 1c

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Boron (cont.)				c) Potentiometric titration (mannitol) (1,3,15)	Buret \$40 pH meter \$200-1000 hot plate \$100	100 ml	\$5-10	0-10% ±5-10%	(C) 1-100 mg/l working range, CO ₂ must be completely expelled; PO ₄ >10 ppm must be removed
				d) AA (11)	AA \$10K	15 ml	\$10-15	Not available Not available	(D) 50-200 mg/l working range; not sensitive enough; nitrous oxide flame
				e) Methylene blue (6)	Spectrophotometer \$500-5K	10 ml	\$5-10	Not available ±2-10%	(E) Sensitive to undescribed interferences; 0.02-2.5 mg/l working range
Bromide		Plastic or glass cool to 4°C storage 24 hrs +	.4-700 mg/l	a) Colorimetric (1,4)	Spectrophotometer \$500-5K	10 ml	\$10-15	Not available ±2-25%	(A) Very sensitive working curve 0-0.1 mg/l Br; interferences include NO ₂ >1 ppm, Mn ²⁺ >3 ppm, Fe ³⁺ , Zn ²⁺ , Ag ⁺ , Co ²⁺ , Ni ²⁺ >1 ppm
				b) Titration (1,2,4,15)	Buret \$40	400 ml	\$5-10	1-17% 5-10%	(B) Measures both Br and I; Br by subtraction; working curve 2-50 ppm; interferences iron, manganese; organics can be easily removed
				c) Phenol red (3)	Spectrophotometer \$500-5K	50 ml	\$5-10	5-15% 10-15%	(C) 0.1-1 ppm working range
				d) XRF (10)	Inst. costs \$50-100K	100 ml	\$50-100 Multielement	Not Available ±10-25	(D) Solid sample necessary detection limit 1-5 ppm
Cadmium	0.2 mg/l toxic to fish	Plastic filter on site acidify to pH<2 HNO ₃ storage 6 mos	0-1 mg/l	a) AA (1,2,3,14)	AA \$10K	10-25 ml	\$5-10	0-20% ±2% at 1 ppm	(A) 0.05-5 mg/l working range, with chelation-extraction, working range is lowered to 0.5 µg/l
				b) Flameless AA (11)	AA \$10-15K graphite furnace \$5K	0.1-1 ml	\$10-15	Not Available ±5-20%	(B)
				c) Dithizone colorimetric (2)	Spectrophotometer \$500-5K	25 ml	\$10	6% 25% at 0.05mg/l	(C) 0.005-0.4 mg/l working range
				d) XRF (10)	Inst. costs \$50-100K	1000 ml	\$50-100 Multielement	Not Available ±10-20%	(D) 5-10 ppm detection limit, quantitative numbers only at higher concentrations, sample must be thin solid
Calcium	Major cation scaling problem	Plastic filter on site acidify to pH<2 HNO ₃ storage 6 mos	.5-40,000 mg/l	e) Neutron activation (9)	Inst. counting \$50-100K		\$100-300	Not Available Not Available	(E) Must use wet chemical separations; detection limit 1 pptillion
				a) AA (1,2,15)	AA \$10K	10-20 ml	\$5-10	0-5% 4% at 1 ppm	(A) 0.2-20 mg/l working range, PO ₄ interferes but can be removed if below 600 ppm, Al interferes
				b) Gravimetric (1,3)	Pt crucibles oven \$300-1000 balance \$1000 hot plate \$100	10-100 ml	\$15-20	±2-5% ±2-5%	(B) Must remove Fe, Mn, Al, PO ₄ , Sr; many steps; working range >10 ppm
				c) EDTA titration (1,2,15)	Hot plate \$100 buret \$40	10-20 ml	\$10-15	±2% ±9% at 100 ppm	(C) Working range 0.5-1000 ppm Sr, Ba >30 ppm interfere

TABLE 1d

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations	
Calcium (cont.)				d) EDTA titration (7)	Buret \$40	3-350 ml	\$10	Not available Not available	(D) Recommended titration procedure for sea water 1-100 mg/l working range	
				e) Flame photometry (7)	Flame emission \$4-15K (AA or other)	10-20 ml	\$10	0-10% ±5-15%	(E) PO ₄ interference, in brines use known addition	
				f) XRF (10)	Inst. costs \$50-100K	10-100 ml	\$50-100 multielement		(F) 5-10 ppm detection limit for thin solid samples	
Chloride	Major anion important to corrosion studies	Plastic or glass no preservative storage up to 7 days	2-184,000 mg/l	a) Mercurimetric titration (1,4)	Buret \$40	1-50 ml	\$10-15	0-3% ±3-5% at 0.26 ppm Cl	(A) Applicable to low solids and low heavy metals containing waters Zn, Pb, Ni, Fe ²⁺ , Cr ³⁺ tolerable up to 100 ppm; Cu tolerable to 50 ppm; Fe ³⁺ must be reduced if above 10 ppm; some I ⁻ , F ⁻ also is titrated; deep color interferes; 0.1-20 ppm Cl working range	
				b) Silver nitrate titration (1,2,3,4,7,15)	Buret \$40 Chloridometer (auto) \$500	1-50 ml	\$5-10	0-3% ±2-4% at 20 ppm	(B) Best for Cl, 20-2000 mg/l good for mineralized water with higher heavy metals; working curve 5-400 ppm; Br, I, S ⁻ are titrated also; PO ₄ >25 ppm interfere	
				c) Colorimetric (1)	Spectrophotometer \$500-5K	1-50 ml	\$5-10	Not available ±10-20%	(C) Working range 0.02-10 ppm; used mainly for relatively clean waters; Br ⁻ , I ⁻ , Cn ⁻ , S ₂ O ₃ ⁻ , NO ₂ ⁻ , color interfere	
				d) XRF (10)	Inst. costs \$50-100K	1-100 ml	\$50-100 Multielement	Not available ±10-25%	(D) Detection limit 10-100 ppm for thin solid samples	
Chromium	Cr ⁺⁶ toxic	Total Cr filter on site acidify to pH<2 HNO ₃ storage	no data	a) Diphenyl carbazide permanganate oxidation (1,3,4)	Spectrophotometer \$500-5K	10 ml	\$10-15	5-27% ±2-10%	(A) Normally used for total Cr 0.5-5 ppm working range; Fe >1000 ppm, V >4 ppm, Mo, Hg >200 ppm; high Cl >250 ppm reduces Cr recovery; can be removed by precipitation	
				b) Diphenyl carbazide hypobromite oxidation (1,3)	Buret \$40 spectrophotometer \$500-5K	10 ml	\$10-15	5-25% ±2-10%	(B) Normally used for total Cr, good in organic rich wastes; Fe >50 ppm and other precipitable hydroxides interfere; Cl >250 ppm reduces Cr recovery; Cl can be removed; large amounts of PO ₄ or alkali earths may cause Cr loss by precipitation	
		Cr ⁺⁶ filter store <3 days		c) Diphenyl carbazide alkaline-per sulfate oxidation (1)	Spectrophotometer \$500-5K	150 ml	\$10	5-25% ±2-10%	(C) Useful for determination of Cr ⁺³ ; Fe >50 ppm and other precipitable hydroxides interfere; Cl does not interfere	
				d) Diphenyl carbazide (1,3,4)	Spectrophotometer \$500-5K	50 ml	\$5-10	5-25% ±2-10%	(D) Cr ⁺⁶ only, working range 0.005-0.4 mg/l Cr; Fe, V >1 ppm interfere with color development	

TABLE 1e

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Chromium (cont.)				e) Atomic absorption (2,4)	AA \$10-15K	10-20 ml	\$10	3-30% ±10-50%	(E) Working range 0.2-10 ppm; with APDC-MIBK chelation Cr ⁺⁶ 0.002 ppm readily detected, Cr ⁺³ must be oxidized to extract
				f) Flameless AA (11)	AA \$10-15K Graphite furnace \$5K	1 ml	\$10-15	Not available ±10-25%	(F) 0.0006 mg/l detectable by direct injection; use known additions to remove matrix dependence; extraction probably necessary on brines
				g) XRF (10)	Inst. \$50-100K	100-1000 ml	\$50-100 multielement	Not available ±5-20%	(G) 1-5 ppm detection limit; water samples must be evaporated or exchanged so that thin solid sample may be mounted
				h) NAA (9)	Reactor Inst. \$50-100K	25-1000 ml	\$100 multielement	Not available ±5-20%	(H) Water sample evaporated, salts directly irradiated and counted 0.0003 mg/l detection limit; wet chemical separations increase range to 3 pptillion
Copper	Health hazard above 1 mg/l	Plastic filter on site acidify pH<2 HNO ₃ storage up to 6 mos	0-5 mg/l	a) Neocuproine (1)	Spectrophotometer \$500-5000	100 ml	\$10-20	2-10% ±5-10%	(A) Can tolerate most water types; possible interferences from sulfide, cyanide, organic matter, and Cr are eliminated; working range 0.2-5 mg/l Cu
				b) Cuprethol (1,3)	Spectrophotometer \$500-5000	100 ml	\$5-10	1-10% ±4-20%	(B) Can tolerate less interference than method A; Na, K, Mg, NH ₄ , Cl, NO ₃ , PO ₄ , SiO ₂ up to 1000 ppm O.K. Bi, Co, Hg, Ni, CN, S ⁼ worst interferences; working range 0.2-4 mg/l Cu; Al >20 ppm, Ca >400 ppm, Fe >20, Mn >10, NO ₂ >20, Zn >20 interfere
				c) AA (1,2,4,14)	AA \$10-15K	10-25 ml	\$5-10	0-5% ±2-10%	(C) Working range 0.1-20 mg/l Cu extraction with APDC-MIBK increases sensitivity 100 fold
				d) Bathocuproine (3)	Spectrophotometer \$500-5000	50 ml	\$5-10	1% at 1 ppm Cu ±4%	(D) Al >100 ppm, Co >1000 ppm, Cr ⁺³ >10 ppm, Fe >100 ppm, Hg >100 ppm, Mn >500 ppm, Na >1000 ppm, Cl >1000 ppm, NO ₃ >300 ppm, SO ₄ >1000 ppm interfere; working range 0.1-5 mg/l Cu
				e) Carbonate (5)	Spectrophotometer \$500-5000	50 ml	\$5-10	10% 10%	(E) Fe, Ca, PO ₄ interferences removed with citric acid; working range 0.1-5 ppm Cu
				f) Flameless AA (11)	AA \$10-15K Graphite furnace \$5K	1 ml	\$10-15	Not available 10%	(F) 0.001 mg/l and above run directly
				g) XRF (10)	XRF \$50-100K	100-1000 ml	\$50-100 multielement	Not available ±5-20%	(G) Detection limit 1-5 ppm; water sample must be evaporated or ion exchanged to get a solid sample
				h) NAA (9)	Reactor Inst. \$50-100K	100 ml	\$100-300	Not available ±5-20%	(H) Wet chemical separations; mandatory detection limit 2 pptillion

TABLE 1f

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Fluoride	Water conc. must be controlled for health reasons	Plastic preferred to glass cool 4°C hold <7 days	0.1-25 mg/l	a) SPADNS (1,3,2)	Distillation apparatus \$100-300 Spectrophotometer \$500-5000	400 ml	\$10-15	1-5% ±5-20%	(A) Fluoride isolated by distillation from waters; working range 0-1.4 mg/l; Al >300 ppm, SiO ₂ >400 ppm, Cl >2500 ppm and oily matter interfere even with distillation
				b) Ion selective electrode (1,3,2)	Probe meter \$200-1000	50 ml	\$5-10	0-5% ±3-5%	(B) Working range 0.1-1000 ppm distillation usually not necessary; method not applicable to brines >10,000 ppm dissolved solids; most interferences removed with buffer solution
				c) Alizarin (3)	Distillation apparatus \$100-300 Spectrophotometer \$500-5000	400 ml	\$5-15	0-10% ±1-20%	(C) After distillation, free of most interferences but Al >0.2 ppm which can be removed by complexation
				d) Zr-Eriochrome cyanine R (4)	Distillation apparatus \$100-300 Spectrophotometer \$500-5000	400 ml	\$10-15	Not available ±5-10%	(D) Distillation recommended working range 0-3 mg/l Fl Al >10 ppm, Cr, Cd, Ni >5 mg/l
Iodide		Plastic or glass cool 4°C store 1 day	0.1-18 mg/l	a) Arsenious-ceric colorimetric (1,3,4)	Spectrophotometer \$500-5000	20 ml	\$10	Not available ±5-25%	(A) Recommended for natural waters with trace amounts of I ⁻ <0.10 ppm. Reducing agents cause positive errors and must be removed by permanganate treatment. Cl <5000 ppm, Na <3000 ppm, alkalinity <1000 ppm, NO ₃ <750 ppm, Ca <250 ppm, Br <5 ppm, Fe 5 ppm acceptable. Working range 0.01-0.1 ppm. Must control temperature and time closely
				b) Titration (1,2,4)	Buret \$40	100-400	\$5-10	1-17% 5-10%	(B) Measures both I ⁻ and Br ⁻ ; applicable to brines, natural waters; working curve 2-50 ppm; interferences iron, manganese, organics easily removed
				c) XRF (10)	Inst. Cost \$50-100K	1000+ ml	\$50-100 Multielement	Not available	(C) Detection limit on thin solid sample 10-50 ppm; water samples would have to be evaporated or ion exchanged
Iron	Reducing conditions shown by Fe ²⁺ Oxidation can cause Fe ppt clogging and scavenging	Plastic filter on site acidify to pH<2 HNO ₃ storage 6 mos Fe ²⁺ /Fe ³⁺ analyze rapidly	0-2200 mg/l	a) Phenanthroline (1,3)	Spectrophotometer \$500-5000	100 ml	\$5-10	1-10% ±1-10%	(A) Use at Fe >0.05 ppm Measures Fe ²⁺ , upon sample reduction measures Fe ³⁺ +Fe ²⁺ If Cu, Co, Cr, Zn exceed 10X Fe there are interferences Ni >2 ppm, Bi, Ag at any concentration interfere and must be removed. Large amounts of PO ₄ interfere. Working range 0.1-5 ppm Fe Detection limit 0.02 ppm. If interferences are severe Fe can be extracted with ether first
				b) Batho-phenanthroline (1,5)	Spectrophotometer \$500-5000	50 ml	\$5-10	Not available	(B) For low iron waters; total iron is measured; use on sea water; working range 0.016-0.8 ppm Fe
				c) Tripyridine (3,4,7)	Spectrophotometer \$500-5000	50 ml	\$5-10	0-15% ±10-50%	(C) Interferences same as method A reagents less expensive than method B

TABLE 1g

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Iron (cont.)				d) Atomic absorption (1,2,3,4, 14)	AA \$10-15K	10-20 ml	\$5-15	0-10% ±5-15%	(D) $\text{SiO}_2 > 200$ ppm interferes; a Ca matrix is used to reduce SiO_2 interferences; working range 0.1-10 mg/l Fe very good above 0.3 ppm Fe extraction procedure APDC-MIBK removes all but trace metal interferences and decreases detection limit to ppb
				e) Flameless AA (11)	AA \$10-15K Graphite furnace \$5K	1 ml	\$10-15	Not available ±10%	(E) Direct determination ppb range
				f) XRF (10)	Inst. cost \$50-100K	1000 ml	\$50-100 Multielement	Not available ±5-15%	(F) Detection limit 1-5 ppm on thin solid sample
				g) NAA (9)	Inst. cost \$50-100K reactor needed	25 ml	\$100-150 Multielement	Not available ±5-10%	(G) Evaporate sample; no separations detection limit 0.001 mg/l
Lead		Plastic, filter on site acidify to pH<2 HNO_3 cool to 4°C store up to 6 mos	0-80 mg/l	a) AA (1,2,3,14)	AA \$10-15K	10-100 ml	\$10-15	0-10% ±20-30% at 1 ppm	(A) 0.34-20 ppm working range if use APDC-MIBK extraction detection limit 100X better (<3 ppb)
				b) Flameless AA (11)	AA \$10-15K Graphite furnace	1-10 ml	\$10-15	0-20% ±10-30%	(B) Direct injection of low salt waters 2 ppb detection; high salt waters extract APDC-MIBK detection limit 0.05 ppb
				c) Dithizone (3)	Spectrophotometer \$500-5000	25 ml	\$15-20	5-15% ±20-50% at 0.5 ppm	(C) Careful technique utmost importance; working range 0.05-1 ppm
				d) XRF (10)	Inst. cost \$50-100K	1000 ml	\$50-100 Multielement	Not available ±10-20%	(D) Detection limit 1-5 ppm on thin solid sample
Lithium		Glass or plastic filter on site acidify to pH<2 cool to 4°C polyethylene bottles often contaminated with Li store up to 6 mos	0-200 mg/l	a) Flame emission (1,3)	Flame photometer \$5-15K	25-50 ml	\$10	5-10% ±10%	(A) Ba, Sr, Ca interfere and can be removed by addition of Na_2SO_4 - Na_2CO_3 solution; Na and Mg above 10; detection limit 0.1 ppm
				b) Atomic absorption (4)	Atomic absorption \$10-15K	25 ml	\$5-10	0-10% ±5-10%	(B) Na >1000 ppm, K >100 ppm, Mg >200 ppm, Ca >200 ppm, Cl >1000 ppm, SO_4 >2000 ppm, NO_3 >100 ppm and Sr 5 ppm interfere; detection limit 0.01 ppm
				c) Flameless AA (11)	AA \$10-15K Graphite furnace \$5K	1-5 ml	\$10-15	Not available 5-15%	(C) Working range 0.01-0.9 ppm
Magnesium	Scale problem major cation	Plastic; filter on site acidify to pH<2 HNO_3 cool to 4°C store up to 6 mos	0-1500 mg/l	a) EDTA titration (1,4)	Buret \$40	50 ml	\$10-15	5-10% ±5-15%	(A) Mg determined by difference of two titrations total (Mg+Ca)-(Ca) Al >5 ppm, HCO_3 >500 ppm, CO_3 >50 ppm, Cl >10,000 ppm, Fe >20 ppm, NO_3 >500 ppm, SiO_2 >100 ppm interfere
				b) Gravimetric (1,3,14)	Balance \$1000 Oven \$1000	10-100 ml	\$10-15	2-10% ±2-15%	(B) PO_4 , Fe, Al, Mn are removed, then Ca is precipitated and finally Mg determined on Ca filtrate by precipitation
				c) AA (2,3,4)	AA \$5-15K	25 ml	\$5-10	0-5% ±3-7%	(C) Add La solution to remove Al interference; Na, K, Ca 400 ppm cause no interference; working range 0.02-2 mg/l
				d) Colorimetric (3)	Spectrophotometer \$500-5000	5-50 ml	\$5-10	3-20% ±1-40%	(D) Ca, Al added to stabilize interference; Fe <2.5 ppm, Cl <250 ppm, F <5 ppm, PO_4 <5 ppm; Ok, Mn, Zn must be absent; working range 2-75 ppm Mg

TABLE 1h

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Manganese		Plastic; filter on site acidify to pH<2 HNO ₃ cool to 4°C store up to 6 mos.	0-1400 mg/l	a) Colorimetric persulfate (1,3)	Spectrophotometer \$500-5K	100-200 ml	\$10-15	0-10% ±10-50%	(A) Color at 525 nm interferes; organic matter, Co interfere
				b) AA (1,2,4)	AA \$5-15K	25-100 ml	\$5-10	1-20% ±3-10%	(B) Working range 0.04-10 ppm; Al >100 ppm interferes
				c) Neutron Activation (9)	Inst. costs \$50-100K	25-100 ml	\$100-300 Multielement	0-10% ±5-15%	(C) Chemical separations necessary after irradiation 0.01 ppb detection limit
				d) XRF (10)	Inst. costs \$50-100K	100-1000 ml	\$50-100 Multielement	0-20% ±5-20%	(D) Detection limit 1-5 ppm, sample must be evaporated or ion exchanged to procure a thin solid sample
				e) Colorimetric (periodate) (3)	Spectrophotometer \$500-5K	25-100 ml	\$5-15	10-25% ±10-30%	(E) Reducing agents must be removed or destroyed; Cl must also be removed
Mercury		High density plastic or glass filtration on site acidify to pH<2 HNO ₃ cool to 4°C storage - 13 days plastic; 30 days glass	0-10 mg/l	a) Cold vapor AA (1,2)	Hg analyzer \$1000	100 ml	\$10-20	0-20% ±10-50%	(A) 0.2-10 µg/l in any waters (brines included); total Hg is analyzed; sulfide <20 ppm, Cu <10 ppm, can be tolerated; corrections for volatile organics may be necessary; some organic mercury types don't quantitatively reduce
				b) Neutron Activation (9)	Inst. costs \$50-100K	100-1000 ml	\$100-300 Multielement	Not available ±10-30%	(B) Wet chemical separations necessary 0.1 ppb detection limit
				c) XRF (10)	Inst. costs \$50-100K	100-1000 ml	\$50-100 Multielement	Not available ±10-20%	(C) Detection limit 1-5 ppm not sensitive for environmental water samples without much preconcentration, sample would have to be evaporated or ion exchanged
Nitrate	Major anion; drinking water standard 45 ppm	Plastic or glass cool to 4°C store in dark analyze with 24 hrs or acidify pH<2 or freeze	0-10 mg/l	a) Colorimetric sulfanilic-brucine (1,2,3)	Spectrophotometer \$500-5K	50 ml	\$10-15	0-10% ±10-30%	(A) Working range 1-10 mg/l NO ₃ ; Beer-Lambert law not followed; standard curve must be carefully constructed, method is very temp. sensitive, high organic matter and oxidizing agents interfere; NO ₂ >7 ppm interferes; Fe, Mn >1 ppm interferes; Ca >100 ppm, Mg >60 ppm, Cl ⁻ >1000, SiO ₂ >200 ppm interfere
				b) Cd reduction (2,3,5)	Spectrophotometer \$500-5K	10-50 ml	\$5-10	0-10% ±5-10%	(B) Working range 0.05 to 5 mg/l NO ₃ ; EDTA added to remove Fe, Cu and other metal interferences; determines both NO ₃ and NO ₂
				c) Phenoldisulfonic acid (12)	Spectrophotometer \$500-5K	100 ml	\$5-10	10-60% ±10-50%	(C) Very sensitive to Cl interference; Cl must be <10 ppm; 0.1 to 2 ppm NO ₃ working curve, not applicable to brines
				d) Specific ion electrode (12)	pH meter \$1000 electrode \$200	25-50 ml	\$5	0-10% ±5-10%	(D) Working range 4-5000 ppm NO ₃ , an ionic strength buffer is necessary to determine concentrations; Cl >500 ppm interferes
				e) Nitrosyl chloride reduction (7)	Spectrophotometer \$500-5K	100 ml	\$5-10	10-50% ±2-20%	(E) Measures both NO ₂ and NO ₃ ; Cl content must be greater than 2000 ppm, working range 0.05-3 ppm NO ₃ ; strict temperature control necessary

TABLE 1i

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instruments Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Nitrite	Presence shows sample is reduced	Plastic or glass; store at 4°C in dark measure preferably within 24 hrs or freeze	no data	a) Diazonium colorimetric (1,2,3,4,5)	Spectrophotometer \$500-5K	100 ml	\$5-10	5-20% ±10-20%	Interferences include amines, oxidizing agents, reducing agents (I^- , Fe^{+2} , S^{2-}); Hg^{+2} , Bi^{+3} , Pb^{+2} , Cu^{+2} , Co^{+2} , Cr^{+3} should be low or absent; working range 0.02-1 ppm NO_2^- ; alkalinity >600 ppm will give low results
				b) Volumetric (1)	Buret \$40	200 ml		Not available ±10-20%	(B) Applicable for waters >3 ppm NO_2^- ; reducing agents interfere
Phosphate	Major cation nutrient capable of causing eutrophication	Plastic or glass; filter at site with preleached filters analyze within 24 hrs or preserve with $HgCl_2$	no data	a) Ascorbic Acid (1,2,3)	Spectrophotometer \$500-5K	50 ml	\$5-10	0-10% ±5-10%	(A) Working range 0.01-2 ppm P, SiO_2 >10 ppm interferes some; Fe^{+3} <50 ppm, Cu <10 ppm do not interfere; also measures As; S^{2-} , NO_2^- are removed; with sample digestion measures other forms of phosphorus; reagents unstable must be prepared frequently
				b) Amino reduction (1)	Spectrophotometer \$500-5K	100 ml	\$5-10	±10-20%	(B) Working range 0.03-3 ppm; up to 40 ppm Fe, 75 ppm CrO_4^{2-} , 1500 ppm Cl allowable, SiO_2 at 20X phosphate concentration causes 2% error; NO_2^- , S^{2-} are removed, if Ca >200 ppm use HCl rather than H_2SO_4 ; with sample digestion measures other forms of phosphorus
				c) Molybdovanado-phosphate (1,3,4)	Spectrophotometer \$500-5K	50 ml	\$5-10	5-20% ±10-20%	(C) Working range 0.7-20 ppm; Fe^{+2} >100 ppm and S^{2-} interfere, cannot be used on highly colored waters; with sample digestion measures other forms of phosphorus, SiO_2 correction necessary
Potassium		Plastic or glass; 0.6-23800 mg/l filter on site acidify to pH 2 HNO_3 store at 4°C 6 mos allowed		d) Stannous Chloride (3,5)		100 ml	\$5-15	5-10% ±10-20%	(D) Similar to molybdovanadophosphate but more sensitive; working range 0.05-2 ppm PO_4^{3-}
				a) Flame photometry (1,3)	Flame \$2-4K	25 ml	\$5-10	10-25% ±5-20%	(A) Working range 1-100 ppm, other alkali earth elements cause interferences
				b) AA (2,4)	AA \$10-15K	25 ml	\$5-10	2-5% ±5-20%	(B) Na interferences removed by addition of large Na^+ concentrations to all samples and std; 0.1-2 ppm working range
				c) XRF (10)	Inst. costs \$50-100K	100 ml	\$50-100 Multielement	Not available ±10-20%	(C) Detection limit 5-10 ppm K, water samples must be evaporated or ion exchanged to obtain a thin solid sample
				d) NAA (9)	Inst. costs \$50-100K Reactor facilities	100 ml	\$100-300 Multielement	Not available ±5-20%	(D) Detection limit 0.05 ppm after chemical separation
Silica	Primary constituent important in scale formation	Plastic or stainless steel cool to 4°C storage 7 days if SiO_2 >100 ppm dilute 1/10 with distilled water	3-1420 mg/l	e) Colorimetric (1)	Spectrophotometer \$500-5K	100-500 ml	\$10-15	Not available ±5-50%	(E) NH_4^+ interferes, high SiO_2 may cause gel, detection limit 5 ppm, tedious method
				a) Gravimetric (1,3)	Oven Pt. crucibles	100-500 ml	\$20-30	0-10% ±5-20	(A) No interferences; detection limit 1 ppm; tedious procedure calling for two evaporations to total dryness, measures total SiO_2 unless sample is filtered; best for samples with >20 ppm SiO_2

TABLE 1j

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Silica (cont.)				b) Molybdate colorimetric (1,2,4,15)	Spectrophotometer \$500-5K	50 ml	\$5-10	4-10% ±4-10%	(B) Turbidity, color and CrO_4^- interfere; working ranges 2-50 ppm; measures soluble SiO_2 ; timing important
				c) Heteropoly Blue (1,2,3,4)	Spectrophotometer \$500-5K	50 ml	\$5-10	2-5% ±5-30%	(C) Turbidity color CrO_4^- interfere; working range 0.04-2 ppm SiO_2
				d) XRF (10)	Inst. costs \$50-100K	50-500 ml	\$50-100 Multielement	Not available Not available	(D) Detection limit 10-100 ppm; water sample would have to be evaporated or SiO_2 ion exchanged onto solid before analysis
				e) AA (11)	AA \$10-15K	25-50 ml	\$5-10	0-15% ±2-10	(E) Working range 0.5-35 ppm; no interferences; N_2O flame
Silver		Plastic filter on site acidify to pH<2 HNO_3 cool to 4°C store in dark 6 mos or less	0-1.5 mg/l	a) AA (2,3,14)	AA \$10-15K	50-500 ml	\$10-15 \$10-25 with extraction	10-20% ±10-20%	(A) Optimum working range 0.1-4 ppm; detection limit 0.01 ppm; with APDC-MIBK extraction, detection limit and working range reduced to 0.1 ppb and 1-40 ppb
				b) Flameless AA (11)	AA \$10-15K Graphite Furnace \$5K	5-50 ml	\$10-25	10-20% ±5-20%	(B) Direct analysis with known addition corrections for matrix effects; 0.4-5 ppb working range direct; with APDC-MIBK extraction 4 pptillion detection limit
				c) XRF (10)	Inst. costs \$50-100K	50-500 ml	\$50-100 Multielement	Not available ±10-20%	(C) Detection limit 5-10 ppm for a thin solid sample; waters would have to be evaporated or ion exchanged onto resin
				d) Neutron activation (9)	Inst. costs \$50-100K Reactor facilities	25 ml	\$100 \$100-300 with separations	10-20% ±10-20%	(D) Detection limit in sea water without separation 1 ppb; with separation 3 pptillion
				e) Dithizone method (1,3)	Spectrophotometer \$500-5K infrared lamp hot plate	100-500 ml	\$25-30	20-50% ±20-60%	(E) Good results require extreme care, other metal interferences are great
Sodium	Major cation releases of high sodium are detrimental to permeability and agriculture	Plastic filter on site acidify to pH<2 HNO_3 cool to 4°C store 6 mos or less	3-79000 mg/l	a) Flame photometry (1,3)	Flame photo \$2-4K	25 ml	\$5-10	10-25 ±5-20%	(A) Other alkali metals interfere, working ranges 0-1 ppm, 0-10 ppm, 0-100 ppm; use internal standards or known addition
				b) AA (2,4,6)	AA \$10-15K	25 ml	\$5-10	2-5% ±2-10%	(B) Optimum working range 0.03-1 ppm; ionization controlled by addition of high K buffer to samples and standards
				c) Neutron activation (9)	Inst. costs \$50-100K Reactor facility	30-100 ml	\$100	0-10% ±5-10%	(C) Detection limit without wet chemical separation 0.01 ppm
Strontium		Plastic filter on site acidify to pH 2 HNO_3 cool to 4°C store 6 mos or less	0.5-400 mg/l	a) AA (1,4)	AA \$10-15K	25 ml	\$5-10	0-10% ±5-10%	(A) Chemical suppression by Si, Al, PO_4 controlled by addition of lanthanum; working range 1-10 ppm; use known additions to correct for matrix effects, K added to suppress effects of Na and K
				b) Flame photometry (3)	Flame photo \$2-4K	25 ml	\$5-10	5-20% ±10-15%	(B) Bulk salt interferes so one must use known addition techniques; detection limit 0.2 ppm
				c) X-ray fluorescence (9)	Inst. costs \$50-100K	25-100 ml	\$50-100 Multielement	5-20% ±10-20%	(C) Detection limit 1-5 ppm for thin solid sample; water would have to be evaporated or ion exchanged onto solid matrix

TABLE 1k

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Sulfate	Major anion potable water limit 250 ppm	Plastic or glass cool to 4°C store up to 7 days	0-5700 mg/l	a) Gravimetric (1,2,3)	Filter \$20 Pt. crucible oven	200 ml	\$10-20	0-5% ±1-5%	(A) Applicable to all types of water; optimum working range 20-100 ppm; sulfites and sulfides may oxidize and interfere, Cr, Fe, alkali metals can cause low results
				b) Turbidimetric (1,2,3)	Spectrophotometer \$500-5K	50 ml	\$5-10	5-10% ±5-25%	(B) Optimum working range 10-100 ppm color and variable salt matrices cause interferences; detection limit 1 ppm; SiO ₂ >500 ppm interferes
				c) Volumetric method (1,4)	Burets \$40 Ion exchange \$20	50 ml	\$10-20	1-20 ±1-5%	(C) Optimum working range 5-1000 ppm; salts interfere by Co precipitation; K, Fe, Al, PO ₄ , F, NO ₃ worst; metallic interferences removed by ion exchange Cl >1000 ppm interfere
				d) Chromate colorimetric (15)	Spectrophotometer \$500-5K	5-50 ml	\$10-15	10-40% ±10-25%	(D) Working range 10-250 ppm SO ₄ ⁼ ; interferences include S ⁼ , CO ₃ ⁼ , HCO ₃ ⁻ which must be removed prior to SO ₄ determination
Sulfide	Only present in reduced environments H ₂ S gas poisonous	Plastic or glass preserve with zinc acetate hold up to 24 hrs	0-30 mg/l	a) Iodine titrimetric (2,3,4,14,15)	Burets \$40 glassware \$50	50 ml	\$10-15	Not available Not available	(A) Detection limit 1 ppm, total acid soluble sulfide unless sample is filtered under N ₂ at collection, sulfite, thiosulfite and iodine consuming substances give positive interferences
				b) Methylene blue (3)	Spectrophotometer \$500-5K	50 ml	\$10-15	10-20% ±10-20%	(B) Strong reducing agents cause low results; sulfide >100 ppm inhibits color formation; dilutions necessary, sulfite <10 ppm have no effect; NO ₂ ⁻ interferes; detection limit 0.05 ppm
				c) Methylene blue modified (7)	Spectrophotometer \$500-5K	50 ml	\$10-15	Not available Not available	(C) Working range 0.032-32 ppm S ⁼ ; used in seawater analyses
Total Soluble Organic Carbon		Glass cool to 4°C if acidify pH<2 H ₂ SO ₄ for only organic carbon store up to 24 hrs		a) Combustion-infrared (1,2,3)	Carbon analyzer \$10-25K	5 ml	\$5-10	0-20% ±5-10%	(A) Optimum working range 2-200 ppm, dissolved carbon only; particles clog injection syringe, organic carbon by difference of total carbon and carbonate carbon; brines greater than 50g/l should be diluted
Zinc		Plastic filter on site acidify to pH<2 HNO ₃ cool to 4°C store up to 6 mos	.01-600 mg/l	a) Colorimetric (zincon) (1,3)	Spectrophotometer \$500-5K	10-50 ml	\$5-10	Not available ±10-50%	(A) Working range 0.02-5 ppm Zn; metal interferences partially removed with cyanide; Cd, Al, Mn, Fe >10 ppm interfere Cr, Ni, Cu, Co >30 ppm interfere
				b) AA (1,2,3,4,14)	AA \$10-15K	100 ml	\$5-10 \$15-20 with extraction	1-10% ±6-25%	(B) Working range 0.02 to 3 ppm; with APDC-MIBK extraction 0.2 ppb and above measurable
				c) Flameless AA (11)	AA \$10-15K graphite furnace \$5K	5 ml	\$15-20	Not available ±10-20%	(C) Direct analysis with known addition techniques for matrix effects, detection limit 0.05 ppb
				d) XRF (10)	Inst. costs \$50-100K	500-1000 ml	\$50-100 Multielement	Not available ±10-20%	(D) Detection limit 1-5 ppm; water sample would have to be evaporated or ion exchanged onto a solid matrix
				e) Neutron Activation (9)	Inst. costs \$50-100K reactor facility	25 ml	\$100 Multielement	Not available ±5-10%	(E) Direct analysis; detection limit 0.2 ppb; with wet chemical separations detection limit 10 pptillion
				f) Dithizone colorimetric (3)	Spectrophotometer \$500-5K	100 ml		10-30% ±10-40%	(F) To be quantitative this technique requires extremely controlled technic; most metal interferences can be removed; Zn ⁺² working range 0-0.5 ppm

TABLE 11

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instrument Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Limitations
Cesium	Minor alkali metal	Plastic filter on site; acidify pH 2 with HNO ₃ ; store 6 months	0.02 to 20 mg/l	a) AA (14)	AA \$10K	20 ml	\$5-10	Not available $\pm 10\%$	(A) Hollow cathode source lamps short life time; detection limit 0.1 ppm
				b) Graphite furnace AA (11)	AA \$10K Graphite Furnace \$5K	5 ml	\$10-15	Not available $\pm 10-25\%$	(B) 0.002 ppm detection limit; run known additions to remove matrix effects
				c) Flame emission (15)	AA \$10K Flame Photometer \$5-10K	20 ml	\$10-15	Not available $\pm 10-25\%$	(C) All other ions in solution affect to some extent the Cs emission; Na and K especially enhance Cs signal; burner must be in first class condition to get good results
				d) XRF (10)	XRF \$50-100K	1000 or more mls	\$50-100 multielement	Not available	(D) Detection limit 10-50 ppm, sample should be converted to solid matrix
				e) NAA (9)	NAA, Counting \$50-100K	25 ml	\$100 multielement	5-10% $\pm 10\%$	(E) Direct measurement, no wet chemical separation needed, detection limit 3 pptillion
Rubidium	Minor alkali metal	Plastic filter on site; store 6 mos acidify pH 2 with HNO ₃ ; store 6 months	0-135 mg/l	a) AA (14)	AA \$10K	20 ml	\$5-10	Not available $\pm 10\%$	(A) Detection limit 0.01 ppm, working range 0.01-5 ppm, add excess Na or K to stabilize flame temperature and reduce Rb ionization
				b) Graphite furnace AA (11)	AA \$10K Graphite furnace \$5K	5 ml	\$10-15	Not available $\pm 10-25\%$	(B) Detection limit 0.001 ppm, use known additions to remove matrix effects
				c) Flame emission (15)	AA or Flame photometer \$5-10K	20 ml	\$10-15	Not available $\pm 10-25\%$	(C) All ions affect especially Na Na and K which enhance signal, burner must be in first class condition
				d) XRF (10)	XRF \$50-100K	100 or more mls	\$50-100 multielement	Not available $\pm 10-20\%$	(D) Detection limit 1-5 ppm, sample should be converted to solid matrix
				e) NAA (9)	Counting \$50-100K	25 ml	\$100 multielement	5-10% $\pm 10\%$	(E) Direct measurement, no wet chemical separations needed; 5 pp billion detection limit
Dissolved Oxygen	Important in controlling oxidation reduction potential and corrosion	May preserve 4-8 hours with H ₂ SO ₄ and sodium azide cool to 10°C if I ₂ demand is low	0-10 ppm	a) Winkler (2,3)	D.O. bottles \$5 Buret \$40	200-300 ml	\$5-10	Varies 3-10%	(A) Oxidizing and reducing agents, NO ₃ ⁻ , Fe ⁺² and organic matter interfere
				b) Azide modification (1,3)	D.O. bottles \$5 Buret \$40	200-300 ml	\$5-10	Varies 1-5%	(B) Most effective method if nitrites interfere; ferrous iron, organic material, sulfites and other oxidizing or reducing substances interfere
				c) Rideal-Stewart modification (1,3)	D.O. bottles \$5 Buret \$40	200-300 ml	\$5-10	Varies 1-5%	(C) Use only if organics and reduced sulfur compounds not present; Ferrous iron content >1 ppm causes low results
				d) Pomeroy, et al. modification (1)	D.O. bottle \$5 Buret \$40	200-300 ml	\$5-10	Varies 1-5%	(D) For high (>15 ppm DO) samples or those with high organic content
		Can be used in field, direct measurement		e) Electrode (2,3)	O ₂ meter and membrane probe \$300	25-100 ml	\$5-10	1-20% $\pm 2-50\%$	(E) Detection limit 0.05 ppm, dependent on total salt content, Cl ₂ , H ₂ S gases interfere, temperature dependent

Notes for Table 2, GASES

1. The constituents listed represent a comprehensive but not all inclusive list of chemicals which have been measured in geothermal vapors.
2. The list of reasons for measuring each constituent is incomplete and often considers only environmental concerns.
3. The ranges in geothermal vapors are based on the volume percentages of gases remaining after water vapor removal. In most cases the bulk of the vapor collected is water vapor (60-98%). The range for each gas was determined from tabulation of readily available documents on geothermal wells and should be used only as a guide.
4. The analytical procedures listed for each gas are not inclusive but do represent commonly used techniques. A very powerful but costly instrumental tool is the coupling of a gas chromatograph and a mass spectrometer. The gas chromatograph separates the gases while the mass spectrometer verifies the mass weight-to-charge ratio and allows positive identification. For relatively simple systems such as geothermal vapors such sophisticated and expensive procedures are usually not necessary.
5. The per sample costs are based on the assumption that a sufficient number of samples would be analyzed such that startup and calibration curve costs would be relatively small. For most chemical analyses, a sample size of 10 to 50 ml would meet this requirement. For smaller sample sizes per sample costs could more than double over those quoted.
6. The accuracy numbers quoted represent bias from the true values and can be calculated from the following equation:

$$\left| \frac{\text{Actual-Observed}}{\text{Actual}} \right| \times 100 = \% \text{ Bias}$$

The precision values represent $\pm$ one standard deviation.
7. The term ppm for gases is based on volumes and not weight.

References Table 2

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TABLE 2
CONSTITUENTS IN GEOTHERMAL VAPORS

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instruments Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Comments
Ammonia	Noxious gas, often found in geothermal waters; denotes reducing conditions	Absorb NH_3 in acid solution, store in glass 48 hrs	0-1.7%	A) Absorption-distillation (4,5)	Distillation apparatus \$100 Spectrophotometer \$500-5000	100-1000 mls	\$10-20	Not available $\pm 10\%$	A) After sorption use Nessler procedure
				B) GC (2)	Gas chromatograph \$5-15K	0.1-10 ml	\$10-20	Not available	B) Detector: thermal conductivity, sensitivity 19.6 $\mu\text{g}/0.01 \text{ mv}$; Column: 40 inch polyethylene or glycol on NaOH washed firebrick
				C) Microwave (5)		1-100 ml	Not available	Not available	C)
				D) Mass spec (14)	Mass Spectrometer \$50-200K	1-10 ml	\$20 to >\$100 Multielement	Not available	D) Instrumentation expensive and sophisticated, detection limit >0.01%
Argon	Minor inert gas commonly found in geothermal waters	Glass, metal samplers OK	0-1.5%	A) Mass spec (14)	Mass Spec. \$50-200K	1-10 ml	\$20 to >\$100 Multielement	Not available	A) Instrumentation expensive and sophisticated, spectral output can be difficult to interpret, detection limit >0.01%
				B) GC (2,7)	GC \$5-15K	1-10 ml	\$10-20	Not available	B) He or CO_2 carrier gas; column: packed activated charcoal or silica gel, or molecular sieve #5A; O_2 can elute at same time therefore lower T° ; increase column length; or catalytically remove O_2 with Pd; detector: thermal conductivity
Carbon Dioxide	Major gas constituent; important in fouling and scaling	Absorb in KOH or NaOH solution (A); absorb in $\text{Ba}(\text{OH})_2$ solution (B,C); absorb in $\text{Ba}(\text{OH})_2$ solution	1-99%	A) Absorption-titration (3,5,6)	Gas Sampling Bottles \$50 Buret \$40 Flow Meter \$100	100 mls to several liters	\$10-20	Not available	A) Excess base titrated with acid; also absorbs other acid gases such as H_2S , HCl , SO_2 ; KOH favored over NaOH
				B) Absorption weighing (8)	Flow Meter \$100 Gas Sampling Bottles \$50 Balance \$1K	100 mls to several liters	\$10-20	Not available	B) Weigh increase; macro amounts of carbon dioxide must be present; can also use solid absorptents such as ascarite
				C) Absorption titration (4,5)	Same as (a)	100 mls to several liters	\$10-20	Not available	C) Titrate excess $\text{Ba}(\text{OH})_2$ with oxalic acid
				D) GC (2)	GC \$5-15K	1-10 mls	\$10-20	Not available	D) Column: activated silica gel, activated carbon, or use molecular sieve No. 5A, the temperature program $10^\circ/\text{min}$; He carrier gas; detector: thermal conductivity; mediocre sensitivity
				E) GC (9)	GC \$5-15K	1-10 mls	\$10-20	Not available	E) Convert CO , CO_2 to methane with Ni catalysis and detect CH_4 by Flame Ionization; good sensitivity; CO , CH_4 , CO_2 must be separated first before catalytic conversion
				F) Mass spec (14)	Mass Spec. \$50-200K	1-10 mls	\$20 to >\$100 Multielement	Not available	F) Expensive and sophisticated instrumentation, spectral data may be difficult to interpret; detection limit >0.01%
Carbon Monoxide	Health hazard to humans	CO not absorbed by acid or base	0-3%	A) GC (2,6,10)	GC \$5-15K	0.1-10 ml	\$10-20	Not available	A) Column: Molecular sieve 5A; 5 meter; separates H_2 , O_2 , N_2 , CH_4 , CO ; but CO_2 , H_2S , H_2O must be removed prior to contact with column; detector thermal conductivity; carrier gas He or Ar

TABLE 2
CONSTITUENTS IN GEOTHERMAL VAPORS

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instruments Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Comments
Ammonia	Noxious gas, often found in geothermal waters; denotes reducing conditions	Absorb NH_3 in acid solution, store in glass 48 hrs	0-1.7%	A) Absorption-distillation (4,5)	Distillation apparatus \$100 Spectrophotometer \$500-5000	100-1000 mls	\$10-20	Not available $\pm 10\%$	A) After sorption use Nessler procedure
				B) GC (2)	Gas chromatograph \$5-15K	0.1-10 ml	\$10-20	Not available	B) Detector: thermal conductivity, sensitivity 19.6 $\mu\text{g}/0.01$ mv; Column: 40 inch polyethylene or glycol on NaOH washed firebrick
				C) Microwave (5)		1-100 ml	Not available	Not available	C)
				D) Mass spec (14)	Mass Spectrometer \$50-200K	1-10 ml	\$20 to >\$100 Multielement	Not available	D) Instrumentation expensive and sophisticated, detection limit >0.01%
Argon	Minor inert gas commonly found in geothermal waters	Glass, metal samplers OK	0-1.5%	A) Mass spec (14)	Mass Spec. \$50-200K	1-10 ml	\$20 to >\$100 Multielement	Not available	A) Instrumentation expensive and sophisticated, spectral output can be difficult to interpret, detection limit >0.01%
				B) GC (2,7)	GC \$5-15K	1-10 ml	\$10-20	Not available	B) He or CO_2 carrier gas; column: packed activated charcoal or silica gel, or molecular sieve #5A; O_2 can elute at same time therefore lower T° ; increase column length; or catalytically remove O_2 with Pd; detector: thermal conductivity
Carbon Dioxide	Major gas constituent; important in fouling and scaling	Absorb in KOH or NaOH solution (A); absorb in $\text{Ba}(\text{OH})_2$ solution (B,C); absorb in $\text{Ba}(\text{OH})_2$ solution	1-99%	A) Absorption-titration (3,5,6)	Gas Sampling Bottles \$50 Buret \$40 Flow Meter \$100	100 mls to several liters	\$10-20	Not available	A) Excess base titrated with acid; also absorbs other acid gases such as H_2S , HCl , SO_2 ; KOH favored over NaOH
				B) Absorption weighing (8)	Flow Meter \$100 Gas Sampling Bottles \$50 Balance \$1K	100 mls to several liters	\$10-20	Not available	B) Weigh increase; macro amounts of carbon dioxide must be present; can also use solid absorpents such as ascarite
				C) Absorption titration (4,5)	Same as (a)	100 mls to several liters	\$10-20	Not available	C) Titrate excess $\text{Ba}(\text{OH})_2$ with oxalic acid
				D) GC (2)	GC \$5-15K	1-10 mls	\$10-20	Not available	D) Column: activated silica gel, activated carbon, or use molecular sieve No. 5A, the temperature program $10^\circ/\text{min}$; He carrier gas; detector: thermal conductivity; mediocre sensitivity
				E) GC (9)	GC \$5-15K	1-10 mls	\$10-20	Not available	E) Convert CO, CO_2 to methane with Ni catalysis and detect CH_4 by Flame Ionization; good sensitivity; $\text{CO}, \text{CH}_4, \text{CO}_2$ must be separated first before catalytic conversion
				F) Mass spec (14)	Mass Spec. \$50-200K	1-10 mls	\$20 to >\$100 Multielement	Not available	F) Expensive and sophisticated instrumentation, spectral data may be difficult to interpret; detection limit >0.01%
Carbon Monoxide	Health hazard to humans	CO not absorbed by acid or base	0-3%	A) GC (2,6,10)	GC \$5-15K	0.1-10 ml	\$10-20	Not available	A) Column: Molecular sieve 5A; 5 meter; separates $\text{H}_2, \text{O}_2, \text{N}_2, \text{CH}_4, \text{CO}$; but $\text{CO}_2, \text{H}_2\text{S}, \text{H}_2\text{O}$ must be removed prior to contact with column; detector thermal conductivity; carrier gas He or Ar

TALBE 2b

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instruments Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Comments
Carbon Monoxide (continued)		Absorb in ammoniacal cuprous chloride		B) Mass spec (14)	Mass Spec \$50-200K	0.1-10 ml	\$20 to >\$100	Not available	B) Instrumentation expensive and sophisticated; spectral data may be hard to interpret
				C) Nondispersive Infrared (1)	CO Analyzer \$5K Sample Pump \$200 Flow Meter \$100	Continuous	\$10-20	Not available $\pm 5\%$	C) Continuous CO monitor; CO ₂ at 150 ppm only causes 0.5 ppm spurious signal, water vapor worst interferent but can be removed, hydrocarbons at 50 ppm give a spurious response of 0.5 ppm CO; detection limit 0.5 ppm
				D) GC (2,9,11)	GC \$5-15K	0.1-1 ml	\$10-20	Not available $\pm 0.1\%$	D) Separate CO from CO ₂ on molecular sieve, convert CO to CH ₄ measure by flame ionization; range 0.1-60000 ppm
				E) Absorption Weighing (3)	Gas Bottles \$100 Balance \$1K	500 ml or greater	\$10-20	Not available	E) O ₂ , acetylene and acid gases dissolve in absorbing solution also; detection limit by weighing absorbed quantity = 500 ppm CO
				F) Colorimetric (3,4)	Spectrophotometer \$500-5K	100-1000 ml	\$10-20	Not available	F) Use diluted blood; CO causes a pink carboxyhemoglobin complex which can be measured colorimetrically
				G) I ₂ titration (3)	Gas Bottle \$100 Buret \$40	100-1000 ml	\$10-20	Not available	G) Addition of I ₂ O ₅ to CO liberates I ₂ which is absorbed in a KI solution and titrated with thiosulfate; apparatus necessitates combustion furnace and several gas traps
Hydrocarbons C ₂ and greater	Potential fuel source; denotes reducing conditions	Collection glass, plastic, or gas bag; store for 3 days in plastic yields 6% loss	0-11.8%	A) GC (1,2)	GC \$5-15K	1 ml	\$10-20	10% $\pm 10\%$	A) This method covers C ₁ -C ₅ , elutes 17 hydrocarbons, detection limit 0.01 ppm, C ₃ -C ₅ can be detected at 0.1 ppb with 100 ml freeze trapped sample; detector: flame ionization; carrier gas: He; column: 8 ft 8/8' oxydipropionitrile on activated alumina; total separation time only 16 min.
				B) Mass spec (14)	Mass Spec \$50-200K	1-10 ml	\$20 to >\$100	Not available	B) Expensive and sophisticated instrumentation; spectral data may be hard to interpret
Hydrogen	Provides data on oxidation reduction environment	Doesn't absorb in typical acid or base reagents but colloidal Pd will absorb H ₂	0-39%	A) GC (2,6)	GC \$5-15K	0.1-10 ml	\$10-20	Not available	A) Molecular sieve 5A separates H ₂ , O ₂ , N ₂ , CH ₄ , CO; interferences CO ₂ , H ₂ S and H ₂ O must be removed; thermal conductivity detection limit on 1 ml sample = 20 ppm H ₂ ; helium flame ionization detection limit 0.3 ppm H ₂ ; He and Ne appear as H ₂ without further separation.
				B) Absorption weighing (3)	Gas Bottles \$100 Balance \$1K	100-1000 ml	\$10-20	Not available	B) CO ₂ , CO, olefins must be removed first before absorption of H ₂ on colloidal Pd; detection limit ~500 ppm
				C) Mass spec (14)	Mass Spec \$50-200K	1-10 ml	\$20 to >\$100	Not available	C) Expensive and sophisticated instrumentation; spectral data may be hard to interpret; detection limit >0.01%
Hydrogen Sulfide	Toxic gas; important indicator of reduced conditions; corrosion agent	Glass sample containers best; absorb H ₂ S in Pb acetate solution or As ₂ O ₃ acid solution B) Zinc acetate absorbing solution	0-42%	A) Absorption weighing (7)	Gas Bottles \$100 Balance \$1K	100-1000 ml	\$10-20	Not available	A) PbS precipitate weighed or CdS or As ₂ S ₃
				B) Absorption titration (3,4)	Gas Bottles \$100 Buret \$40	100-1000 ml	\$10-20	Not available	B) Add excess iodine and back titrate with thiosulfate; detection limit 2 ppm H ₂ S, SO ₂ interferes

TABLE 2c

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instruments Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Comments
Hydrogen Sulfide (continued)		Collect H ₂ S in KOH, NaOH, or Cd(OH) ₂		C) Absorption colorimetric (3,4)	Gas Bottles \$100 Spectrophotometer \$500-5K	100-1000 ml	\$10-20	Not available	C) Use methylene blue colorimetric technique
				D) GC (2)	GC \$5-15K	1-10 ml	\$10-20	Not available	D) Column: silica gel at 25°C, detector: thermal conductivity; detection limit 50 ppm H ₂ S; separates sulfur gases from each other; using flame photometric detection 50 ppb H ₂ S
		No preservation		E) Direct titration (3)	Gas Bottles \$100 Buret \$40	100 ml	\$10	Not available	E) Gas sample directly titrated with I ₂ ; H ₂ S gas cannot be stored for very long analysis must be performed right after sampling; detection limit for 100 ml sample 0.3 ppm H ₂ S by volume, SO ₂ must be removed first
Mercury	Potential health hazard	Nonmetallic gas sampling bottle	No data	A) Direct cold vapor (1,2)	Hg Analyzer \$1000 or AA	100-1000 ml	\$10-30	Not available	A) Modification of standard Hg in water procedure
		Collect on iodized activated carbon		B) Absorption cold vapor (4)	Same as A plus Induction furnace \$1K	100-1000 ml	\$10-30	Not available	B) Activated carbon heated to drive off Hg then standard procedure
Methane	Common hydrocarbon in geothermal wells	Glass, metal or plastic OK	0-15%	A) GC (2,6,10)	GC \$5-15K	1-10 ml	\$10-20	Not available	A) Column: molecular sieve 5A will separate H ₂ , O ₂ , N ₂ , CH ₄ and CO; thermoconductivity detector; CO ₂ , H ₂ S, H ₂ O must be removed before column separation; for more sensitivity a flame ionization detector is used
				B) Mass Spec (14)	Mass Spec \$50-200K	1-10 ml	\$20 to >\$100	Not available	B) Instrumentation expensive and sophisticated spectral data may be hard to interpret
Nitrogen	Major inert gas	Glass, metal or plastic OK	0.5-80%	A) GC (2,6,10)	GC \$5-15K	1-10 ml	\$10-20	Not available	A) Column of molecular sieve 5A will separate H ₂ , O ₂ , N ₂ , CH ₄ and CO; thermoconductivity detector, helium carrier gas
				B) Mass Spec (14)	Mass Spec \$50-200K	1-10 ml	\$20 to >\$100	Not available	B) Instrumentation expensive and sophisticated, spectral data may be hard to interpret; detection limit >0.01%
				C) Manometrically (3)	Mercury Manometer \$100	100 ml	\$10	Not available	C) Remove all reactive gases with acid, base absorbents, combust organics; also measures Noble gases as N ₂ , tedious many removal steps; measure residual volumes
Nitrous Oxides	Important role in smog formation	Absorb NO ₂ in AZO dye reagent, analyse within 5 hrs, or collect on silica gel	No data	A) NO ₂ Griess-Saltzman Reaction (1,3)	Spectrophotometer \$500-5K	100 ml - 12 liters	\$10-15	Not available ±1%	A) Working range 0.005-5 ppm by volume (0.01 to 10 µg/l); read pink color; ten fold ratio of SO ₂ /NO ₂ causes no interference; if strong oxidizing and reducing agents are present measure color within 1 hour; a bubbler and gas collection rate of <0.4 liters/min is most efficient; absorbing agent is sulfanilic acid - N-(1-naphthyl)-ethylene diamine dihydrochloride. If analysis must wait collect NO ₂ on silica gel elute in lab and treat with reagents

TABLE 2d

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instruments Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Comments
Nitrous Oxides (continued)		Absorb in H ₂ O ₂ and dilute H ₂ SO ₄		B) NO, NO ₂ Phenoldisulfonic acid procedure (1)	Spectrophotometer \$500-5K	1000 ml	\$15-25	Not available ±10%	B) Working range 5 to several thousand ppm by volume; oxides converted to NO ₃ and read colorimetrically; SO ₂ and halides interfere
				C) GC (2)	GC \$5-15K	1-10 ml	\$10-20	Not available	C) N ₂ O inert easily separated from other oxides of nitrogen; porous polymer column (Porapak), He carrier gas at 27°C separates NO, N ₂ O, CO ₂ , detector: argon ionization detector; NO ₂ , NO separation using 20 ft activated charcoal - 2% squalene, He carrier gas, detector thermal conductivity N ₂ O can be separated from other gases with silica gel, activated charcoal or molecular sieve, thermal conductivity detection limit 50 ppm; helium ionization detector more sensitive
Oxygen	Important for oxidation-reduction reactions	Absorb in alkaline pyrogallate	0-20%	A) Absorption weighing (3,5)	Gas Bottles \$100 Balance \$1K	100 ml to several liters	\$10-20	Not available	A) Pyrogallol absorbs O ₂ at temperatures >7°C; acid gases must be removed first (CO ₂ , SO ₂ , NO ₂)
				B) Shaw Method (3)	Spectrophotometer \$500-5K	100-1000 ml	\$10-20	Not available	B) Gas treated with freshly precipitated ferrous hydroxide, acidify, determine Fe+3 colorimetrically
				C) Winkler (3)	Gas Bottles \$100 Buret \$40	100 ml	\$10-20	Not available	C) Manganese hydroxide absorbs O ₂ , changes to manganic hydroxide. When a little KI and H ₂ SO ₄ added manganic hydroxide dissolves and liberates I ₂ which is titrated with thiosulfate. Detection limit 0.14% O ₂ .
				D) GC (2,6)	GC \$5-15K	1-10 ml	\$10-20	Not available	D) Molecular sieve 5A; detector thermal conductivity, separates H ₂ , CH ₄ , CO, N ₂ , O ₂ after removal of CO ₂ , H ₂ S, H ₂ O vapor
				E) Absorb O ₂ in colorless alkaline solution of anthraquinone-8-sulfonate (4)	Spectrophotometer \$500-5K	100 ml	\$15-20	Not available	E) Working range 10-1000 ppm O ₂ by volume, take absorbing solution and reduce with reducing agent (amalgamated zinc) turns red color; unaffected by small quantities of hydrocarbons, CO, CO ₂ or sulfur compounds
				F) Mass spec (14)	Mass Spec \$50-200K	1-10 ml	\$20 to >\$100	Not available	F) Instrumentation expensive and sophisticated; spectral data may be hard to interpret
Oxides of Sulfur	Corrosion agent; harmful to environment	Absorb SO ₂ in solution of potassium or sodium tetrachloromercurate; can store 30 days if refrigerate to 5°C	3-31%	A) Absorption-colorimetric (West-Baeke) (1)	Spectrophotometer \$500-5K Manometer \$100 Gas Flow Meter \$100	25 or more liters	\$10-20	Not available ±5%	A) Working range 0.003-5.0 ppm SO ₂ ; interferences of oxides of nitrogen and heavy metals minimized with treatment of absorbing solution; formaldehyde and acid-bleached pararosaniline containing phosphoric acid added to form colored solution; measure; need high sample volume
		Collect gas in acidified H ₂ O ₂		B) Conductometric (1)	Conductivity Meter \$400 Gas Flow Meter \$100	100 mls to several liters	\$10-20	Not available	B) Not specific to SO ₂ , measures all electrolyte forming gases (halogen acid gases, nitrogen oxides), NH ₃ ; CO ₂ does not interfere significantly; absorb SO ₂ forming SO ₄ ⁼ , measure conductance; detection limit 0.01 ppm SO ₂

TABLE 2e

Constituent	Reason For Measurement	Storage Container Preservation	Range in Geothermal Waters	Procedure	Instruments Requirements and Costs	Sample Volume Requirements	Per Sample Cost	Accuracy and Precision	Comments
Oxides of Sulfur (continued)		Absorb in acidified bromide solution		C) Electrolysis (continuous method) (1)	Redox Sensors \$200 mv meter \$500	Air flow 1 liter/min	\$10	5-10% ±2%	C) 0.1 ppm SO ₂ detection, 0.1-10 ppm working range; measures all oxidizable sulfur gases including H ₂ S; NO ₂ causes low results
		May collect directly on silica gel		D) GC (2)	GC \$5-15K	0.1-10 ml	\$10-20	Not available	D) Sulfur compounds easily separated from themselves and other gases; silica gel columns OK but each batch may act differently; porous polymer materials or silicone oil or grease on firebrick also separate SO ₂ ; detection by thermal conductivity or argon ionization is typically used
		Absorb SO ₂ in tetrachloromercurate -EDTA solution		E) SO ₂ Elec- trode (13)	Electrode \$300 Meter \$500-1K	100 ml	\$10	Not available	E) 0.001 ppm - 4 ppm working range

Notes for Table 3

Summary of Published Methods

I. Purpose: Table 3, "Summary of Published Methods," was compiled to allow geothermal water analysts and researchers to quickly survey published methods of laboratory water analysis. No recommendation of the applicability of the methods to geothermal brines should be assumed since the intent of the table is to encourage and solicit comments and discussion leading to recommended analytical procedures for geothermal waters and research.

II. Scope: Table 3 covers commonly analyzed properties and dissolved or colloidal solids and gases found in water.

III. Limitations of Table 3:

- A. Although a comprehensive list of the available methods of water analysis is presented, the list is by no means all inclusive.
- B. Four readily available publications and one college text (see Bibliography) were used in the literature search. Hence, the data base must be considered representative rather than comprehensive.
- C. Only those properties and constituents in the liquid phase of a geothermal sample are covered; for example, gases listed in the table are considered to be dissolved gases. (See Table 2 for gas analysis)
- D. Financial considerations, sample storage and sample size requirements are not covered in Table 3. (See Tables 1 and 2 for these data.)
- E. Equipment requirements are inferred in most cases. Equipment is explicitly described only in those procedures requiring special apparatus. (See Tables 1 and 2 for equipment for equipment requirements.)

IV. Table 3 Organization:

A. General Organization

- 1. Constituents: See the alphabetical listing for the specific properties and constituents included in Table 3.
- 2. Method: Not all possible analytical methods are presented for the given constituent. The method is first given as a generic type, such as electrometric, titrimetric, colorimetric, atomic absorption, etc., then any commonly accepted or a brief descriptive name is listed in parentheses after the generic title. Reference listings (see "References" for details) follow the method name.

3. Range: The range denotes the minimum and maximum concentration values usually in milligrams of constituent per liter of brine unless otherwise noted. In many cases, such as colorimetric or atomic absorption methods, the range represents the linear response of the method. The range is not included where this datum is not readily available from the listed references.
4. Precision/Accuracy: The precision of a method is assumed to be the percentage relative standard deviation at the 67% probability level while accuracy may be assumed to be computed as percentage relative error. Not all references indicate the conditions upon which these values are based, hence data from different sources may not be readily compared. Precision and accuracy values are omitted where they are not readily available.
5. Description: The description of the method usually includes a cursory explanation of the chemistry and mechanical manipulations involved in the analysis.
6. Comments: This heading covers reported interferences peculiar to the method, special equipment needs, safety hazards, time considerations and other important details pertaining to the method. Comments are drawn from the references and from personal experiences.

B. Listing of Properties and Constituents

1. General Properties

Table 3 - Page Number

pH	3.1
Redox Potential	3.1
Conductivity	3.1
Alkalinity/Acidity	3.1 & 3.2
Suspended Solids (non-filtrable residue)	3.3
Dissolved Solids (filtrable residue)	3.3
Turbidity	3.4
Color	3.4 & 3.4
Specific Gravity	3.5 & 3.6

2. Alphabetical Listing of Chemical Constituents

Constituent	Table 3 Page Number
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Aluminum	3.6 & 3.7
Ammonia	3.8
Argon	3.9
Barium	3.9 & 3.10
Boron	3.10
Bromide	3.10 & 3.11
Cadmium	3.12
Calcium	3.12 & 3.13
Carbon Dioxide	3.13 - 3.15
Carbon Monoxide	3.15
Cesium	3.15
Chloride	3.15 - 3.17
Chromium	3.18 & 3.19
Copper	3.19 & 3.20
Fluoride	3.21 & 3.22
Helium	3.22
Hydrazine	3.22
Hydrogen	3.22 & 3.23
Iodide	3.23 & 3.24
Iron	3.24 - 3.26

Constituent	Table 3 Page Number
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Lithium	3.26
Lead	3.26 & 3.27
Magnesium	3.27 & 3.28
Manganese	3.29 & 3.30
Mercury	3.30
Methane	3.30 & 3.31
Nitrate	3.31 & 3.32
Nitrite	3.33
Nitrogen	3.33
Oil	3.33 & 3.34
Oxygen	3.35
Phosphate	3.36 & 3.37
Potassium	3.37 & 3.38
Rubidium	3.38
Silica	3.38 & 3.39
Sodium	3.39
Sulfate	3.39 & 3.40
Sulfide	3.40 & 3.41
Vanadium	3.42
Zinc	3.42 & 3.43

V. Abbreviations used in Table 3

addn	addition	F&P*	Fischer and Peters
APHA*	American Public Health Association	mass spec.	mass spectrometry
API*	American Petroleum Institute	MIBK	methyisobutylketone
ASTM*	American Society for Testing and Materials	mv	millivolt
cmpds	compounds	PMT	photomultiplier tube
dme	dropping mercury electrode	SCE	saturated calomel electrode
EDTA	ethylenediaminetetracetic acid	soln	solution
epm	equivalents per million	USGS	U.S. Geological Survey

* Bibliographic reference

VI. Bibliography and References

A. Reference system: References appear immediately after the method title under the Method column.

1. The numbers following the APHA, ASTM and API references refer to procedure numbers found in these references. Page numbers may change from edition to edition, but procedure numbers usually do not.
2. The numbers following the F&P and USGS references are page numbers.

B. Bibliography

Taras, Michael J., chmn. ed., Standard Methods for the Examination of Water and Wastewater, 13th ed., American Public Health Association, Washington, DC, 1971.

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Presser, T.S. and Ivan Barnes, Special Techniques for Determining Chemical Properties of Geothermal Water, WRI-22-74, U.S. Geological Survey, Menlo Park, CA, August 1974.

Fischer, Robert B. and Dennis G. Peters, Quantitative Chemical Analysis, 3rd ed., W.B. Saunders Co., Philadelphia, PA, 1968.

Table 3.1

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
pH	Electro- metric APHA 144, ASTM D1293-65, API 2.1	----	±0.02% ±0.05%	The pH of a solution is determined by measuring the potential of the solution between glass and reference electrodes. The pH may be determined in batch form with dip type electrodes or flo-thru form using flo-thru cells.	1. Interferences: temp. must be controlled, glass electrode suffers from Na ion interference at high pH and acid interference at low pH, poorly buffered sample difficult to analyze (unless flo-thru is used), oil and grease coat electrodes, no interferences from color, turbidity, oxidants, reductants or colloidal matter. 2. Standard buffers required.
Redox Potential	Electro- metric ASTM D1498-59	----	±13%	Redox potential is measured with a SCE-Pt (or other noble metal) electrode system. Voltage (in MV) is read from a voltmeter.	1. Interferences: a nonreversible system gives erratic results, oil and residue coat electrodes, temp. dependent. 2. ASTM type A & C voltmeters are recommended for measurements.
Conductivity	Conductivity Bridge APHA 154, 226, ASTM D1125-64 API 2.91	----	±5% ±5%	Conductivity is measured with an electrode of known cell constant and a Wheatstone bridge.	1. Interferences: temp. dependent, oil and residue foul electrodes. 2. Cell constant at different temp. must be determined with standard KCl solutions or samples must be measured at constant temp. (e.g., 25°C). 3. Cell constant should be measured with standard KCl solutions.
Alkalinity Acidity	Titration to a Designated Endpoint APHA 101, 102, ASTM D1067-70B, API 2.21-2.22	10-500 mg/l as CaCO ₃	±0.2-9% ±0.6-23%	The sample is titrated with a strong acid (H ₂ SO ₄ or HCl) to separate equivalence points for CO ₃ ²⁻ , HCO ₃ ⁻ , and OH ⁻ . Equivalence points are determined either potentiometrically or with visual indicators.	1. Interferences: determinations of OH ⁻ , CO ₃ ²⁻ and HCO ₃ ⁻ contributions to total alkalinity possible only with absence of other weak bases; residual Cl ₂ , color, and turbidity affect visual indicator titrations; loss or gain of atm. CO ₂ affects results; erratic results obtained when oxidizing or reducing species are present; some constituents may cause buffering at endpoint.

Table 3.2

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Alkalinity Acidity (contd)	Titration to a Designated Endpoint (contd)				2. Useful for routine control of water.
	Titration (Electro- metric) ASTM D1067-70A	----	----	Standard acid or base is added in increments to a sample to be analyzed and the pH recorded after each increment is added. pH versus volume of titrant is plotted to yield the titration curve.	1. Interferences: formation of precipitates may make glass electrode sluggish causing high results; slow equilibria; temp. dependent. 2. Regions of buffer capacity defined. 3. Method considered most precise of any of the alk-acidity methods.
	Color Comparison Titration ASTM D1067-70C	----	----	The sample is titrated with standard acid or base to a predesignated pH endpoint. The color of the endpoint indicator is compared to the color of the same indicator in a standard solution buffered at the desired pH.	1. Interferences: some constituents cause buffering at endpoint or destroy indicator; natural color or turbidity masks endpoint color; oxidizing or reducing species. 2. Useful for routine control of water. 3. Indicator blank correction recommended.
	Titration (Color Change After Boiling) ASTM D1067-70D	----	----	Method is similar to the designated endpoint procedure except that slowly hydrolyzable constituents are driven off from the acidified sample before titrating. Basic samples must be acidified before using this method.	1. Interferences: same as designated endpoint method, volatile acids or bases contributing to total acidity or alkalinity may be lost upon boiling. 2. Basic samples must be acidified, boiled, and back-titrated. 3. Useful for routine analysis.
	Titration (Color Change After Oxidation and Boiling) ASTM D1067-70E	----	----	Method is similar to previous procedure except that H_2O_2 is added prior to boiling to expedite oxidation of oxidizable species [e.g., Fe(II)]. Sample must be acidic before titrating.	1. Interferences: color masks indicator change, suspended solids slow glass electrode response, Fe(II) (which contributes H^+ upon oxidation) is removed.

Table 3.3
SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Suspended Solids (Non-filtrable Residue)	Filtration APHA 148C, 224C, ASTM D1888-67A,B	----	±13% ----	Suspended solids (nonfiltrable residue) are usually determined in conjunction with filtrable solids and total solids content. Suspended solids may be determined indirectly by the difference between total solids and filtrable solids or directly by filtering sample through a tared filter, drying and weighing.	1. Interferences: clogging of filter with matter.
Dissolved Solids (Filtrable Residue)	Filtration and Evapora- tion APHA 148B, ASTM D1888-67A,B	----	---- ----	A sample is filtered through a membrane filter, evaporated in a tared drying dish, oven dried and weighed for filtrable residue. Samples may be ignited at 600°C to determine volatile residue.	1. Interferences: colloidal as well as dissolved solids pass filter, dried residue is hygroscopic (must be weighed quickly), some solid residues [e.g., $(\text{NH}_4)_2\text{CO}_3$] decompose at drying and ignition temps., some liquids (e.g., glycerol or H_2SO_4) are not volatile at drying temps. 2. Considered most accurate method. 3. Automatic evaporator helpful.
	Calculation API 2.11	----	---- ±5%	A sum of the total cation/anion content of a sample is made.	1. Interferences: not all ionic and suspended species are always analyzed. 2. Not subject to loss of components upon heating. 3. Requires all anions and cations of a sample be analyzed.

Other possible methods: estimation from 1) specific gravity, 2) conductance measurements, or 3) ion exchange.

Table 3.4

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Turbidity	Nephelo- metric APHA 163A, ASTM D1889-71	<25 Jackson Candle Units	---- ----	Scattered light from a turbidity sample is (usually) measured at right angles to the incident light in a nephelometer and compared with standard formazin turbidity solutions.	1. Interferences: true color, air bubbles, quickly settleable matter, dirty glassware. 2. Standards required. 3. Does not measure absolute turbidity. 4. Results reported in nephelos units.
	Jackson Candle APHA 163B, ASTM D1889-71	25-1000 Jackson Candle Units	---- ----	Turbidity is measured as the depth of sample in a specially graduated tube necessary to extinguish the image of a standard candle when viewed vertically through the sample tube.	1. Interferences: true color, air bubbles, settleable matter, dirty glassware. 2. Standards not required. 3. Does not measure absolute turbidity. 4. Results reported as Jackson Candle turbidity units.
	Absolute Turbidity ASTM D1889-71	----	---- ----	Absolute turbidity is determined with an integrating sphere apparatus which gives an approximate sum of scattered light in all directions.	1. Interferences: true color (not as severe an interference as other methods), rapidly settleable matter, air bubbles, dirty glassware. 2. Type and size of instrument subject to size of particles in suspension.
Color	Pt - Co Comparison APHA 118	----	---- ----	Color is determined as mg/l Pt by comparison with cobalt-platinum standard solutions. Alternative field method uses standardized colored glass.	1. Interferences: turbidity (usually removed by centrifuge), color varies with pH. 2. Color should be determined immediately after sampling to minimize physical and chemical changes. 3. Standards required.

Table 3.5

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Color (contd)	Spectro- photometric APHA 206A	----	----	Color is defined and measured spectro- photometrically in terms of dominant wavelength, hue, luminance and purity. The pH of the sample is adjusted to 7.6, centrifuged and filtered before determining the color properties.	1. Interferences: nonfiltrable turbidity. 2. Considered most precise and accurate method. 3. Special charts required for interpretation of data. 4. Many data points must be taken.
	Tristimulus Light Filter APHA 206B	----	----	Three special tristimulus filters and a special light source (W lamp at 3000 K) are used to determine the color characteristics of a filtered, pH adjusted sample.	1. Interferences: nonfiltrable turbidity. 2. Requires special chromaticity diagrams. 3. Does not require large number of data points. 4. Probably more rapid method than the spectrophotometric method, but not as accurate.
Specific Gravity	Pycnometer ASTM D1429-60A, API 2.33	----	±0.2% ±0.5%	The weight of a clean, dry pycnometer, the weight of the pycnometer contain- ing distilled water and finally the weight of the pycnometer containing the sample are determined at 15.6°C. The weight of the pycnometer is sub- tracted from the other two determina- tions and the specific gravity of the sample is computed as the weight of the sample divided by the weight of the water.	1. Interferences: uncontrolled temp. during weighing procedure (corrections can be applied). oil in sample. 2. Not suitable for muds and/or sludges.

Table 3.6

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Specific Gravity (contd)	Erlenmeyer Flask APHA 227, ASTM D1429-60B	----	±0.5% ----	Method is similar to the pycnometer method except that an erlenmeyer flask or other container is used instead of a pycnometer.	1. Interferences: uncontrolled temp. during weighing. 2. Suitable for muds and/or sludges.
	Hydrometer API 2.31	----	±0.5% ----	A hydrometer is a weighted bulb with a graduated stem; the depth to which the hydrometer sinks in the sample is an indication of the specific gravity of the sample.	1. Interferences: oil in sample. 2. Temp. compensation necessary. 3. Not considered as accurate as specific gravity balance method or pycnometer method.
	Specific Gravity Balance API 2.32	----	±0.5% ----	The specific gravity balance is an analytical balance which uses a plummet to measure the weight of liquid by displacement. The balance is standardized against distilled water.	1. Interferences: oil in sample. 2. Temp. compensation necessary.
Aluminum	Atomic Absorption APHA 129, USGS-6	----	±22% ±10%	Al is complexed in the aqueous sample with 8-quinolinol, then extracted from the aqueous phase with chloroform. The chloroform solution is then aspirated directly into an N ₂ O-acetylene burner and the absorption measured at 309.3 nm.	1. Interferences: formation of Al oxides in flame. 2. Sensitivity: 1 mg/l Al per 1% absorption. 3. Standards required.
	Colorimetric (Aluminon or Eriochrome Cyanine R) APHA 103B	0.02-0.3 mg/l	±50% ±9%	Dilute Al solutions form a red to pink complex with Eriochrome cyanine R dye at pH 6. The complex is measured colorimetrically at 535 nm.	1. Interferences: F ⁻ ; polyphosphates; >10 mg/l PO ₄ ; alkalinity; Fe and Mn are removed by adding ascorbic acid; color and turbidity compensated by using sample water for blank with Al complexed by EDTA; reaction influenced by pH, time, temp., and concentration of other ions. 2. Standards required. 3. Close control of pH, time, and temp. required.

✓
2

Table 3.7

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Aluminum (contd)	Fluoro- metric (Morin) ASTM D857-69A	0-0.005 mg/l	±0.5-6.4% ----	The fluorescence of the Al-morin complex is measured at pH 3 and the Al concentration determined from a calibration curve.	1. Interferences: most heavy metals (see table in reference); Ca (>1 mg/l); F ⁻ (>5µg/l); NH ₄ ⁺ (>0.5 mg/l); PO ₄ ³⁻ (>3µg/l); SiO ₂ (1 mg/l); SO ₄ (>1 mg/l). 2. Standards required.
	Colori- metric (8-quinolinol with Ion- Exchange Clean-up) ASTM D857-69B	0-0.5 mg/l	±2% ----	Al is complexed with NaF to prevent its reaction with 8-quinolinol while interfering cations are removed by ion-exchange and chloroform extraction. The Al is then made reactive to 8-quinolinol by pH adjustment and the chloroform extracted quinolate is measured at 380 nm.	1. Interferences: (see table in reference) Cu(II), Mn ²⁺ , PO ₄ ³⁻ , polyphosphate, F ⁻ , Fe(III), Mg ²⁺ , Ca ²⁺ . 2. Determines total Al. 3. Standards required. 4. Ion exchange and extraction with CHCl ₃ necessary.
	Colori- metric (Ferron) ASTM D857-69C	0-2 mg/l	±2-7% ----	Al reacts with ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid) to form a water soluble complex which is measured colorimetrically at 370 nm.	1. Interferences: (see table in reference) Fe is major interference which is determined as its 1,10-phenanthroline complex and a correction applied to Al conc.; Mn, Pb, Co, F ⁻ (beryllium used to tie up F ⁻). 2. Determines only soluble Al. 3. Standards required. 4. Simple, rapid.

Table 3.8

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Ammonia	A distillation procedure prior to determination of ammonia content is often advisable to help remove chemical interferences. APHA 132A, ASTM D1426-58A				
	Colori- metric (Nessler) APHA 132B ASTM D1426- 58A, B	0.005-0.5 mg/l (5 cm cell)	±20% ±5%	A basic solution of $\text{HgI}_2 + \text{KI}$ is added to the sample to form $\text{NH}_2\text{Hg}_2\text{I}_3$ which has a yellow to brown hue that is measured between 450 and 500 nm.	1. Interferences: many interferences eliminated by distillation; others (in nondistilled samples) eliminated by addition of basic ZnSO_4 to precipitate Ca^{2+} , Fe , Mg^{2+} , and H_2S ; addition of EDTA or Rochelle salts prevents Ca^{2+} and Mg^{2+} from precipitating during determinations; S^{2-} , hydrazine, urea, and other hydrolyzable organic amides and amino acids will interfere. 2. Standards required.
	Colori- metric (Phenate) APHA 132C	0.04-2 mg/l	±13% ±6%	The reaction of ammonia, hypochlorite, and phenol is catalyzed by manganous ion to form the blue compound indo-phenol which is measured colorimetrically at 630 nm.	1. Interferences: >500 mg/l alkalinity and >100 mg/l acidity (removed by distillation), hydrolyzable organic compounds. 2. Standards required.
	Titri- metric (Formaldehyde Indirect) API 3.13	>5 mg/l	±2% ±5%	Formaldehyde reacts with ammonium ion to produce hexamethylene tetramine, acid and water. The acid is back-titrated with standard base and the ammonia concentration calculated from the titration.	1. Interferences: HCO_3^- and S^{2-} eliminated by addition of acid and boiling; nitrogen containing organics which hydrolyze. 2. Reagent blank required.
	Specific Ion Electrode USGS 5	>0.02 mg/l	---- ----	Ammonia is determined with a pIon or millivolt meter and an ammonium specific electrode in the pH range of 10-14.	1. Interferences: volatile amines, S^{2-} , Hg(II) . 2. Standards required (ammonia standards not stable).

Other possible methods: gas chromatography, mass spectrometry.

Table 3.9
SUMMARY OF PUBLISHED METHODS

CONSTITUENT	METHOD	RANGE	PRECISION ACCURACY	DESCRIPTION	COMMENTS
Argon	Possible methods: gas chromatography, mass spectrometry.				
Barium	Atomic Absorption APHA 129	----	----	Barium is aspirated directly from an aqueous sample into a N ₂ O-acetylene flame and the absorbance of the Ba resonance line at 553.6 nm is measured.	1. Interferences: ionization of Ba (reduced by introduction of cation with similar or lower ionization potential). 2. Standards required.
	Plasma Arc Emission API 4.1	----	±4-6% ----	An acidified sample of Ba is diluted with propanol, mixed with an internal standard (lanthanum) and aspirated into the plasma arc. The intensity of the excitation spectral lines is measured with either photographic plates or PMT.	1. Interferences: most interferences corrected by addition of La. 2. Standards required. 3. Quick and simple when PMT used.
	Flame Photo- metric API 4.7	----	±5% ±8%	Barium is separated and concentrated from a sample by precipitation with chromate in an acid environment. The precipitate is redissolved in HNO ₃ and diluted with aqueous alcohol. The solution is then aspirated into the flame and the intensity of the BaO(H) band peak at 873 nm is measured.	1. Interferences: Ca interferes at 872 nm (removed by precipitation). 2. Standards required.
	Gravi- metric API 3.31	----	----	Barium is precipitated as its chromate, filtered, dried and weighed.	1. Interferences: Ca and Sr removed by a second precipitation; Fe removed by precipitating Fe oxide; Al, Mn, Mg and SiO ₂ interfere by occlusion if Ba conc. <10 mg/l. 2. Time consuming.
	Turbidi- metric API 3.32	----	----	Barium is measured turbidimetrically at 420 nm as its sulfate.	1. Interferences: polyphosphate (removed by acid digestion), high concentration of organic acids or complexing agents, >4500 mg/l Ca.

Table 3.10

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Barium (contd)	Turbidi- metric (contd)				2. Close control of addn. rates, mixing times and other factors required. 3. Requires standards.
Boron	Colori- metric (Curcumin) APHA 107A	0.1-1 mg/l	±22.8% ----	An acidified sample containing boron is evaporated in the presence of circumin to produce rosocyanine which is mea- sured colorimetrically at 540 nm.	1. Interferences: >20 mg/l NO_3^- ; >100 mg/l Ca^{2+} and Mg^{2+} may be removed. 2. Requires standards. 3. Close control of evaporating times, volumes and other variables required.
	Colori- metric (Carmine) APHA 107B, ASTM D3082-72T	0.2-5 mg/l	±35.5% ±0.6%	Carmine in concentrated H_2SO_4 changes from bright red to bluish-red in the presence of boron. Color is measured at 585 nm.	1. Interferences: NH_4^+ , Mo, Ce, Ge, Cl^- , SO_4^{2+} , Ca, Mg, Na and K do <u>not</u> interfere; F^- , SiO_2 and PO_4^{3-} create slight interference. 2. Requires standards.
	Potential- metric Titration (Mannitol) APHA 107C	0.1-5 mg/l	±8.3% ±1.1%	Boron in solution is determined by adjusting the pH to 7, adding mannitol (which lowers the pH) and readjusting the pH with standard NaOH to 7. The volume of NaOH used to readjust the pH is proportional to the concentration of boron.	1. Interferences: PO_4^{3-} , Ge, V(IV), buffering agents, e.g., NH_4^+ , CO_3^{2-} , PO_4^{3-} , and CO_2 ; absorption of CO_2 , HCl or NH_3 from atmosphere into solution. 2. Standards recommended.
Other possible methods: atomic absorption.					
Bromide	Colori- metric (Phenol Red) APHA 108	0.1-1 mg/l (1 cm cell)	---- ----	Bromide reacts with phenol red in the presence of chloramine T at pH 5.0-5.4 to form a reddish-violet complex which is measured colorimetrically at 590 nm.	1. Interferences: Cl_2 forms during reaction, may be removed by addition of $\text{Na}_2\text{S}_2\text{O}_3$. 2. Standards required.

Table 3.11

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Bromide (contd)	Colori- metric (Iodine- Permanganate) ASTM D1246-68B	0-0.1 mg/l	±50% ----	Bromide catalyzes the oxidation of I_2 to periodate by permanganate and hence affects the reaction rate. For a given time, pH, temperature and reactant concentrations, the concentration of bromide is inversely proportional to the unreacted I_2 . The I_2 is extracted with CCl_4 and measured colorimetrically at 515 nm.	1. Interferences: any substance which oxidizes I_2 , or reduces IO_3^- or MnO_4^- ; free Cl_2 must be removed by boiling; >1.0 mg/l NO_2^- , 3 mg/l $Mn(II)$, 1 mg/l $S_2O_3^{2-}$, $Fe(III)$, Zn^{2+} , Ag^+ , Co^{2+} and Ni^{2+} give positive deviations; dilution may decrease interferences to tolerable levels. 2. Close control over time, pH and temperature necessary. 3. Standards required.
	Titri- metric (For Bromide and Iodide) ASTM D1246-68C, API 3.16	<50 mg/l	±3% ±6%	Iodide in a sample is oxidized with bromide to iodate; the excess bromide is then destroyed. Iodine is then formed by oxidizing iodide with the iodate and the resulting iodine is determined by titration with thiosulfate. Iodide and bromide are then determined together by oxidizing both with ClO^- to iodate and bromate. Excess ClO^- is destroyed; the iodine is liberated and determined with thiosulfate. The bromide content is taken as the difference between the iodide and bromide content and the iodide content.	1. Interferences: Fe, Mg and organic material (removed prior to determination with CaO).
	Colori- metric (CCl_4 Extrac- tion) API 3.14	8-80 mg/l (5 cm cell)	±15% ±12%	Bromide is oxidized by chromic acid to bromine, then extracted from the aqueous phase with CCl_4 . The CCl_4 solution is then measured at 417 nm for bromine content.	1. Interferences: Cl^- and I^- do not interfere. 2. Standards required.

Table 3.12

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Cadmium	Atomic Absorption APHA 129, ASTM D2576-70	0.05-5 mg/l	±1-29% ----	Solutions of Cd may be aspirated directly into an air-acetylene flame, or extracted from the aqueous phase as a pyrrolidine dithiocarbamate complex into MIBK. Determinations are made at 228.8 nm. N ₂ O-acetylene flame may also be used.	1. Interferences: few, if any. 2. Requires standards.
	Colori- metric (Dithizone) APHA 109B, 211(II)B	>0.5 µg/l	±24.6% ±6%	Cadmium ions are complexed with dithizone, extracted with chloroform, and measured colorimetrically at 518 nm.	1. Interferences: <250 mg/l Pb, <120 mg/l Zn and <40 mg/l Cu are tolerable; most polyvalent metals do not interfere. 2. Standards required. 3. Uses toxic compound: CN ⁻ .
	Polar- ography APHA 211(III)B	>0.1 mg/l	---- ----	Cadmium may be determined qualitatively and quantitatively by its E _{1/2} and the current height of its polarographic wave.	1. Interferences: strong oxidizing or reducing agents, components with similar E _{1/2} 's. 2. Standards recommended.
Other possible methods: cadmium specific electrode, plasma arc emission.					
Calcium	Gravimetric (Oxalate) APHA 110A, ASTM D1126-67A, D511-52, API 2.52	<0.5 epm and greater	±3.7% ±1.9%	Calcium is precipitated from a solution of carefully controlled pH with ammonium oxalate. The calcium oxalate precipitate is ignited at 1100-1200°C and weighed as CaO.	1. Interferences: Sr, Si, Al, Fe, Mn, PO ₄ ³⁻ , Ba, suspended solids; most removed by preliminary precipitations and by reprecipitation of CaC ₂ O ₄ . 2. Magnesium may also be determined during this method as an ammonium orthophosphate precipitate. 3. Time consuming, but quite accurate.

Table 3.13

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Calcium (contd)	Titri- metric (Permanganate) APHA 110B, API 2.51	<250 mg/l	±3.5% ±2.8%	Calcium is precipitated as its oxalate, redissolved in acid solution, and the oxalate is titrated with permanganate. The amount of permanganate required to oxidize the oxalate is proportional to the calcium concentration.	1. Interferences: same as gravimetric procedure.
	Complexi- metric (EDTA) APHA 110C, ASTM D1126-67B, API 2.4	0-24 epm	±9.2% ±1.9%	Calcium may be compleximetrically titrated with EDTA without interference from Mg at pH 12-13. At pH 10 Mg and Ca may be determined together. The endpoint is determined visually with a compleximetric indicator.	1. Interferences: PO_4^{3-} precipitates Ca at pH used in method; 30 mg/l alkalinity (as CaCO_3); Sr; Ba; Fe (removed by complexing or ion exchange); see table in ASTM reference. 2. High pH values used in method means samples must be titrated immediately after addition of base. 3. Fast rapid method for Ca and Mg determination.
	Atomic Absorption ASTM D2576-70	0.3-15 mg/l	±7-17% ----	Samples containing calcium are aspirated into an air-acetylene flame and determined by the absorption of the calcium resonance line at 422.7 nm	1. Interferences: <600 mg/l PO_4^{3-} eliminated by acidifying solution. 2. Standards required. 3. Fast, easy to use for routine measurements.
Other possible methods: thermometric titration, specific ion electrode, plasma arc emission, polarography.					
Carbon Dioxide	Precise Evolution ASTM D513-71A	>1 mg/l	±0.5-25% ----	CO_2 is liberated by acidifying and boiling the sample in a closed system. The liberated CO_2 is trapped by bubbling into a $\text{Ba}(\text{OH})_2$ solution; excess $\text{Ba}(\text{OH})_2$ is then titrated with standard HCl and the CO_2 species content determined by calculation from the titration and the pH of the sample.	1. Interferences: NH_3 and SO_2 removed by chromic acid cleaning solution; H-S removed by I_2 scrubbing solution; temperature dependent; color, turbidity and most common water constituents do not interfere. 2. Blank determination necessary.

Table 3.14

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Carbon Dioxide (contd)	Precise Evolution (contd)				3. Use of computer program recommended. 4. CO_3^{2-} , HCO_3^- and H_2CO_3 concentration determined by this method. 5. Use of activity coefficients of various CO_2 species in system necessary for meaningful results.
	Abridged Evolution ASTM D513-71B	----	----	Carbonate and bicarbonate are fixed as SrCO_3 precipitate by adding strontium chloride and sodium hydroxide to the sample. The solution is then neutralized, carbon dioxide is removed by aeration in the presence of excess acid, and the quantity of carbon dioxide removed is then determined by back titration of the acid with standard base.	1. Interferences: $>200 \text{ mg/l PO}_4^{3-}$; $>50 \text{ mg/l Fe, Si or Al}$; $>25 \text{ mg/l NH}_4^+$; method unuseable when Fe and PO_4^{3-} both present; Mg^{2+} interferes with titration. 2. Blank determination required. 3. CO_3^{2-} , HCO_3^- , and H_2CO_3 may be determined. 4. Meaningful results requires use of activity coefficients.
	Bicarbonate Titration APHA 111B, ASTM D513-71C	100-1600 mg/l	$\pm 1\%$ ----	The carbon dioxide concentration is determined from the pH and the direct titration of the sample to pH 8.3 and then to pH 4.5 with standard HCl.	1. Interferences: temperature dependent, variable ionic strength of solution. 2. CO_3^{2-} , HCO_3^- , and H_2CO_3 may be determined. 3. Meaningful results requires use of activity coefficients.
	Differential Titration ASTM D513-71D	$>1 \text{ mg/l}$	$\pm 1-33\%$ ----	The sample is titrated to pH 8.5, then to pH 5.0 using standard acid and base as needed. The sample is then acidified, boiled to remove CO_2 , and re-titrated to the same two endpoints.	1. Interferences: acidic components, e.g., H_2S . 2. CO_3^{2-} , HCO_3^- , and H_2CO_3 may be determined. 3. Meaningful results requires use of activity coefficients.

Table 3.15

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Carbon Dioxide (contd)	Direct Titration ASTM D513-71E	----	±10% ----	The carbon dioxide in a sample is reacted with sodium hydroxide to form bicarbonate. The solution is then titrated with standard sodium hydroxide to a pH 8.3 endpoint.	1. Interferences: components which affect carbonate equilibria, e.g., Al, Fe, Cr, Cu (these may also introduce a color or turbidimetric error); NH_3 , PO_4^{3+} , BO_3^{3+} , S^{2-} and NO_3^- .
	Nomographic APHA 111A	----	±1% ----	Given the pH, total alkalinity, temperature and the total mineral content, the total carbon dioxide content may be determined from charts.	1. Interferences: any constituent which significantly affects pH, e.g., superchlorination; coagulation; poorly buffered systems; Cl^- , SO_4^{2-} . 2. Precision of method affected by analyst's ability to read charts.
Other possible methods: gas chromatography, mass spectrometry.					
Carbon Monoxide	Possible methods: gas chromatography, mass spectrometry.				
Cesium	Possible methods: atomic absorption, flame emission, plasma arc emission, Cs specific electrode.				
Chloride	Titrimetric (Mercuric Nitrate) APHA 112B, ASTM D512-67A	----	±3.3% ±2.9%	The chloride sample is titrated with mercuric nitrate titrant; the endpoint is detected by diphenylcarbazone which forms a purple complex with excess Hg(II).	1. Interferences: Br^- ; I^- ; >10 mg/l CrO_4^{2-} , Fe(III) and SO_3^{2-} ; color. 2. pH range of titration must be 2.1-2.8. 3. Blank determination recommended.

Table 3.16

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Chloride (contd)	Titrimetric (Mohr) APHA 112A, ASTM D512-67B, API 2.8, F&P 375	----	±4.2% ±1.7%	Silver chloride precipitates quantitatively as silver nitrate titrant is added to the sample. The endpoint is marked by the formation of red silver chromate. The pH range of the solution must be 7-10.	1. Interferences: Br^- , I^- , CN^- , S^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} (S^{2-} , SO_3^{2-} , and $\text{S}_2\text{O}_3^{2-}$ may be removed); PO_4^{3-} ; color; Fe(III) may mask endpoint color.
	Titrimetric (Fajan) F&P 386	----	----	Silver chloride precipitates quantitatively as silver nitrate titrant is added. The endpoint is detected visually by adsorption of a fluorescent indicator onto the colloidal silver chloride precipitate. A surfactant is added to keep the precipitate colloidal.	1. Interferences: same as preceding method, Fe(III) offers no visual problems. 2. pH range of titration must be 4-10 if dichlorofluorescein is indicator.
	Titrimetric (Volhard indirect) F&P 379, 381	----	----	A known amount of silver nitrate is added to the chloride sample in excess. Silver chloride precipitates and the excess silver ion is back titrated with KSCN. The endpoint is detected visually by the formation of the red Fe(III)-thiocyanate complex.	1. Interferences: same as preceding methods; metathesis of AgCl occurs upon addition of KSCN titrant (can be compensated). 2. pH of solution must be <2.
	Titrimetric (Potentiometric) APHA 203C, F&P 388	----	----	AgCl precipitates quantitatively as silver nitrate titrant is added to the sample. The endpoint is detected with a glass-Ag,AgCl electrode system and an electrometer.	1. Interferences: ferricyanide causes high results; CrO_4^{2-} ; $\text{Cr}_2\text{O}_7^{2-}$; Fe(III) in excess of the concentration of Cl interferes; Br^- and I^- will also precipitate, but give different endpoint potentials from Cl, hence halide mixtures may be titrated to separate observable endpoints (coprecipitation of the other halides in a mixture does occur). 2. pH range not critical.

Table 3.17

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Chloride (contd)	Titrimetric (Conducti- metric) F&P 742	----	---- ----	AgCl precipitates quantitatively as silver nitrate titrant is added; the endpoint is indicated by plotting conductance data versus volume increments of silver nitrate added. The intersection of the two lines on the plot indicate the endpoint.	1. Interferences: CN^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, Br^- , I^- , S^{2-} , PO_4^{3-} . 2. Endpoint "break" on conductance plot may not be distinct. 3. Not useful for rapid determinations.
	Gravimetric (Silver Chloride) F&P 181	----	---- ----	Chloride is quantitatively precipitated with silver ion, collected, dried and weighed as silver chloride.	1. Interferences: anions which form insoluble salts with Ag^+ , e.g., S^{2-} , PO_4^{3-} , Br^- , I^- , etc.; precipitate may contain occluded materials from mother liquor; AgCl precipitate subject to photodecomposition (procedure must be done in darkened room with incandescent lamp); peptization of precipitate may occur during washing. 2. Time consuming.
	Colori- metric (Mercuric- thiocyanate) ASTM D512-67C	0.02-10 mg/l	$\pm 5\%$ ----	Chloride reacts with mercuric thiocyanate, displacing the thiocyanate ligand from the mercuric ion. Thiocyanate forms stable Fe(III) thiocyanate; the Fe(III) is supplied by ferric alum. The amount of ferric thiocyanate formed is determined colorimetrically at 460 nm.	1. Interferences: Br^- , I^- , CN^- , $\text{S}_2\text{O}_3^{2-}$, NO_2^- , NH_4^+ , color, contamination of blank and/or standard solutions from glassware. 2. Standards required.

Other possible methods: Cl^- selective electrode, AgNO_3 titration with Ag, AgS electrode.

Table 3.18

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Chromium	Atomic Absorption APHA 129, ASTM D2576-70	0.2-20 mg/l	---- ----	Cr may be determined by directly aspirating the aqueous sample into an air-acetylene flame and measuring the absorbance of the Cr resonance line at 357.9 nm.	1. Interferences: few, if any. 2. Sensitivity: 0.15 mg/l per 1% absorbance. 3. Standards required. 4. Fast, easy method.
	Colorimetric (Diphenyl- carbazide) APHA 117A, ASTM D1687-67	0.005-0.4 mg/l	±3% ----	Cr(VI) reacts with diphenylcarbazide to produce a reddish-purple color in slightly acid medium after 5 minutes. The color is measured at 540 nm.	1. Interferences: Hg(I and II) (only slightly), >1 mg/l Fe forms yellow complex, V (interference negligible 10 minutes after addition of diphenylcarbazide), CN^- , $\text{S}_2\text{O}_3^{2-}$ and organic material reduce Cr(VI) to Cr(III) upon acidification; color; turbidity. 2. Determines Cr(VI) only. 3. Method useful for relatively clean water samples. 4. Standards required.
	Colorimetric (Diphenyl- carbazide, Permanganate Oxidation) APHA 117C, 211(II)C, ASTM D1687-67A	0.5-5 mg/l	±3% ----	Cr(VI) is reduced by thiosulfate to Cr(III); the sample is then evaporated and fumed with sulfuric acid to destroy organic material. Cr(III) is then reoxidized to Cr(VI) with a slight excess of permanganate. Sodium azide is added to destroy the excess permanganate and the Cr(VI) is reacted with 1,5-diphenylcarbazide in acid solution to form a reddish-purple color measured at 540 nm.	1. Interferences: >100 mg/l organic matter (it is not all destroyed by digestion), >1000 mg/l Fe(III), Cu, >4 mg/l V (negligible after 10 minutes reaction time), >200 mg/l Mo (VI), (Cu, Fe, Mo and V removed in additional steps), >200 mg/l Hg(I and II), >250 mg/l Cl^- (removed as AgCl); Pb, Ag and other heavy metals form explosive azides with NaN_3 . 2. Determines total Cr. 3. Standards required. 4. Uses dangerous compound: NaN_3 (explosive potential).

Table 3.19 9

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Chromium (contd)	Colorimetric (Diphenyl- carbazide, Hypobromite Oxidation) APHA 117D, ASTM D1687-67B	0.5-5 mg/l	±26% ±27%	Samples are digested with nitric acid and hydrogen peroxide to remove organic interferences. All Cr in the sample is then oxidized to Cr(VI) with NaOBr solution. Excess NaOBr is destroyed with phenol, and diphenylcarbazide is added to produce a reddish-purple color measured at 540 nm.	1. Interferences: >100 mg/l organic matter do not interfere, >50 mg/l Fe, >250 mg/l Cl ⁻ (removed as AgCl), large amounts of PO ₄ and alkali earths precipitate with Cr during alkaline oxidation. 2. Standards required. 3. Method useful if large amount of organics present. 4. Determines total Cr.
	Colorimetric (Diphenyl- carbazide, Persulfate Oxidation) ASTM D1687-67C	0.5-5 mg/l	±1-9%	Cr(VI) is removed from the sample by batch treatment with a strong base type I anion resin. The remaining Cr(III) is oxidized to Cr(VI) with alkaline persulfate; excess persulfate is destroyed with sulfuric acid. Diphenylcarbazide is added and the resulting color measured at 540 nm. Total Cr may be determined by omitting the ion exchange procedure.	1. Interferences: >100 mg/l organic matter, >50 mg/l Fe; Cl ⁻ does not interfere. 2. Standards required. 3. Method useful for determination of Cr(III) concentration.
Other possible methods: Cr specific electrode, plasma arc emission.					
Copper	Atomic Absorption APHA 129, ASTM D2576-70	0.1-20 mg/l	±2% ----	Samples containing Cu are directly aspirated into an air-acetylene flame and determined by absorption of the Cu resonance line at 324.7 nm.	1. Interferences: few, if any. 2. Standards required. 3. Fast, easy method.

Table 3.20

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Copper (contd)	Colorimetric (Cuprethol) APHA 119B, ASTM D1688-68C	>0.05 mg/l	±17.5% ±8.5%	Cu(II) forms a yellow colored chelate with cuprethol (bis(2-hydroxyethyl)-dithiocarbamate) which is measured colorimetrically at 435 nm.	1. Interferences: Bi, Co, Hg(I), Ag, Ni, CN ⁻ , S ²⁻ , (chelate complex may be extracted with isoamyl alcohol to rid interferences if necessary). 2. Standards required. 3. Good for trace analysis in relatively clean water. 4. Easily adapted to field determinations.
	Colorimetric (Bathocuproine) APHA 119C	>0.02 mg/l (5 cm cell)	---- ----	Cu(II) in solution is reduced to Cu(I) with hydroxylamine hydrochloride which then forms an orange complex with bathocuproine disulfate (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline disulfonate). The orange complex is measured at 484 nm.	1. Interferences: (see table in reference), relatively high degree of freedom from interferences; CN ⁻ , SCN ⁻ , persulfate, and EDTA interfere. 2. Standards required.
	Colorimetric (Neocuproine) APHA 211-(II)E, ASTM D1588-68A,B	0.002-5 mg/l	±1-31% ----	Cu(II) in the sample is reduced to Cu(I) with hydroxylamine hydrochloride and complexed with neocuproine (2,9-dimethyl-1,10-phenanthroline) between the pH of 3-9. The complex is then extracted with chloroform-methanol. The orange colored solution is measured at 457 nm.	1. Interferences: method relatively interference free; large amounts of Sn ²⁺ , Cr, S ²⁻ , CN ⁻ and organic compounds which interfere may be eliminated. 2. Standards required (system follows Beer's law).
	Polarography APHA 211(III)B	>0.1 mg/l	---- ----	Cu may be determined qualitatively and quantitatively by its E _{1/2} and by the relative current height of the polarographic wave.	1. Interferences: large quantities of other reducible species with E _{1/2} 's similar to Cu; 100 mg/l Cr, Fe and organics had no detectable effects. 2. Standards recommended.

Table 3.21

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Fluoride	Distillation Procedure APHA 121A, 208	----	----	Fluoride is distilled away from chemical interferences in the sample by acidifying the sample with concentrated sulfuric acid and distilling off the volatile HF which is formed at 180°C. Silver sulfate is added to samples of high chloride content during distillation.	<p>1. Interferences: procedure designed to rid sample of Al(III), Cl⁻, Fe(III), hexametaphosphate, PO₄³⁻, SO₄²⁻, color and turbidity; SO₄²⁻ contamination possible if distillation not done carefully.</p> <p>2. Procedure quantitative within the accuracy and precision of F⁻ determination methods.</p> <p>3. Time consuming: still must be flushed by distilling pure H₂O before and after distilling HF.</p> <p>4. Safety hazard: H₂SO₄ can hydrolyze violently with sample.</p>
	Fluoride Specific Electrode APHA 121B, ASTM D1179-72B	>0.1 mg/l	±0-5% ±0-5%	Fluoride concentration is measured with a fluoride specific electrode containing a lanthanum fluoride crystal and an electrometer or pIon meter.	<p>1. Interferences: polyvalent cations, e.g., Al(III), Fe(III) and Si(IV), complex F⁻ (may be eliminated by using TISAB with a complexing agent); distillation often not necessary.</p> <p>2. pH must be controlled with TISAB.</p> <p>3. Method quick, simple to use.</p>
	Colorimetric (SPADNS) APHA 121C, ASTM D1179-72A	0.05-1.4 mg/l	±17% ±7%	Fluoride reacts with zirconium dye lake to produce a colorless zirconium hexafluoride species. The dye becomes lighter in color with the increasing concentration of fluoride. The color is measured at 570 nm.	<p>1. Interferences: similar to above procedure, may be removed by distillation; Cl₂ removed by addition of NaAsO₂.</p>

Table 3.22

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Fluoride (contd)	Colorimetric (Alizarin) APHA 121D	0.05-1.4 mg/l	±5-52% ±0-30%	The principle is similar to the SPADNS method; 3-alizarinsulfonic acid is the dye used instead of SPADNS. (This method is given as a visual comparison method, but an adaptation to a colorimetric or spectrophotometric procedure could be made.)	1. Interferences: removed by distillation. 2. 1 hr required for color development. 3. Standards required.
Helium	Possible methods: gas chromatography, mass spectrometry.				
Hydrazine	Colorimetric (4-methyl- aminobenzal- dehyde) ASTM D1385-67	0.002-0.05 mg/l	±3-29% ----	Hydrazine reacts with 4-dimethylamino-benzaldehyde to form a yellow compound which obeys Beer's law at 458 nm.	1. Interferences: turbidity, color, strong oxidizing agents, e.g. O ₂ , collected with the sample or absorbed from air. 2. Requires standards.
	Other possible methods: gas chromatography, mass spectrometry.				
Hydrogen	Thermal Conduc- tivity ASTM D1588-60A	ca. 0.001 mg/l range	±5% ----	Hydrogen in solution is scrubbed out with air from a thermostated liquid sample. The mixture of hydrogen and air saturated with water vapor is passed through one side of a Wheatstone type thermal conductivity bridge while air saturated with water passes through the other side. The difference in the thermal conductivities of the two gas mixtures is measured and attributed to the hydrogen gas content.	1. Interferences: other volatile gases in solution. 2. Requires special equipment and calibration.

Table 3.23

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Hydrogen (contd)	Volumetric ASTM D1588- 60B	ca. 0.001 mg/l range	---- ----	Dissolved gases (including hydrogen) are removed from solution by boiling. The collected gases are sent through an Orsat type gas analysis apparatus. Carbon dioxide and water are pulled from the system by running the collected gases through appropriate absorption tubes. The volume lost from this procedure is noted, then any hydrogen is pulled from the system by running the gas through hot copper oxide and the change in volume again noted. This change is related to the amount of H ₂ present.	1. Interferences: hot CuO may prompt decomposition of volatile organic compounds; other gases not removed during the process. 2. Requires special apparatus. 3. No calibrations required.
Other possible methods: gas chromatography, mass spectrometry.					
Iodide	Colorimetric (Arsenious- Ceric) ASTM D1246-68A	<0.1 mg/l	±16% ----	The iodide concentration affects the first order reaction rate of AsO ₃ with Ce(IV) in acid solutions. Samples and standards are reacted in a constant temperature bath at 30°C for 30 minutes and the remaining yellow Ce(IV) ion is measured at 450 nm.	1. Interferences: see table in reference, oxidizing agents, e.g., Cl ₂ and >0.1 mg/l Hg; reducing agents (removed with MnO ₄ ⁻). 2. Recommended for low concentrations of I ⁻ . 3. Standards required. 4. Time and temperature must be closely controlled.
	Titrimetric (For Bromide and Iodide) ASTM D1246-68C, API 3.16			Procedure identical to that listed under bromide.	

Table 3.24

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Iodide (contd)	Colorimetric (Arsenious- Ceric-Ferric thiocyanate) APHA 123A	0.0002- 0.0008 mg/l (optimum)	---- ±2%	Procedure is similar to the arsenious- ceric colorimetric method listed above, except the reaction of Ce(IV) with the arsenious ion is quenched with ferric alum and thiocyanate to form the red Fe(III) thiocyanate complex which is measured at 510 or 525 nm.	1. Interferences: I_2 , Cl^- , Hg(II), and Ag(I) are minimized by adding excess NaCl to bring solution to a stable maximum Cl^- concentration. 2. Quenching procedure overcomes rapid change in Ce(IV) concentration during measurements. 3. Requires careful control of time and temperature. 4. Standards required.
	Colorimetric (CCl_4 Extrac- tion) API 3.15	10-50 mg/l	±1-2% ±1-2%	Iodide is oxidized to iodine by nitrous acid (potassium nitrite in sulfuric acid). The iodine is then extracted with CCl_4 and measured colorimetrically at 517 nm.	1. Interferences: H_2S is removed by boiling an acidified sample.
Iron	Colorimetric (1,10-Phenan- throline) APHA 124A, 124C, 211(II)F, ASTM D1068-68A	0.02-4 mg/l	±1-31% ----	Iron is reduced to Fe(II) with hydroxyl- amine hydrochloride and complexed with 1,10-phenanthroline between pH 2.9-3.5 to give an orange-red complex which is measured at 510 nm.	1. Interferences: most interferences over- come by extracting Fe-phenanthroline complex from aqueous solution with diisopropyl ether, (Cu, Co, Cr, Zn and >2 mg/l Ni interfere; Bi and Ag precipitate with phenanthroline; Cd, Hg, Mo interfere; CN^- , NO_2^- , F^- and PO_4^{3-} complex with Fe; strong oxidizing agents). 2. Total iron determined. 3. Standards required.
	Colorimetric (Bathophenan- throline) ASTM D1068-68B	<0.2 mg/l	±7% ----	Procedure is similar to 1,10-phenan- throline method: iron is reduced to Fe(II), complexed with 4,7-diphenyl- 1,10-phenanthroline, extracted with n-hexane or isoamyl alcohol and mea- sured at 533 nm.	1. Interferences: the following ions do not interfere if the pH of the aqueous phase is 3.3-3.7 and if present in <1 mg/l quantities: Cu, Mg, Al, Zn, Mg, Na, Si, NO_3^- , PO_4^{3-} . 2. Total iron determined.

Table 3.25

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Iron (contd)	Colorimetric (Bathophenan- throline) (contd)				3. Standards required. 4. System obeys Beer's law.
	Colorimetric (Tripyridine) APHA 124B, API 3.62	0.02-4 mg/l	±62% ±13%	Iron is reduced to Fe(II) with hydroxylamine hydrochloride and is complexed with 2,2',2''-tripyridine in a solution buffered with ethylenediamine. The reddish-purple complex is measured at 555 nm.	1. Interferences: strong oxidizing agents, color, turbidity, CN^- , NO_2^- (may be removed); PO_4^{3-} and heavy metals do not interfere; probably one of most interference-free methods. 2. Total iron determined. 3. System obeys Beer's law. 4. Standards required.
	Colorimetric (Mercapto- acetic) API 3.61	----	----	Iron forms a reddish-purple complex with mercaptoacetic acid which is measured at 540 nm.	1. Interferences: trace: CN^- , uranyl ion, Ni; amounts equal to iron: Co, Pb, Bi, Au; amounts > iron: NO_2^- , Mo, Cu, As(III), Sn(II), Zn, Cd, Mn, Hg(I). 2. Standards required. 3. Odiferous compound used: mercaptoacetic acid.
	Titrimetric (Dichromate) API 3.63	----	----	Iron is reduced to Fe(II) with Sn(II) and titrated with dichromate using barium diphenylamine sulfonate as the endpoint indicator.	1. Interferences: strong oxidizing and reducing agents, Cu, V, As, Sb, W, Au, Mo, Pt, organic matter. 2. Total iron determined.
	Titrimetric (EDTA) API 3.64	>1 mg/l	----	Iron is oxidized to Fe(III) with peroxide and titrated with EDTA at pH 2.4. Salicylic acid is used as the visual endpoint indicator.	1. Interferences: H_2S is removed by boiling acidic sample, most divalent cations do not interfere. 2. Determines total iron.

Table 3.26

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Iron (contd)	Atomic Absorption APHA 129	----	----	Aqueous samples of iron are aspirated directly into an air-acetylene flame and the absorbance of the Fe resonance line at 248.3 nm is measured.	1. Interferences: few, if any. 2. Sensitivity: 0.3 mg/l per 1% absorbance. 3. Standards required. 4. Quick, easy for routine iron samples.
	Polar- ography APHA 211(III)B	>0.1 mg/l	----	Iron may be determined qualitatively and quantitatively by its $E_{1/2}$ and the relative current height of its polarographic wave.	1. Interferences: large quantities of compounds with $E_{1/2}$'s similar to iron; Cr, oxidizing and reducing species, organics, Cl^- and turbidity may interfere (can be eliminated). 2. Standards recommended.
Other possible methods: plasma arc emission.					
Lithium	Flame Photo- metric APHA 126A, API 4.5	>0.1 mg/l	±3% ±6%	Lithium may be determined quantitatively by aspirating the sample into a gas flame and analyzing the intensity of the resonance line at 670.8 nm.	1. Interferences: Ba, Sr, and Ca are removed by precipitation and filtration; Na and Mg interfere in concentrations >10 mg/aliquot; standard addition technique helps compensate for interferences. 2. Standards recommended.
Other possible methods: atomic absorption, plasma arc emission.					
Lead	Colori- metric (Dithizone) APHA 125A, 211(II)G	>0.002 mg/l	±42.1% ±8.5	Lead is extracted from the aqueous phase with dithizone in CCl_4 to form a red color which is measured at 510 nm.	1. Interferences: most common polyvalent metal cations will interfere (may be eliminated), organic material must be acid digested, dithizone is light sensitive. 2. Time consuming and subject to contamination.

Table 3.27

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Lead (contd)	Colori- metric (contd)				3. Useful for detecting small quantities of lead. 4. Standards required. 5. Uses toxic compound: CN^- .
	Atomic Absorption APHA 129, ASTM D2576-70	0.34-40 mg/l	$\pm 23.5\%$ $\pm 19.0\%$	Lead is extracted from the aqueous phase with pyrrolidine dithiocarbamate in MIBK. The extraction is then aspirated into an air-acetylene flame and the absorbance of the resonance line at 283.3 nm measured.	1. Interferences: few, if any. 2. Detection limits larger than dithizone method. 3. Fast, easy to use. 4. Requires standards.
	Polar- ography APHA 211(III)B	>0.1 mg/l	---- ----	Lead is determined qualitatively and quantitatively by its $E_{1/2}$ and the current height of its polarographic wave.	1. Interferences: strong organic oxidizing or reducing species, components with $E_{1/2}$'s similar to Pb. 2. Relatively fast, interference free method. 3. Standards recommended.
Other possible methods: plasma arc emission, Pb^{2+} specific electrode.					
Magnesium	Gravi- metric (Pyrophos- phate) APHA 127A, ASTM D1126-67A, D511-52, API 2.61	----	$\pm 0.1-2\%$ ----	Diammonium hydrogen phosphate pre- cipitates magnesium quantitatively in an ammoniacal solution as magnesium ammonium phosphate. The precipitate is ignited and weighed as magnesium pyrophosphate. A double precipitation of the precipitate is desirable. (This method is usually used concur- rently with the oxalate precipitation of calcium in hardness determinations.)	1. Interferences: Al, Ca, Fe, Mn, Si, Sr, suspended matter (most may be removed); ammonium salts, e.g., ammonium chloride, in high concentrations interfere. 2. Procedure time consuming, but is rela- tively accurate and interference free.

Table 3.28

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Magnesium (contd)	Titri- metric (EDTA) APHA 122B, ASTM D1126-67B, API 2.4	----	±1-2% ±4-5%	Magnesium is determined volumetrically by titrating with EDTA in the presence of a compleximetric indicator dye at pH 10. This method is usually used in conjunction with a simultaneous calcium determination for total water hardness.	1. Interferences: most other polyvalent metal cations (may be removed), Ca will interfere if only Mg is to be determined. 2. Relatively rapid procedure providing few interferences are present.
	Colori- metric (Brilliant Yellow) APHA 127C	1-75 mg/l	±2-50% ±2-40%	Magnesium hydroxide is precipitated in the presence of brilliant yellow; the dye is adsorbed onto the precipitate and changes color from orange to red. A stabilizer solution is added to keep the precipitate in colloidal suspension. The color is measured at 525 nm.	1. Interferences: Ca, Al (may be eliminated), >5 mg/l PO_4^{3-} , 0.5 mg/l Cl_2 , >2.5 mg/l Fe, >250 mg/l Cl^- , 5 mg/l F^- ; Mn, Zn. 2. Uses unstable solutions which must be replaced every few days. 3. Requires standards.
	Atomic Absorption APHA 129, ASTM D2576-70	0.05-3.5 mg/l	±8-40% ----	Solutions containing magnesium are aspirated directly into an air-acetylene flame and the absorbance of the resonance line at 285.2 nm is measured.	1. Interferences: PO_4^{3-} and Al eliminated by addition of La. 2. Rapid, accurate method. 3. Standards required.

Other possible methods: plasma arc emission, thermometric titration.

Table 3.29

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Manganese	Colorimetric (Ammonium persulfate) APHA 128B, 211(II)H, ASTM D858-65	0.025-15 mg/l	±50% ±7.2%	Manganese (II) is oxidized to permanganate with ammonium persulfate in the presence of silver nitrate. The resulting permanganate color is measured colorimetrically at 525 nm.	1. Interferences: Cl^- (minimized by addn. of Hg(II)), Br^- , I^- , organics, Co (most interferences may be minimized). 2. Standards required. 3. Method preferred over other oxidation methods because of the use of Hg(II) to suppress Cl^- and rapid color development.
	Colorimetric (Periodate) APHA 128C, API 3.7	0.005-15 mg/l	±36% ±25%	Manganese (II) is oxidized to permanganate with periodate or paraperiodate and measured colorimetrically at 525 or 545 nm.	1. Interferences: Cl^- , Br^- , I^- , Fe(II) , organics and other reducing agents capable of reacting with IO_4^- or MnO_4^- may be removed with H_2SO_4 or HNO_3 ; H_3PO_4 used to decolorize Fe(III) ; SiO_2 may cause turbidity; colored species may be compensated. 2. Standards required. 3. Most suited for samples containing >0.01 mg/l Mn and few interferences.
	Atomic Absorption APHA 129, ASTM D2576-70	0.04-10 mg/l	±13.5% ±6%	Manganese may be determined by aspirating the aqueous sample directly into an air-acetylene flame and measuring the absorbance of the resonance line at 279.4 nm.	1. Interferences: SiO_2 removed by addn of Ca. 2. Standards required. 3. Rapid, accurate method. 4. Considered method of choice for Mn determinations.
	Flame Photometry API 4.8	----	±3% ±6%	Manganese is extracted from an aqueous sample with 3-hydroxyquinoline in chloroform. The chloroform is evaporated and the metal complex is redissolved in n-propanol. This solution is aspirated into the flame and the intensity of the resonance triplet at 403.2 nm is measured.	1. Interferences: Ga (may be corrected). 2. Standards required.

Table 3.30

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Manganese (contd)	Other possible methods: plasma arc emission.				
Mercury	Cold Vapor Atomic Absorption ASTM D3223-73	0.002- 0.01 mg/l	±30-50% ----	Mercury is oxidized to its Hg(II) state, then reduced to elemental mercury. The mercury vapor is circulated through a cell in an atomic absorption instrument and the absorption of the mercury resonance line at 253.7 nm is measured.	1. Interferences: S^{2-} (may be eliminated), >10 mg/l Cu, Cl^- , Cl_2 , and volatile organics (may be compensated). 2. Standards required.
Other possible methods: Hg ⁺ specific electrode.					
Methane	Combustible Gas Indi- cator APHA 130A	>0.2 mg/l	±10% ----	The partial pressure of methane above an aqueous sample is determined by oxidizing the gas on a heated Pt filament which is part of a Wheatstone bridge. The heat generated by the combustion process raises the resistance in the wire and unbalances the bridge. The imbalance may then be measured.	1. Interferences: other oxidizable volatile species, e.g. ethane, H_2 and H_2S . 2. Calibration with standards recommended. 3. Fast, simple, relatively accurate.
	Volumetric APHA 130B, 225A	>2 mg/l	±1-20% ----	Oxygen, carbon dioxide and hydrogen are removed from the gas sample; the remaining gas is passed slowly over a heated Pt wire in the presence of excess oxygen to convert the product to carbon dioxide and water. The volume of carbon dioxide formed is equivalent to the original amount of methane and is measured volumetrically in an Orsat type system. Nitrogen is assumed to be the only other gas present.	1. Interferences: other volatile oxidizable species. 2. Method is more accurate for large volumes of CH_4 than the combustible gas indicator method.

Table 3.31
SUMMARY OF PUBLISHED METHODS

CONSTITUENT	METHOD	RANGE	PRECISION ACCURACY	DESCRIPTION	COMMENTS
Methane (contd)	Other possible methods: gas chromatography, mass spec.				
Nitrate	Colori- metric (Phenoldisul- fonic Acid) APHA 133A, 213D	0.01-12 mg/l	±74% ±38%	Nitrate and phenoldisulfonic acid react to form a yellow color which is measured colorimetrically at 410 or 480 nm.	1. Interferences: 10 mg/l Cl^- (Cl^- must be removed by Ag_2SO_4 precipitation before accurate determination made); color, turbidity and NO_2^- affect method. 2. Standards required.
	Colori- metric (Direct Measurement) APHA 133B	0.04-11 mg/l	---- ----	Nitrate has an absorption band in the near UV which follows Beer's law at 220 nm. A baseline correction for organic components present is taken at 275 nm.	1. Interferences: dissolved organics, NO_2^- , Cr(VI) and surfactants may be compensated by preparing individual correction curves; OH^- , and CO_3^{2-} may be compensated by acidifying; Cl^- does not interfere. 2. Standards required. 3. Useful for routine NO_3^- control in water with negligible organic content.
	Colori- metric (Sulfanilic Acid - Zinc Reduction) APHA 213A	0.01-6.2 mg/l (10 cm cells)	±2-70% ±33-70%	Nitrate is reduced to nitrite with Zn(II) . The nitrite is then measured by reacting it with sulfanilic acid to form diazosulfanilic acid which then couples with naphthylamine to form a reddish-purple azo dye. The dye is measured colorimetrically at 520 nm.	1. Interferences: strong oxidizing or reducing agents, Sb(III) , Au(II) , Bi , chloroplatinate, Fe(III) , Hg(I) , metavanadate, Ag(I) , Cu(II) , color. 2. Standards required. 3. Slope of calibration curve temperature dependent. 4. Indigenous NO_2^- destroyed before reducing NO_3^- to NO_2^- . 5. Uses carcinogenic compound: naphthylamine.

Table 3.32
SUMMARY OF PUBLISHED METHODS

CONSTITUENT	METHOD	RANGE	PRECISION ACCURACY	DESCRIPTION	COMMENTS
Nitrate (contd)	Colori- metric (Cadmium Reduction) APHA 213B	0.01-0.8 mg/l	±9-96% ±1-47%	Nitrate is reduced to nitrite by passing the solution through a column of cadmium-mercury amalgam. The nitrate reduced to nitrite is then diazotized with sulfanilamide and coupled to N-(1-naphthyl)-ethylene-diamine. This azo dye is then measured colorimetrically at 543 nm.	<ol style="list-style-type: none"> 1. Interferences: unknown. 2. Standards required. 3. Correction for indigenous nitrate needed. 4. Requires special preparation of Cd/Hg amalgam and reduction column for procedure. Column must be periodically reactivated. 5. Uses carcinogenic compound: N-(1-naphthyl)-ethylenediamine.
	Colori- metric (Brucine) APHA 213C, ASTM D992-71	1-50 mg/l	±6-67% ±0-8%	Nitrate ion is reacted with brucine in a strong sulfuric acid environment with precise temperature and time controls. The reaction yields a yellow color which is measured colorimetrically at 410 nm.	<ol style="list-style-type: none"> 1. Interferences: strong oxidizing and reducing agents; >5 mg/l Cl_2 (eliminated with NaAsO_2); high concentrate of organics (minimized by addn of $\text{Al}(\text{OH})_3$ and activated carbon); >0.5 mg/l NO_2^-; >1 mg/l Fe(II), Fe(III) and Mn(IV); Cl^- masked by addn of excess Cl^-. 2. Requires standards.
	Colori- metric (Chromo- tropic Acid) APHA 213E	0.25-20 mg/l	±1-64% ±0-13%	Two moles of nitrate react with one mole chromotropic acid to form a yellow reaction product which is measured colorimetrically at 410 nm.	<ol style="list-style-type: none"> 1. Interferences: Cl_2, some oxidizing agents and NO_2^- yield yellow color with chromotropic acid (Cl_2 and oxidizing agents eliminated with SO_3^{2-}; NO_2^- eliminated with urea); Cl^- and FeCl_3 (complexed with Sb); Ba, Pb, Sr, I^- and IO_3^- interfere; >20 mg/l Cr(VI). 2. Standards required. 3. Color is stable after 10 min to 24 hr.

Table 3.33

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Nitrite	Colori- metric (Diazoti- zation) APHA 134, ASTM D1254- 67A	0.015-0.15 mg/l (5 cm cell)	±21% ±12%	Nitrite is determined in acidic solution by diazotization of sulfanilic acid and subsequent coupling with naphthylamine to produce a reddish-purple azo dye which is measured colorimetrically at 520 nm.	1. Interferences: oxidizing agents (Cl_2 , NCl_3 , Cr(VI) , Cr(III) , MnO_4^- , ClO_3^- , ClO_4^- , IO_4^- , trisulfatocerate, peroxydisulfate, tungstate); reducing agents (I^- , Fe(II) , SnCl_4 , S^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-}); heavy metals precipitate (antimonious, Au(III) , Fe(III) , Bi , Pb(II) , Hg(I) , Ag(I) , PtCl_5 , metavanadate); Cu(II) catalyzes decomposition of diazonium salt; amines and NH_3 react with NO_2^- ; Co(II) , and Cr(III) contribute to color; Hg(II) , bacterial interferences on storage. 2. Requires standards, NaNO_2 standards unstable. 3. Uses carcinogen: naphthylamine hydrochloride.
	Titri- metric (Permanganate- Oxalate) ASTM D1254- 67B	3-600 mg/l	±1-5% ----	A sample containing nitrite is pipetted below the surface of a known volume of acidified permanganate. The solution is heated, a known amount of oxalate is added in excess to destroy the remaining permanganate and the excess oxalate is then back titrated with permanganate.	1. Interferences: other reducing agents. 2. Does not require nitrite standards.
Nitrogen	Possible methods: gas chromatography, mass spec.				
Oil	Separatory Funnel Extraction APHA 137, ASTM D2778- 70	----	----	Organic matter present in an aqueous sample is partitioned between water and an immiscible organic solvent (e.g. pet ether). Solvent extractions are made in separatory funnels with the aqueous phase adjusted consecutively to pH 7,	1. Interferences: oxidation of organic compounds, emulsions, inability of solvent to extract all organic components. 2. Reproducibility dependent upon exact maintenance of procedure for each replicate determination.

Table 3.34

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Oil (contd)	Separatory Funnel Extraction (contd)			3, and 11. Extracted material may then be determined gravimetrically or instrumentally.	3. Relatively rapid procedure.
	Soxhlet Extraction (Filtration) APHA 209A	----	----	A sample is acidified to hydrolyze metallic soaps and any solid or viscous oils are separated by filtration. The filter and filtering apparatus are wiped clean of the collected oil and grease with solvent soaked filter paper which is then extracted with hexanes in a Soxhlet extractor. Determination of oil content is gravimetric.	1. Interferences: adsorption of oxygen from air (causes weighing errors and oxidation of organic compounds), loss of volatile species. 2. Reproducibility is similar to previous method. 3. Requires ca. 6 hr elapsed time.
	Soxhlet Extraction (Activated Charcoal) ASTM D2910- 71T	----	----	Procedure is similar in theory to the above Soxhlet extraction except that organic constituents are collected on an activated charcoal column which is eluted in a Soxhlet extractor. Final determination may be instrumental.	1. Interferences: similar to above Soxhlet method. 2. Reproducibility is similar to above methods. 3. Requires ca. 10-hr elapsed time.
	Turbidimetric API 3.17	----	----	Oil is extracted from the water sample with chloroform in a separatory funnel. The amount of oil in the extraction is determined turbidimetrically against clean chloroform and the absorbance reading compared to standard curves.	1. Interferences: extractable color, e.g. organic dyes, metal chelates, etc. 2. Claimed to be reproducible and accurate. 3. Rapid method. 4. Standards required.

Other possible methods: gas chromatography, mass spec.

Table 3.35

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Oxygen	Titri- metric (Iodometric) APHA 218(A-E) ASTM D1589- 60(A-C), D888-66(B-D), API 3.41	----	---- ----	Alkaline iodide is added to the sample to be determined, followed by the addition of Mn(II). The Mn(II) is oxidized to higher oxidation states by dissolved oxygen; oxidized Mn in turn oxidizes iodide to iodine in acid media. The liberated iodine is then titrated using standard thiosulfate. There are several modifications to help reduce interferences: azide, permanganate, alum, and the copper sulfate-thiocarbamic acid modifications.	1. Interferences: strong oxidizing or reducing agents, NO ₂ (removed by azide method), Fe(II) (removed by permanganate method) Fe(III) (removed by using H ₃ PO ₄), suspended solids (removed by flocculation methods), H ₂ S and SO ₂ . 2. Standards not necessary. 3. Rapid, relatively reliable. 4. Blanks usually required.
	Colori- metric (Indigo Carmin) ASTM D888- 66A	>0.06 mg/l	±6% ----	Dissolved oxygen reacts in alkaline solution with indigo carmine to produce a color change from yellow-green through red, through blue, to blue-green. The color is visually compared to colored standards which represent different oxygen contents.	1. Interferences: Fe(II), Cu, >1 mg/l tannin, hydrazine, sulfite, >4 mg/l Fe(II), cyclohexylamine, morpholine. 2. Gives rapid, precise, accurate results.
	Membrane Electrode APHA 218F, API 3.43	----	---- ----	Dissolved oxygen is measured using an electrode consisting of a cathode and anode surrounded by an electrolyte encased in a Teflon or polyethylene membrane. Oxygen diffuses through the membrane and is reduced electrically. The current thus formed is proportional to the oxygen content.	1. Interferences: H ₂ S, CO ₂ , oil, SO ₂ , Cl ₂ , Br ₂ , I ₂ , N _x O _y ; turbidity, color, sampling technique and most ionic components do not interfere. 2. Method dependent upon temperature and ionic strength of solution. 3. Electrode is submersible, good for field determinations.
	Polaro- graphic ASTM D185- 60D, API 3.42	>0.1 mg/l	---- ----	Oxygen in solution may be determined qualitatively and quantitatively by the E _{1/2} and the current height of the polarographic wave. The dme or rotating Pt electrode may be used.	1. Interferences: gaseous and volatile oxidants (e.g., halogens) stronger than O ₂ , certain heavy metal ions, high concentrations of soaps and detergents. 2. Blank determinations somewhat uncertain.

Table 3.36

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Phosphate	Colori- metric (Ascorbic Acid Reduc- tion) APHA 223F, ASTM D515-72A	0.01-0.5 mg/l	±4-9% ±4-10%	Orthophosphate reacts with ammonium molybdate and Sb-K tartrate to form an antimony phosphate tartrate complex which is reduced by ascorbic acid to a blue molybdenum complex. The complex is measured colorimetrically at 880 or 625-650 nm.	1. Interferences: >50 mg/l Fe; >10 mg/l SiO ₂ ; As; Cr(VI); NO ₂ ⁻ and S ²⁻ interferences removed by Br ₂ -H ₂ O or sat. KMnO ₄ . 2. Low concentrations of PO ₄ ³⁻ measured at 880 nm, higher concentrations at 625-650 nm. 3. Method specific for orthophosphate; other phosphate forms may be converted to orthophosphate for total phosphate determinations.
	Colori- metric (Amino Reduction) ASTM D515-72B, API 3.9	0.03-3 mg/l	±0.2-10% ±5%	Orthophosphate reacts with ammonium molybdate in acid medium forming a molybdophosphate which is reduced to a molybdenum blue complex with aminonaphthol sulfonic acid. The color intensity is measured at 650 nm. An addition of bismuth nitrate to the procedure increases the sensitivity four-fold.	1. Interferences: >40 mg/l Fe; >75 mg/l Cr(VI); >50,000 mg/l Cl ⁻ or >1500 mg/l Cl ⁻ when Bi(NO ₃) ₃ is used; NO ₂ ⁻ interference eliminated by addn of sulfamic acid; SiO ₂ concentrated 20X greater than phosphate causes 2% error; S ²⁻ eliminated by addn of MnO ₄ ⁻ ; CaSO ₄ precipitation eliminated by using HCl in procedure. 2. Requires standards. 3. Uses carcinogenic compound: 1-amino-2-naphthol-4-sulfonic acid.
	Colori- metric (Molybdo- vanado- phosphate) APHA 223D, ASTM D515-72C	1-20 mg/l	±5-22% ±9-75%	Orthophosphate is determined by formation of the yellow colored molybdo-vanadophosphoric acid specie when ammonium molybdate and ammonium vanadate are added to the sample. Color intensity is measured at 400-420 nm or, for increased range, 470-490 nm.	1. Interferences: high Fe(III) content, color (e.g. tannin), Si, As, arsenate, F ⁻ , Th, Bi, S ²⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ , excess molybdate, >100 mg/l Fe(II), >75 mg/l Cl ⁻ if HNO ₃ used in test. 2. Requires standards. 3. Determines orthophosphate; other phosphates determined by digestion to orthophosphate. 4. Contamination from lab glassware possible (glassware for test should be kept separately).

Table 3.37

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Phosphate (contd)	Colori- metric (Stannous Chloride) APHA 223E	0.007-2 mg/l (using 10, 2, and 0.5 cm cells)	±8-20% ±4-29%	In acid solution molybdate is added to form molybdophosphoric acid which is reduced to the molybdenum blue complex by stannous chloride. The complex is extracted by benzene-isobutanol and measured at 625 nm.	1. Interferences: similar to molybdovanado-phosphate method, most overcome by extraction procedure. 2. Determines orthophosphate; other phosphates determined by digestion to orthophosphate. 3. Standards required. 4. Temperature and time require close control.
Potassium	Gravimetric (Tetraphenyl Boron) API 3.11	----	±2% ±5%	Potassium is precipitated by tetraphenyl boron. The precipitate is washed to remove most interferences and dried to constant weight.	1. Interferences: Rb, Cs, NH_4^+ coprecipitate (NH_4^+ may be removed).
	Flame Photometric APHA 147A, ASTM D1428- 64, API 4.4	1-100 mg/l	±3% ±6%	Potassium is determined by aspirating the sample into the flame of a flame photometer. The intensity of the potassium line at 769.9 nm is measured and is proportional to the potassium concentration.	1. Interferences: self absorption eliminated by using standards, Al, other alkali metals, suspended matter (filter), Ca, Mg (when Mg concentration >100X K); most interferences may be eliminated by using internal Li standard, including major interferences in standards and operating in the lowest possible K range. 2. Standards required. 3. Probably easiest to use method if few interferences present.
	Colori- metric (Sodium cobalti- nitrite) APHA 147B	>5 mg/l (15 cm cell)	----- ±9%	Potassium is precipitated by trisodium cobaltinitrite and oxidized by standard chromic acid; the excess dichromate is measured colorimetrically at 425 nm.	1. Interferences: NH_4^+ ; SiO_2 causes turbidity, but may be removed. 2. Standards required. 3. Method dependent upon mixing rates, temperature, and time.

Table 3.38

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Potassium (contd)	Other possible methods: atomic absorption, specific ion electrode, plasma arc emission.				
Rubidium	Possible methods: atomic absorption, plasma arc emission				
Silica	Gravimetric APHA 151A, ASTM D859-68A	>20 mg/l	±1% ----	Silica in water is concentrated and precipitated as partially dehydrated silica by evaporation with HCl. The residue is ignited at 1000-1200°C and weighed; subsequently the silica present is converted to volatile silicon tetrafluoride by addition of HF. The silicon tetrafluoride is driven off by a second ignition and the difference between the weights of the remaining residue and the residue before HF treatment is considered to be the silica content.	1. Interferences: common water constituents offer no interference; atmospheric dust may contaminate. 2. Method determines total silica in water. 3. Procedure tedious and time consuming. 4. Uses dangerous compounds: HF.
	Colorimetric (Heteropoly Blue) APHA 151C, ASTM D859-68B,C	0.02-1 mg/l	±5-27% ±3-5%	Soluble silica reacts with molybdate ion to produce a greenish-yellow complex which is then reduced by 1-amino-2-naphthol-4-sulfonic acid to produce a blue complex which is measured at (preferably) 815 nm or, with reduced sensitivity, at 640-700 nm.	1. Interferences: turbidity, Fe, S ²⁻ , tannin, color; PO ₄ removed by oxalic acid. 2. Uses carcinogen: amino-naphthalene.
	Colorimetric (Molybdosilicate) APHA 151B	>1 mg/l	±8-14% ±4-10%	Procedure is similar to preceding method except that the blue indicating complex is omitted; the yellow silica-molybdate complex is measured directly at 410 nm.	1. Interferences: contamination from glassware, Fe, color, turbidity, S ²⁻ , PO ₄ ³⁻ , tannin. 2. Standards required. 3. Conflicting statements made about the applicability of Beer's law to system.

Table 3.39

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Silica (contd)	Other possible methods: atomic absorption.				
Sodium	Flame Photometry APHA 153A, ASTM D1428- 63, API 4.3	>0.1 mg/l	±3% ±6%	Solutions containing sodium are aspi- rated into an atomizing flame and the emitted energy measured by a PMT at 589 nm.	1. Interferences: other alkali metals, Al, suspended matter clogs burner, Ca, large amounts of Mg, Cl^- , SO_4^{2-} , and HCO_3^- (most interferences may be eliminated). 2. Internal standards or known adds required.
	Specific Ion Electrode ASTM D2791- 73	>0.0001 mg/l	---- ----	A sodium specific electrode is used to measure sodium ion activity in a solu- tion with the pH buffered at 11.0.	1. Interferences: Ag^+ , Li^+ , H^+ , K^+ , NH_4^+ . 2. Relatively rapid, easy method. 3. Requires standards.
	Gravimetric (Zinc uranyl acetate) APHA 153B	----	±11.3% ±0.5%	Sodium is precipitated by zinc uranyl acetate hexahydrate by the addition of the reagent to the sample. The par- tially water soluble precipitate is carefully washed and dried in air before weighing.	1. Interferences: Li^+ ; 25 mg/ml K^+ ; PO_4^{3-} , organic acids, SO_4^{2-} (especially when large amounts of K^+ present); SiO_2 may precipitate out. 2. Precipitate is unstable.
	Other possible methods: atomic absorption, plasma arc emission.				
Sulfate	Gravimetric APHA 156A,B, ASTM D516-68A, API 2.71	20-100 mg/l	±5% ±2%	Sulfate is precipitated as barium sulfate which is dried and weighed.	1. Interferences: SiO_2 , Fe(III), NO_3^- , NH_4^+ , heavy metals and insoluble matter; SiO_2 may be removed by dehydration with HCl, HClO_4 or by $\text{H}_2\text{SO}_4 + \text{HF}$; SO_3^{2-} and S^{2-} may oxidize and precipitate with BaSO_4 .

Table 3.40

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Sulfate (contd)	Turbidi- metric APHA 156C, ASTM D516- 68B, API 2.72	10-100 mg/l	±5-9% ±1.2%	Sulfate is converted to a barium sulfate colloidal suspension under controlled conditions. The concentration of the sulfate is then determined turbidimetrically.	1. Interferences: Fe(III), insoluble suspended matter (removed by filtration), color; most other anions present will not interfere. 2. Standards required. 3. Reaction conditions must be closely controlled.
	Titri- metric ASTM D516- 68C	5-1000 mg/l	±1% ----	Sulfate is titrated in an alcoholic solution with controlled acid conditions using barium chloride titrant and thorin as the visual endpoint indicator.	1. Interferences: K, Cr(VI), Fe, Al, PO_4^{3-} , F^- , NO_3^- , S^{2-} , SO_3^{2-} , and Cl^- interfere by coprecipitating with $BaSO_4$; many metallic ions interfere by complexing with indicator; most interferences may be removed by cation exchange pretreatment and other methods. 2. Method may be less time consuming than other methods when a minimum of pretreatment is necessary.
Other possible methods: colorimetric.					
Sulfide	Unless sample is analyzed for sulfide content immediately, sample should be pretreated with zinc acetate to precipitate the sulfide for later analysis..				
	Titri- metric (Iodine) APHA 228A API 3.10.1, USGS 7	>1 mg/l	---- ±1.5%	Sulfide is indirectly determined by stripping hydrogen sulfide from an acidified sample with an inert gas. Hydrogen sulfide is collected in zinc acetate solution to which excess iodine in water is added to oxidize sulfide to elemental sulfur. Excess iodine is titrated with thiosulfate.	1. Interferences: SO_3^{2-} , $S_2O_3^{2-}$ and hydro-sulfite decompose in acid yielding erratic results; volatile iodine consuming substances give high results. 2. Requires special gas rack apparatus. 3. Considered more accurate than colorimetric analyses.

Table 3.41

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Sulfide (contd)	Titrimetric (Iodine) (contd)				4. All sulfide forms may be determined by measuring pH of sample and calculation. (Activity coefficients necessary for meaningful results).
	Colorimetric (Methylene Blue) APHA 228B,C, API 3.10.2	0.02-20 mg/l	---- ±10%	Methylene blue is formed when sulfide is reacted with 4-amino-N,N-dimethylaniline in the presence of ferric chloride. Ammonium phosphate is then added to destroy excess Fe(III). The color is measured at 600 nm.	1. Interferences: strong reducing agents inhibit color formation; high sulfide concentration (ca. 100 mg/l) inhibit reaction; >10 mg/l $S_2O_3^{2-}$ and SO_3^{2-} interfere (may be eliminated). 2. Standards required. 3. All sulfide forms may be determined by measuring sample pH and calculation (meaningful results require use of activity coefficients). 4. Uses poisonous compound: 4-amino-N,N-dimethylaniline.
	Titrimetric (Electrometric) API 3.10.3	3-15 mg/l	±3% ----	Sulfide is titrated with standard silver nitrate using a glass-silver, silver sulfide electrode system to detect the endpoint.	1. Interferences: free from most major sources of interference: there are usually different enough potential breaks between insoluble Ag precipitates to determine separate constituents; coprecipitation of insoluble Ag compounds a problem. 2. Not suitable for field use.

Other possible methods: gas chromatography, mass spec.

Table 3.42

SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Vanadium	Colori- metric (Gallic Acid) APHA 164A	>0.025 mg/l	±20% ±0%	Vanadium exerts a catalytic effect on the reaction rate of the oxidation of gallic acid by persulfate in acid medium. The extent of the reaction is dependent upon the amount of vanadium present, and is measurable at 415 nm.	1. Interferences: Cr(VI), Co(II), Cu(II), Fe(II) and (III), Mo(VI), Ni(II), Ag, U(VI), Br ⁻ , Cl ⁻ , I ⁻ ; see table in ref. 2. Standards required. 3. Requires close control of reaction conditions.
Other possible methods: atomic absorption, plasma arc emission.					
Zinc	Atomic Absorption APHA 129, ASTM D2576- 70	0.02-3 mg/l	±1.3% ----	A sample containing zinc is aspirated directly into an air-acetylene flame and the absorbance determined at 213.8 nm.	1. Interferences: few, if any. 2. Standards required. 3. Considered method of choice.
	Colori- metric (Dithizone) APHA 165B, 211(II)K	>0.001 mg/l	±18.2% ±25.9%	Zinc reacts with diphenylthiocarbazon (dithizone) at pH 4.0-5.5 to produce a reddish-violet chelate complex. The complex is extracted into CCl ₄ and measured at either 535 or 620 nm.	1. Interferences: Bi, Cd, Co, Cu, Au, Pb, Hg, Ni, Pl, Ag, Sn, Fe(III), Cl ₂ (most interferences may be compensated); contaminated glassware. 2. Standards required. 3. Dithizone reagent unstable in light and heat.
	Colori- metric (Zincon) APHA 165C, ASTM D1691- 67	0.002-5 mg/l	±13.9% ±17.4%	Zinc forms a blue colored complex with 2-carboxy-2'-hydroxy-5'-sulfoformazyl-benzene (zincon). Chloral hydrate and KCN are used to suppress interferences. The complex is measured at 620 nm.	1. Interferences: Cu, Co, Ni, Cr, Fe(II) and (III), Al, Mn, Cd (suppressed with CN ⁻); most common anions (Cl ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻) do not interfere; (see table in APHA reference). 2. Requires standards. 3. Uses poisonous and/or controlled substances.

Table 3.43
SUMMARY OF PUBLISHED METHODS

<u>CONSTITUENT</u>	<u>METHOD</u>	<u>RANGE</u>	<u>PRECISION ACCURACY</u>	<u>DESCRIPTION</u>	<u>COMMENTS</u>
Zinc (contd)	Polar- ography APHA 211(III)B	>0.1 mg/l	---- ----	Zinc is determined qualitatively and quantitatively in the presence of other metals by its $E_{1/2}$ and the current height of its polarographic wave.	1. Interferences: compounds with $E_{1/2}$'s similar to Zn. 2. Standards recommended.

Other possible methods: Zn specific electrode, plasma arc emission.

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