Simplified Testing for Lead and Copper in Drinking Water

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By Charles R. Gibbs

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Introduction

Effects and Sources of Lead and Copper

Legend has it that one of the reasons for the collapse of the Roman Empire in ancient times was the use of lead for water pipes and wine goblets. Today, scientific evidence shows elevated levels of lead in blood can cause serious mental and physical health problems, especially for children. When the United States Environmental Protection Agency (USEPA) issued regulations covering lead and copper in drinking water, a rather extensive list of health effects was included. (Ref.1)

Lead produces negative effects in the body as low as 10 µg/dL of blood or less. It accumulates in the body from a variety of sources: water, paint, dust, air, soil and food. Lead interferes with a number of biochemical processes on the cellular level. In children, this results in altered physical and mental development, interference with growth, and deficits in intellect, attention span and hearing. Elevated levels of lead in women result in low birth weights and premature births. Blood pressure increases in both men and women when lead levels in the blood are elevated, and evidence indicates lead probably is a human carcinogen. Because there is an accumulation of effects with blood lead levels, the USEPA has determined there is no "safe" threshold below which lead has no negative effects. Furthermore, lead serves no purpose in the body and is not required for life.

Conversely, copper is beneficial at low levels and is required for certain biochemical processes. But there can be too much of a good thing. High copper concentrations in water can cause stomach and intestinal distress. High levels may also be hazardous to persons with Wilson's Disease, a genetic disorder involving copper metabolism. Copper appears to have no effect when the daily intake is below 5 mg.

Neither lead nor copper is commonly found in raw or treated drinking water as it enters the distribution system. Less than one percent of source water contains more than 0.005 mg/L lead or 1.0 mg/L copper. Both metals may appear in the consumer's tap water as a result of corrosion of pipes and fixtures by "aggressive" water in the distribution systems. Among the sources for lead are pipes in older plumbing and distribution systems, solder, and brass or bronze fixtures which commonly contain lead. The amount of lead leached depends on many factors. Among them are the amount and age of the materials susceptible to corrosion, the contact time, and the corrosivity of the water (which is affected by pH, hardness and alkalinity). Because the first two factors can vary within a building, it is important to realize that *lead levels can vary greatly from tap to tap in the same structure.* The presence of copper at the tap results mainly from low-pH water dissolving copper from the copper piping used in plumbing systems.

Lead and Copper Regulations

Current USEPA regulations for lead and copper are long, complex and comprehensive. Maximum contaminant level goals (MCLG) and action levels, as well as treatment techniques and monitoring requirements, are mandated. The usual requirements for public notice, record keeping and reporting, variances, exemptions, and compliance schedules (based on system size) are in effect. In addition, analytical methods and laboratory certification requirements stipulate applicable data must be reported to the USEPA. Any method may be used for testing conducted for process control, system surveys or customer education purposes.

Goals of the regulations are to provide customers with water containing 0 µg/L lead and less than 1.3 mg/L copper right from the time they turn on the tap in the morning. However, the action level for lead contamination is 15 µg/L of lead (0.015 mg/L) in "first-draw" samples from high risk locations. The action level for copper is the same as the goal. Treatment techniques are required to minimize corrosion if the highest 10 percent of the samples tested exceed the action levels. Source water treatment also may be required. In addition, educational materials must be distributed to help people avoid exposure to lead. A comprehensive packet of information—titled "Lead and Copper: How to comply"—is available for purchase from the American Water Works Association, 6666 W. Quincy Avenue, Denver, CO 80235, telephone 303-794-7711. Consumers should obtain the packet if they suspect they might be affected by these regulations.

Test Methods for Determining Metals in Water

The most common ways of determining the amount of a metal dissolved in water involve spectroscopy of various sorts. The least expensive and simplest is colorimetry. It involves reacting the metal ions in water with chemicals which produce a colored complex. The concentration of the metal can be determined by measuring the amount of color when shining a light through the solution. Cost to initiate testing would range from $300 to $1600 depending on the instrument (colorimeter or spectrophotometer) chosen. The cost per test would be $0.25 (for copper using CuVer® reagent) to $4.50 (for lead using the LeadTrak® system) plus labor. Technical training is not required if these Hach simplified methods are used.

Atomic absorption spectroscopy (AAS) is more complex and expensive than colorimetry. After sample preparation, the liquid is vaporized with a flame or furnace and carried through a light beam. Individual atoms absorb particular ultraviolet wavelengths of light. The amount absorbed is related to the amount absorbed by a standard and the quantity of metal in the water is determined. Costs for initiating testing would range from $10,000 to $100,000 depending on the instrument and other equipment needed. The sensitivity needed for drinking water testing requires the use of the graphite furnace AAS instruments (GFAAS) at

the more expensive end of the range. The cost per test would be about $20.00 to $35.00 based on commercial laboratory charges. A technical background in chemistry is required to obtain accurate results.

Inductively coupled plasma (ICP) emission spectroscopy is the most complex and expensive method, but multiple elements can be measured at the same time when this method is used. The sample is vaporized in an extremely hot plasma torch. The atoms become so hot they emit light—a different wavelength for a given element. The amount of light is measured to determine the amount of the element present. In some cases, notably lead, a mass spectrometer is coupled to the ICP device to gain greater sensitivity in detection. Such instruments cost $100,000 to $250,000. Costs per test ranges from $15 to $50 and a technical background is required.

Other methods of testing for metals in water, including various electrochemical methods such as ion selective electrodes and polarography, tend to be limited in application for a variety of reasons. Certain methods are required for obtaining test results to be reported to the federal government. In addition, the testing must be done in a certified laboratory. However, tests which are not going to be reported to the government can be done by anyone using any method. The USEPA has approved two furnace AAS techniques and the use of ICP coupled with mass spectroscopy for lead analyses and three AAS techniques and two ICP methods for copper analyses for their drinking water test requirements.

Comparison of Atomic Absorption and Colorimetric Methods

The table below summarizes the characteristics of the atomic absorption and colorimetric methods used in determining the level of lead in drinking water. Generally speaking AAS is most useful for large laboratories doing a large number of tests—20 or more per day—several days per week. The Hach LeadTrak colorimetric method is most useful for running a smaller number of tests per week or for anyone doing on-site testing for surveys, screening or education. A limited number of test results—determined in a certified laboratory where approved methods are used—must be reported to the government. However, LeadTrak methods are ideal for the additional tests conducted. Accurate results are achieved immediately and savings, in both time and money, are significant. Numerous studies have shown the accuracy, precision and reliability of results obtained while using the LeadTrak method are comparable to atomic absorbance results. These research reports are covered in subsequent material.

Lead Test Comparison Table

Characteristic	GFAAS	LeadTrak
1. Can be done		
on site	no	yes
in laboratory	yes	yes
2. Approved by USEPA for reporting	yes (furnace)	pending (note 1)
3. Skill level needed	high	low/med
4. Time required		
to set up	30 minutes	3 minutes
per test	5 minutes	10minutes
5. Cost		
to set up	$10-100,000	$300-1600
per test	$20-35	$4-5
6. Detection limit	1 µg/L	2 µg/L
7. Range	1-100 µg/L	2-150 µg/L
8. Calibration	weekly/ daily check	direct reading/ weekly check
9.Interferences	"molecular absorbance as well as chemical and matrix effects" (note 2)	See list in method

Notes:
(1) Submitted data to USEPA for approval in January, 1990. As of February 1, 1994 no determination had been made.
(2) *Standard Methods for the Examination of Water and Wastewater* 17th edition, pages 3-32

Applications and Benefits of Simplified On-site Testing

On-site testing, once considered useful for "rough estimates" only, is increasing rapidly. Reasons for the increased usage include advances in portable microprocessor instruments and analytical methods. It is now possible to obtain immediate results on site that are comparable in accuracy and precision to those obtained days later in the laboratory. This aspect of immediacy offers great advantages:

- Sources of lead can be immediately tracked and identified.
- Results are available for follow-up testing while personnel is on the site.
- Screening prioritizes samples for laboratory confirmation.
- Results can be used for demonstration and education.

Compared to atomic absorption instrumentation, the LeadTrak system offers a cost-effective way to perform the broad surveys needed when operating a small to medium-sized drinking water system. Checks of only a few sites in the distribution system are not sufficient. Sources for high levels of leached lead—the sites, coolers and fixtures—must be located. Even within the same building there can be a wide variation. For example, a study of school water coolers showed wide variations within the same school (Ref. 2). Operators using the LeadTrak test kit checked all the coolers and replaced only those with water measuring too high in lead—no more and no less. Similar tests in a

Hach employee's home showed 2 ppb lead in the kitchen tap but 32 ppb in an upstairs bathroom tap (Ref. 3).

Other benefits of on-site testing include education and contamination source identification. If a sample taken after the water has stood in the fixture for eight hours (a first draw sample) shows lead contamination, a second sample can be taken after flushing the line. If this does not show lead, then the source can be isolated to fixture corrosion. The water customer can be educated to flush the lines before use to avoid ingesting lead. For example, the lead level dropped from 32 to 1 ppb after flushing the Hach employee's bathroom faucet referred to above. Conversely, if the flushed sample shows a significant lead level, lead service lines should be considered as a source of contamination and other preventive strategies pursued. Finally, if no lead is found in either sample, a customer who has observed the test can be reassured drinking water in the structure is safe. This would be particularly useful if initial action level violations had been followed by public notification and corrosion treatment changes.

Comparability of Results Between Methods

How Methods Are Compared

As an alternative to comparability studies, many analysts are turning to a demonstration of accuracy appropriate to their specific application. Most commonly this is done by "spiking" a sample to show acceptable recovery of the spike. This is called "standard additions" or "known additions". For example, if the analyst found 10 µg/L of lead in a drinking water sample, the analyst could then add a small amount of concentrated standard to increase the concentration by another 10 µg/L. If the second test showed a result of 18-22 µg/L (within 10 % of the expected value), the analyst could be reasonably confident the method worked on the sample type and the technique of the analyst was good. If the second result was outside those limits, then further work might be considered. Hach has published a technical paper which discusses the application of standard additions. It is available upon request (Literature Code 7004).

When reporting to a government agency is required, and the agency has an approved method, comparison of the approved method and another method may be necessary. This is done by splitting the sample and analyzing it with the two methods. Typically, if the level of analyte is low, the sample is spiked before splitting it. Often each portion is tested several times by each method to make allowance for normal variance. When split samples are tested it is necessary to be sure that each method, including any sample preservation techniques, is followed exactly. Several studies, cited below, developed problems because samples were not split before preserving them for the LeadTrak method. In addition, the wrong preservative was used.

A number of samples, representing the cross section of conditions expected to be encountered, need to be tested for a more rigorous statistical study. For example, the USEPA protocol for Alternative Test Procedure (ATP) approval calls for: (Ref. 4)

- 10 different water source samples
- 3-4 sub-samples from each, and
- 3 analyses using each of the 2 methods

This is a total of 180-240 tests plus a number of quality control (QC) checks. Screening tests are also required to determine if the samples contain a detectable level of analyte. If not, they must be spiked.

The data manipulation for proving the two sets of results are equivalent is quite complex. The first step is to obtain an average value (mean) and standard deviation for the four tests run on each of the 30 samples by each method. From this point, two methods of evaluation can be used. Regression analysis uses a graphical plot of one test method's mean values versus the other test method's results. A best straight line fit is calculated and the slope, intercept and r values are determined. See Figure 1 for an illustration. The second method calculates the collective mean and standard deviation for both test methods and uses specific statistical approaches to determine if the means and variances are the "same" at an acceptable confidence level—usually 95%.

A third approach, gaining in popularity, is to simply evaluate the proposed method carefully to see if the data produced meets the needs for which the testing is being done. This is commonly called a Data Quality Objectives approach. (Ref. 5) Often the approved or standard method will be evaluated in parallel as a comparison. The EPA study on the LeadTrak kit (Ref. 6,7), discussed below, was evaluated in parallel. Obtaining data which has an accuracy and precision level sufficient for the purpose of your test is the goal. For example, a survey to determine where the greatest lead hazards from plumbing corrosion occurs does not require absolute accuracy in case of legal challenges. But it should enable the analyst to make decisions in the field about follow-up samples or laboratory confirmation. Similarly, if process changes are being made, rapid trend-indicating results are necessary. The data quality objectives in these cases would be quite different from the data required to report to a governmental agency—where a 0.5 ppb difference might indicate non-compliance.

The introduction to the Schock-George paper (Ref. 6) offers a good general discussion of how to evaluate a method. Their analysis is very rigorous and the data they obtained is broadly applicable. Most water system laboratories would not have to be as rigorous in their testing because:

1. the water in the system being tested is assumed to have consistent characteristics; and

2. once a comparability study has been done and consistent results are obtained, the compared method may be used by anyone.

The variation in the water system or geographic area determines the number and make-up of the water samples to be tested. The authors suggest obtaining the following values for each method:

- lowest concentration that can be reliably detected
- sensitivity
- range of use without dilution
- precision and accuracy of results over the range
- interferences and their effects
- ability of different analysts to obtain the same result
- need for changes in the sample handling routine

Comparability Studies on CuVer and LeadTrak

CuVer Methods for Copper

A comparability study to obtain EPA approval for wastewater (NPDES) reporting was performed using Hach's CuVer Copper Reagent 1 method versus Atomic Absorption. (AA). Two different laboratories tested a number of effluent types which included electroplating, refining and chemical plant outfalls. The EPA's statistical analysis showed no significant difference between the results generated by the two methods. CuVer was approved as an alternate test procedure by the EPA. (Ref. 8) This data, and added samples, was compiled in a paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. (Ref. 9)

Because wastewater reporting data requires determination of total copper, the samples above required mild digestion. However, drinking water samples generally contain only dissolved copper and no digestion is needed. If complexing agents are added to the water, CuVer 2 should be used, as it determines both complexed and free copper. If the sample has been preserved with nitric acid, the instructions in the method for pH adjustment must be followed because excess acidity causes sample turbidity. pH adjustment may be performed before adding CuVer, or afterward if turbidity occurs. Since copper levels in drinking water are much higher than limits in wastewater effluent, the analyst can be confident using CuVer for system surveys or other drinking water applications.

LeadTrak Method for Lead

Because of interest in low-cost on-site analytical methods for lead in drinking water, many independent studies have compared LeadTrak to AAS methods. These studies were done to find a screening method that could rapidly determine the effects of treatment changes on tap lead levels. Using LeadTrak reduces both cost and response time. Often, only samples that exceed a screening action level are sent to the laboratory for Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS) confirmation.

Additionally, if high levels are found, on-site results can guide the selection of other sampling points to aid in the location of lead sources. Changes to water conditions (such as flushing lines, changing hardness or pH, etc.) can be immediately checked for effectiveness. The U.S. Postal Service study found that "the field kit screening techniques can be utilized as a very effective means of reducing costs associated with a water testing program." (Ref. 10) Most importantly, all of the studies found that LeadTrak results were comparable in accuracy to the GFAAS reference method at the 95-99% confidence level.

Three major studies have compared data gathered using the LeadTrak method versus GFAAS:

1. Hach/Enseco USEPA Alternate Test Procedure Protocol (Ref. 11)
2. U.S. Postal Service/Roy F. Weston Inc. Federal Facilities Survey (10)
3. USEPA-Drinking Water Research Division/Technology Applications Inc. Test Kit Evaluation (6,7)

In addition, the Seattle School District and Economic and Engineering Services, Inc. (Ref. 2) conducted a small study that found, as long as correct sample preservation methods are followed, a greater than 99% statistical assurance that the two methods give similar results. Patrick Wiese, inventor of the LeadTrak method at Hach Company, also reported similar results at the American Water Works Association (AWWA) Annual Conference in 1989. (Ref. 12) Perhaps the most impressive data presented was the precision of a 105 ± 11% recovery of a small 9 ppb spike on real-world samples. In addition, the relative standard deviation of 7.1% on 8 replicates of a 10-ppb standard yields a method detection limit of 2.0 ppb. Other studies have yielded a detection limit ranging from 2-4 ppb.

The Hach/Enseco study covered five different sources of drinking water. As designed by the USEPA for their Alternate Test Procedure Approval program, six samples were taken at the inlet to each water system. Each sample was split and each half tested four times by each method being compared, resulting in 240 data points (5x6x8). Half of the samples were tested by Enseco's Houston Laboratory and half by Enseco's Rocky Mountain Analytical Laboratory. The data (see Appendix 1) was submitted to the EPA in January 1990 with a request for approval of LeadTrak as an Alternate Test Procedure.

At this time (February, 1994) Hach has not received a ruling on the request. Simultaneously with the submittal, Hach evaluated the data using the USEPA statistical protocol. This evaluation showed the LeadTrak method is equivalent to the reference GFAAS method in accuracy and precision at the 95% confidence level.

The results submitted to the EPA were on samples preserved and digested according to EPA protocol for total lead. As noted in the LeadTrak method, this required the additional step of neutralizing the excess acid. This apparently did not affect the comparability but adds additional steps. To determine if the digestion was necessary, a set of data using both GFAAS and LeadTrak methods was generated on non-digested samples Interestingly, the LeadTrak dissolved and total results were

comparable at the 93% level to each other but the GFAAS results were not comparable with each other.

A July 1993 article by Lytle et al. of the USEPA (Ref. 13) reports hot acid digestion is not required to solubilize lead from particulate matter. Their data "indicates that lead and lead-containing particles are completely dissolved by the standard preservation technique of acidification to 0.15 percent HNO_3". Preservation "should give essentially the same concentration results as hot acid digestion for virtually all important lead sources in drinking water, reducing the need for burdening small laboratories and utilities with complicated procedures that introduce sample-handling variability, potential sources of contamination, and additional safety concerns." The article also discloses in January 1992, there was a change or clarification to the [digestion] requirement that specifies only water samples having a turbidity >1 NTU be subjected to the additional digestion step when they are being analyzed by AAS methods. There is, however, no technical reason why this should not also be applicable to the LeadTrak method which also uses a nitric acid preservation.

The study by Stofferahn et al. for the U.S. Postal Service, demonstrated that using the LeadTrak kit for screening samples in a survey is both technically feasible and cost effective. The LeadTrak method "can be utilized as a very effective means of reducing costs associated with a water testing program." This was true even when labor costs associated with the screening effort were considered. The screening procedure is cost-effective when screening is conducted on the entire sample population and when selectively performed on sample types shown to exhibit a high rate of frequency of elevated lead concentrations.

The screening results were used for two purposes in this study; both reduced analysis costs. First, if the on-site LeadTrak result on a first-draw sample was above 12 ppb, an additional flush sample was taken to locate and quantify the potential source(s) of lead contamination. Secondly, a screening action limit (SAL) was calculated. The SAL is the minimum concentration that would trigger laboratory analysis of that sample. In this case, a SAL of 9.5 ppb was used to eliminate samples considered to be "clean" from the laboratory analysis. The regression analysis showed it is technically feasible to obtain the SAL by the LeadTrak screening procedure.

A major study by Schock and George (USEPA and Technology Applications, Inc., respectively) also evaluated the LeadTrak kit. The work was motivated by the needs of field investigators doing corrosion control studies for small water systems. The goal was to control costs of analysis and reduce result turnaround time. The evaluation of the kit included:

- precision and accuracy on a range of standards
- determination of operator-related bias
- comparison of results to GFAAS results on standards
- effects of interferences
- recovery of spikes in various drinking waters
- sample preservation and QC considerations

Precision and Accuracy of Standards

While the authors' purpose was not to approve the test kit, the results are encouraging for using the kit as a practical field analysis method. They found the detection limit of the test kit to be 4 µg/L. Above that level they determined that "the accuracy of the GFAAS and test kit procedures in spiked deionized water [standards] were comparable". The precision of the test kit was not as high as GFAAS at low concentrations but the authors noted that "for screening work, the difference is of little practical consequence". For example, they noted the uncertainty at a 95% confidence level in the estimation of a single 15-µg/L value for an unknown was 17% (2.6 µg/L) for GFAAS and 18% (2.7 µg/L) for LeadTrak.

Operator Related Bias

The examination of "operator bias" attempts to determine if the method is designed so that no special technique or analysis experience is needed. The study used one person who had performed several hundred LeadTrak analyses versus two first time users of the test kit. When using the test kit in the laboratory to analyze for levels of lead between 0 and 80 µg/L, statistically no operator bias was seen at the 95% confidence level. It was also noted that for students, engineers, technicians, or chemists somewhat familiar with water testing, considerable skill can be obtained with water testing with very little practice and the test kit can be employed reliably in a short time. The study also found that the pooled slope of their test kit calibration curves agrees with the present instrument curve within the computed statistical uncertainty limits. Analysts using the LeadTrak method can place a high level of confidence in the direct read-out capabilities of Hach instruments.

Graphing the values of standards found by the two methods against each other enabled a slope and intercept of the best straight line to be calculated. The regression analysis of the data showed good statistical agreement between the two methods at the 90% confidence level. This is indicated by a slope not statistically different from unity and an intercept not statistically different from zero. The results are also very nearly equivalent at the 95% confidence level.

Another comparison of the methods involved spiking samples of drinking water collected from various locations. This was similar to the Enseco-Hach comparability study, but on a smaller scale. Each method was applied to six different samples which had been spiked with lead standard solution to produce a 15 µg/L concentration. One sample showed an extremely high GFAAS recovery value (over 150%) and was discarded. The average recovery on the five GFAAS samples was 106% while the recovery on the six LeadTrak samples was 94%. The statistical analysis showed that the differences between percent lead recoveries at 15 µg/L for single samples was not significant at the 95% confidence level.

Effects of Interferences

Schock and George also evaluated the effects of potentially interfering cations and anions on a 25 µg/L lead standard. The ion concentrations were chosen to be extreme values to simulate worst case levels in actual drinking water systems. The results generally were consistent with those previously reported by Wiese and included in the method description. Several polyphosphates tested at the 5 mg/L level suppressed recovery of lead. However, since there were no other metal ions present in the standard, this effect may not occur in real-world samples. It is always advisable to test the water supply for interferences by the use of spike recovery or standard addition checks on actual samples.

Sample Preservation

Schock and George also found the method does require neutralization of nitric acid added for preservation (per instructions). They determined the best approach for split sample comparison was to split the sample and them use the appropriate preservative for each half—pPb-1 for LeadTrak samples and nitric acid for GFAAS samples. pPb-1 cannot be used as a preservative in GFAAS samples because it causes low recoveries of standards unless an alternative matrix modifier is used. This new matrix modifier for GFASS is described in the paper and has been adopted for routine lead analyses in the author's laboratory.

Conclusion

The Hach LeadTrak method has been studied by several groups. Although very low concentrations affected precision and repeatability, accuracy was found to be comparable to the EPA-accepted Graphite Furnace Atomic Absorption method. The detection limit of the LeadTrak method is 2 to 4 µg/L and the groups agree that LeadTrak is an excellent method for screening samples for the action lead level of 15 µg/L. The LeadTrak method offers cost savings and rapid turn-around of results. The CuVer copper method offers similar advantages. Application of both methods provide rapid feedback when developing new corrosion treatment strategies.

References

1. *Federal Register,* 56 FR 26460 (June 7, 1991).

2. L. Odell, Report: "Reducing Lead in School's Drinking Water: A Case Study", p. 1-9 (1991).

3. P. Wiese, Hach Co. unpublished data (1989).

4. United States Environmental Protection Agency, Office of Research and Development, "Protocol for Nationwide Approval...." Revision 1.4, (July 14, 1993).

5. For example, R. G. Mealy, "Data Comparability and Defensibility," *Environmental Testing and Analysis,* p. 36-43, (March/April, 1993).

6. M.R. Schock and G. K. George, "Evaluation of a Field Test Kit for Monitoring Lead in Drinking Water", *Journal AWWA*, Vol. 85 No. 8, pp. 90-100. (August 1993)

7. G. K. George et al, "A Comprehensive Evaluation of a Field Test Kit for Lead", *WQTC Proceedings, 1991,* p.263-288.

8. 40 CFR Sec. 136.3 p. 305 (July 1, 1992).

9. C. Gibbs, "A Statistical Evaluation of the DREL/4 Portable Laboratory versus 'Standard Methods'", presented at the Pittsburgh Conference on Analytical Chemistry, March 5, 1979.

10. J. Stofferahn et al, "Assessing the Occurrence and Distribution of Lead in Drinking Water—A Federal Facilities Perspective", *Proceedings Water Environment Federation 1992 Annual Conference,* p. 353-363.

11. Hach Co. unpublished data. (1990)

12. P. Wiese, "Monitoring Method for Lead in First-Draw Drinking Water Samples", presented at the 1989 AWWA Annual Conference (June 19-23, 1989).

13. D. A. Lytle et al, "Investigating the Preferential Dissolution of Lead from Solder Particulates", *Journal AWWA,* Vol. 85 No. 7, pp. 104-110, (July, 1993).

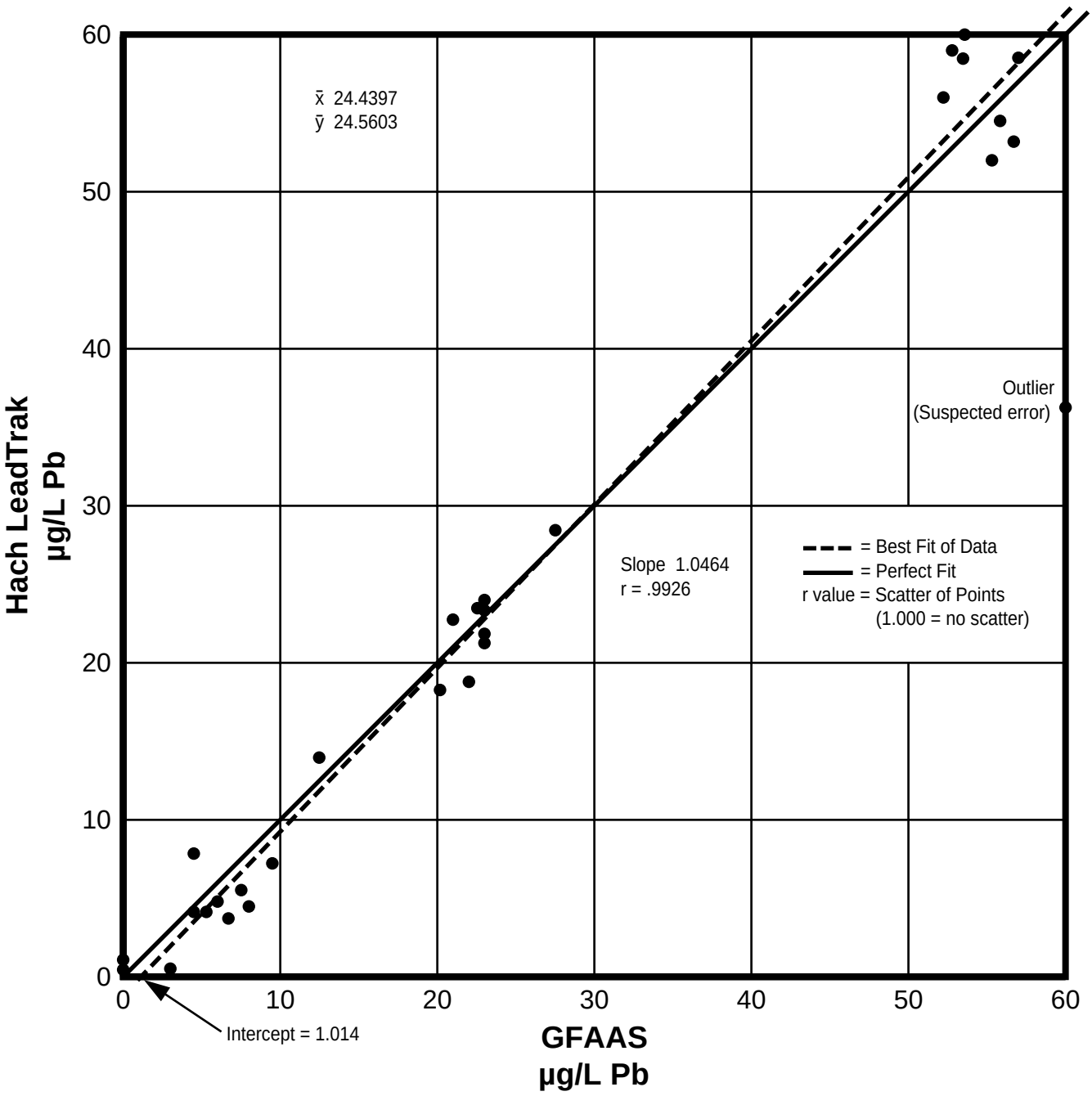
Comparability Data: LeadTrak Method vs GFAAS Method

Data from two independent commercial laboratories comparing results from the Hach LeadTrak method and Graphite Furnace Atomic Absorption method on split real-world samples. Most were spiked at varying levels due to non-detectable natural lead levels.

Sample	Meth.	Spike	Repl 1	Repl 2	Repl 3	Repl 4	x	s.dev	Recov	Range Recov.
S-1-1	AA	0	0	0	0	0	0	0.0	–	–
	LT	0	2	0	0	0	0.5	1.0	–	–
S-1-2	AA	5	5	5	4	5	4.75	0.5	95%	80-100
	LT	5	8	7	7	9	7.75	1.0	155%	140-180
S-1-3	AA	0	12	13	12	13	12.5	1.0	–	–
	LT	0	14	14	14	14	14.0	0.0	–	–
S-1-4	AA	20	21	22	23	22	22.0	0.8	110%	105-115
	LT	20	22	14	19	20	18.75	3.4	94%	70-110
S-1-5	AA	50	56	58	58	56	57.0	1.2	114%	112-116
	LT	50	58	60	59	57	58.5	1.3	117%	114-120
S-1-6	AA	50	51	54	51	53	52.25	1.5	105%	102-108
	LT	50	56	55	56	57	56.0	0.8	112%	110-114
S-2-1	AA	5	6	4	4	3	4.25	1.3	85%	60-120
	LT	5	6	5	6	4	5.25	1.0	105%	80-120
S-2-2	AA	5	4	5	7	8	6.0	1.8	120%	80-160
	LT	5	4	5	5	5	4.75	0.5	95%	80-100
S-2-3	AA	20	20	20	20	21	20.25	0.5	101%	100-105
	LT	20	20	18	18	17	18.25	1.3	91%	85-100
S-2-4	AA	20	17	22	24	21	21.0	2.9	105%	85-120
	LT	20	21	24	23	23	22.75	1.3	114%	105-120
S-2-5	AA	50	56	55	57	55	55.75	1.0	112%	110-114
	LT	50	55	54	53	56	54.5	1.3	109%	106-112
S-2-6	AA	50	56	56	55	54	55.25	1.0	112%	108-112
	LT	50	54	49	52	53	52.0	2.2	104%	98-108
S-3-1	AA	5	10	10	9	9	9.5	0.6	190%	180-200
	LT	5	11	5	7	6	7.25	2.6	145%	100-220
S-3-2	AA	5	7	4	0	7	4.5	3.3	90%	0-140
	LT	5	4	4	4	5	4.25	0.5	85%	80-100
S-3-3	AA	20	23	20	23	25	22.75	2.1	114%	100-125
	LT	20	22	22	21	20	21.25	1.0	106%	100-110
S-3-4	AA	20	23	22	24	22	22.75	1.0	114%	110-120
	LT	20	21	23	25	25	23.5	1.9	118%	105-125
S-3-5	AA	50	56	57	57	57	56.75	0.5	114%	112-114
	LT	50	53	55	54	51	53.25	1.7	107%	102-110
S-3-6	AA	0	0	0	0	0	0	0	–	–
	LT	0	0	2	2	0	1.0	1.2	–	–
S-4-1	AA	5	8	8	8	8	8	0	160	160-160
	LT	5	4	3	6	5	4.5	1.3	90	60-120
S-4-2	AA	5	7	6	7	7	6.75	0.5	135	120-140
	LT	5	4	3	4	4	3.75	0.5	75	60-80
S-4-3	AA	20	22	23	23	23	22.75	0.5	114	110-115
	LT	20	21	18	24	23	21.5	2.6	108	90-120
S-4-4	AA	20	28	27	27	28	27.5	0.6	138	135-140
	LT	20	28	30	28	28	28.5	1.0	143	140-150
S-4-5	AA	50	53	53	54	55	53.75	1.0	108	106-110
	LT	50	58	62	59	61	60.0	1.8	120	116-124
S-4-6*	AA	50	59	60	59	60	59.5	0.6	119	118-120
	LT	50	37	34	42	34	36.75	3.8	74	68-84
S-5-1	AA	0	3	3	3	3	3	0.0	–	–
	LT	0	1	1	0	0	0.5	0.6	–	–
S-5-2	AA	5	8	7	8	7	7.5	0.6	150	140-160
	LT	5	6	6	5	5	5.5	0.6	110	100-120
S-5-3	AA	20	23	23	23	23	23	0.0	115	115-115
	LT	20	21	25	24	24	23.5	1.7	118	105-115
S-5-4	AA	20	23	23	23	23	23	0.0	115	115-115
	LT	20	23	24	23	24	23.5	0.6	118	115-120
S-5-5	AA	50	53	53	52	53	52.75	0.5	106	104-106
	LT	50	60	56	62	58	59.0	2.6	118	112-124
S-5-6	AA	50	53	54	53	54	53.5	0.6	107	106-108
	LT	50	60	57	58	59	58.5	1.3	117	114-120

*outlier - suspect error
x = average
std. dev. = standard deviation
recov. = average recovery of spike
LT = LeadTrak
AA = Atomic absorption
Data Source: ENSECO - RMAL
Data Source: ENSECO Houston

Figure 1.
Graph of Comparability Data



LeadTrak Fast Column Extraction Method Chemistry Explained

Hach's ingenious LeadTrak™ test is accurate, yet requires neither cyanide complexing agents not organic solvents to produce results in the parts per billion (ppb) range.

Add pPb-1 Acid Preservative Solution to the sample. Because pPb-1 Solution also preserves samples, testing can be done up to six months later.

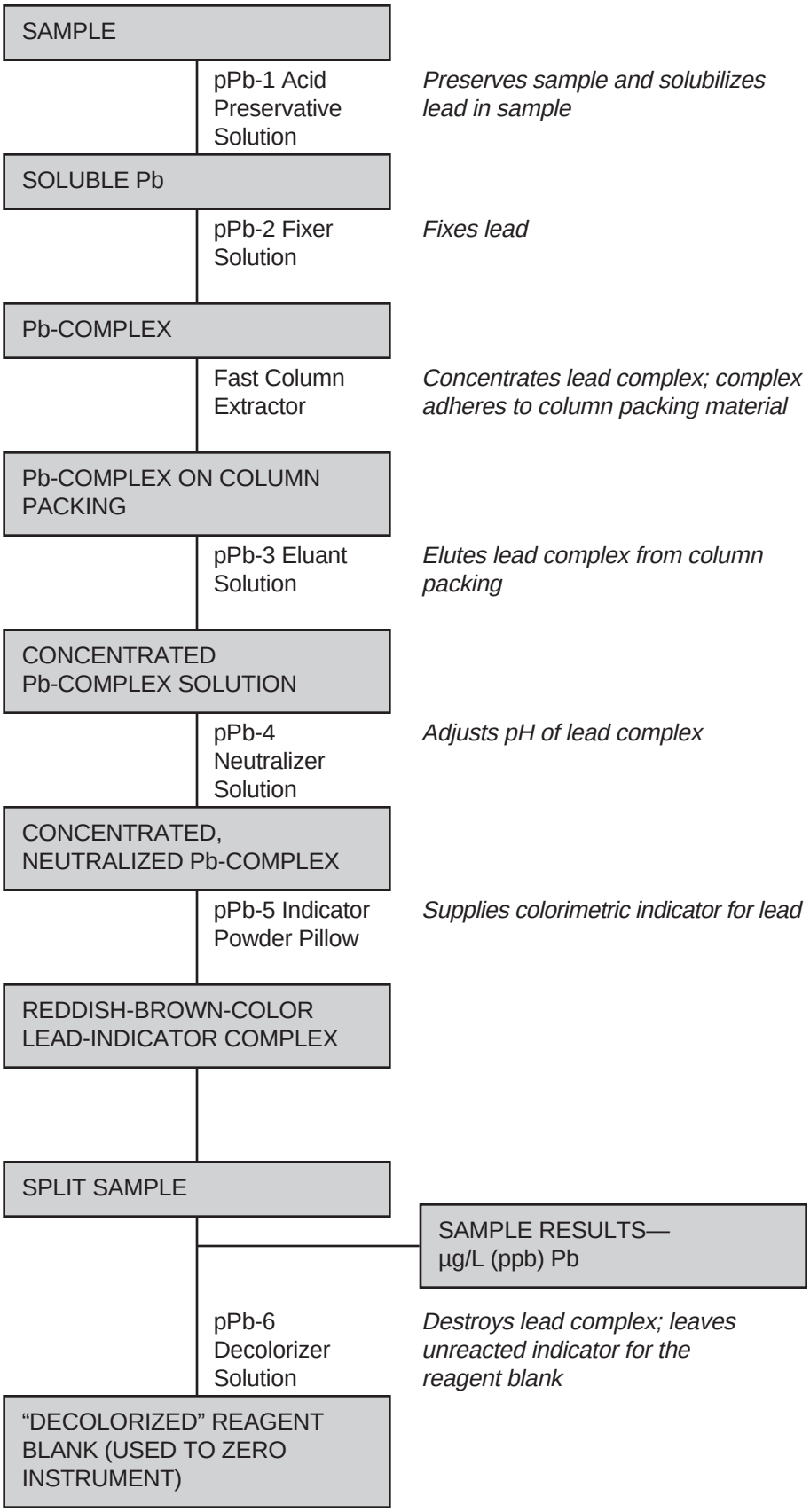
After mixing and allowing a two-minute reaction (in order to solubilize lead that may be present), add pPb-2 Fixer Solution. Next, pour the sample through the Fast Column Extractor to separate the lead from interferences and fix the lead on the column. Then, elute or "liberate" lead from the column packing material by adding pPb-3 Eluant Solution. Neutralize the eluted sample with pPb-4 Neutralizer Solution.

Your sample now is ready for colorimetric analysis. Simply add the contents of one pPb-5 Indicator Powder Pillow and mix thoroughly. Any lead present will react with the indicator, forming a reddish-brown colored complex, within two minutes.

Next, prepare a reagent blank by decolorizing half of the treated sample. Use pPb-6 Decolorizer Solution. This will destroy the lead-indicator complex and leave only the indicator remaining. This reagent blank may not be visually different from the remaining treated sample due to the excess indicator present. Use this reagent blank to zero a DR 100 LeadTrak Colorimeter or a spectrophotometer set at 477 nm. Read levels from the other (not decolorized) portion. Hach DR/2000 and DR/3000 Spectrophotometers* and the LeadTrak DR 100 Colorimeter supply results directly in µg/L lead.

*Sample is not split when using a DR/3000. Sample is read before and after the addition of pPb-6 to give results directly in µg/L lead.

LeadTrak is a Hach Company trademark.



Copper Bicinchoninate Method Chemistry Explained

Introduction

Although copper comprises only 0.007% of the earth's crust, it is a very important element. copper occurs free and combined in nature in many minerals. Copper may occur in natural waters, wastewaters and industrial waste streams as soluble copper salts, or as copper compounds precipitated on suspended solids. Forms of copper in water can be classified as insoluble, dissolved (free and complexed) and total recoverable. Insoluble copper includes precipitates such as copper sulfides and hydroxides. All copper in solution is known as dissolved copper. Included are Cu^{1+} (cuprous) and Cu^{2+} (cupric) ions and copper chelates such as CuEDTA.

Copper concentrations in potable water usually are very low. Copper is not considered a health hazard to humans although more than 1 mg/L can impart a bitter taste to water and large oral doses can cause vomiting and eventually may cause liver damage. Copper salts, such as copper sulfate, $CuSO_4$, may be used to control algae, however, they also may be toxic to fish and wildlife. Hach's simplified test procedures for copper use a variety of reagents, depending on the range of detection desired and the form of copper to be measured. The table below lists the Hach proprietary reagents and their applications.

Chemistry of the Bicinchoninate Method

Copper can be determined by the reaction of copper with 2.2'-biquinoline-4,4'-dicarboxylic acid (bicinchoninic acid). Bicinchoninate reacts with Cu^{1+} to produce a purple-colored complex.

Bicinchoninate does not react readily with Cu^{2+}. Determination of Cu^{2+} begins by reducing it to Cu^{1+}. CuVer® 1 Reagent combines the bicinchoninate reagent with a buffer and reducing agent to allow determination of Cu^{1+} and Cu^{2+}. Total recoverable copper can be determined with this method if the sample is digested first to convert all of the copper present (including insoluble forms and complexed forms) to free copper.

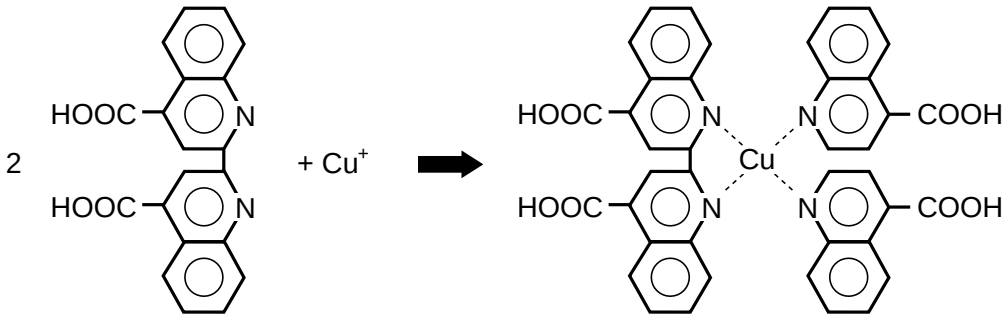
Hach Copper Reagents

Reagent	Form Measured		Application
	without pretreatment	with digestion	
CuVer 1	Free	Total Recoverable	water, wastewater
CuVer2	Total Dissolved Copper	Total Recoverable	
Free Copper Reagent	Free	Total Recoverable	hard water, wastewater, seawater

Complexed copper forms such as CuEDTA react directly with CuVer 2. Digestion is not necessary and high levels of hardness do not interfere. The results will be in terms of total dissolved copper (free and complexed). When using CuVer 1, digestion is necessary and high levels of hardness interfere.

If free copper is to be determined separately from complexed copper, use Free Copper Reagent Powder Pillows. These powder pillows contain bicinchoninate, a reducing agent and an inhibitor to eliminate calcium and magnesium interference. The results will be in terms of free copper. Complexed copper may then be determined by addition of Hydrosulfite Reagent repeating the analysis.

Reaction of Cu^{1+} and Bicinchoninic Acid



Ordering Information

LeadTrak Method

Required Reagents

Description	Qty/ Test	Unit	Cat.No.
LeadTrak, reagent set, 20 tests/pkg	1		23750-00

Required Apparatus

Cylinder, graduated, polypropylene, 100 mL	1	each	1081-42
Cylinder, graduated, polypropylene, 25 mL	1	each	1081-40
Beaker, polypropylene, 250 mL	1	each	1080-46
Beaker, polypropylene, 150 mL	1	each	1080-44
Support, ring stand	1	each	563-00
Clamp, two-prong extension	1	each	21145-00
Clamp, holder	1	each	326-00
Clippers, small	1	each	936-00
Adapter, AccuVac	1	each	43784-00
Sample Cell, 10 mL, with cap	2	each	21228-00

Optional Reagents

Lead Standard Solution, 1000 mg/L	100 mL	12796-42
Lead Standard Solution, Voluette ampule, 50 mg/L as Pb^{2+}, 10 mL	16/pkg	14262-10
Nitric acid, ACS	500 mL	152-49
Nitric Acid Standard Solution, 0.1 N	100 mL	23328-42
pPb-1 Acid Preservative Reagent	237 mL	23685-31
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Water, deionized	3.78 L	272-17

Optional Apparatus

Bottle, sampling, 125 mL	each	23240-43
Bottle, sampling, 125 mL	48/pkg	23240-73
Bottle, sampling, 1000 mL	each	23242-53
Bottle, sampling, 1000 mL	24/pkg	23242-83
Dropper, plastic, Squeezers	10/pkg	21247-10
Flask, volumetric, plastic, 100 mL	each	20995-42
Flask, volumetric, plastic, 1000 mL	each	20995-53
pH meter, portable	each	43800-00
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet, TenSette, tips for 19700-01	50/pkg	21856-96
Pipet, volumetric, 1.0 mL	each	14515-35
Pipet, volumetric, 5.0 mL	each	14515-37
Pipet filler	each	12189-00
Pipettor, 100 µL	each	22753-00
Stopper, hollow	6/pkg	14480-00

Copper Bicinchoninate Method

Required Reagents (Using Powder Pillows)

Description	Qty/ Test	Unit	Cat.No.
CuVer 1 Copper Reagent Powder Pillows	1	50/pkg	14188-66

Required Reagents (Using AccuVac Ampuls)

CuVer 2 Copper Reagent AccuVac Ampuls	1	25/pkg	25040-25

Required Apparatus (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968-00

Required Apparatus (Using AccuVac Ampuls)

Adapter, AccuVac vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

Optional Reagents

Copper Standard Solution, 100 mg/L	118 mL	128-14
Copper Standard Solution, Voluette ampule, 75 mg/L	16/pkg	14247-10
CuVer 2 Reagent Powder Pillows	25/pkg	21882-68
Formaldehyde, 37%	118 mL*	2059-37
Free Copper Reagent Powder Pillows	100/pkg	21186-69
Hydrochloric Acid Solution, 6 N	500 mL	884-49
Hydrosulfite Reagent Powder Pillows	100/pkg	21188-69
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	473 mL	2540-11
Potassium Chloride Solution, saturated	59 mL	765-26
Potassium Hydroxide Standard Solution, 8.0N	118 mL*	282-37
Sodium Hydroxide Solution, 5.0 N	118 mL*	2450-37
Water, deionized	3.78 L	272-17

Optional Apparatus

Cylinder, graduated, polypropylene, 25 mL	each	1081-40
Cylinder, graduated, 100 mL	each	508-42
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Filter Pump	each	2131-00
Flask, volumetric, 100 mL	each	547-42
Funnel, polypropylene, 65 mm	each	1083-67
Hot Plate, 3 1/2" diameter, 120 Vac	each	12067-01
Hot Plate, 3 1/2" diameter, 240 Vac	each	12067-02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, Hach One	each	43800-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 1.00 mL	each	515-35
Pipet Filler, safety bulb	each	14651-00
Pour-Thru Cell Assembly Kit	each	45215-00

*Contact Hach for larger sizes.