

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION
ANALYSIS OF DRINKING WATER

APPENDIX TO METHOD 200.7
REVISION 1.3

"Inductively Coupled Plasma Atomic Emission Spectrometric
Method for Trace Element Analysis of Water and Wastes"

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1. Scope and Application

- 1.1 This procedure is designed to be a supplement to Method 200.7 (1) and is to be used in processing drinking water supply samples prior to inductively coupled plasma-atomic emission spectrometric (ICP-AES) analysis. This appendix does not supercede Method 200.7, but provides elaboration on the analysis of drinking water using Method 200.7. For a listing of the recommended wavelengths, Definitions, and discussions on Safety, Reagents and Standards, and Sample Handling and Preservation see the appropriate Sections of Method 200.7.
- 1.2 This procedure is to be used for the total element determination of primary and secondary elemental drinking water contaminants included in Method 200.7. It is only to be used for compliance monitoring when the determined method detection limit (MDL) (2) for a particular contaminant is no greater than 1/5 its respective maximum contaminant level (MCL) concentration. For these reasons, mercury and selenium have been omitted from this edition of the appendix. A listing of the contaminants for which the procedure is applicable along with their MCLs and MDLs is given as Table 1.
- 1.3 This procedure is to be used in all pneumatic nebulization ICP analyses for compliance monitoring of drinking water, and is recommended for the analysis of ground and surface water where determination at the drinking water MCL is requested.
- 1.4 This procedure also can be used to determine the concentration of calcium (Ca) for calculating corrosivity and for the required monitoring of sodium (Na). Since these two elements can occur in waters at concentrations greater than 25 mg/L, particular care must be taken that concentrating the sample does not cause the analysis of these two elements to exceed the calibration limit of linearity. If standardization of the instrument does not include provision for non-linear calibration, a more convenient and allowable determination of these two elements is the direct aspiration analysis of the acidified unprocessed sample.

2. Summary of Method

- 2.1 For a description of the analytical technique and method summary see Section 2 of Method 200.7.

2.2 Analytical Discussion

- 2.2.1 The analysis of drinking water for elemental contaminants requires that a "total" element determination be made. Irrespective of the valence state or chemical species, the term "total" refers to the sum of the elemental concentration in the dissolved and suspended fractions of the sample. The sample is not filtered, but immediately preserved with nitric acid to pH of less than 2 at the time of collection.

- 2.2.2 Although most finished drinking waters are free of suspended matter, all samples must be subjected to a pretreatment acid dissolution to solubilize that portion of the contaminant that may be occluded or adhering to minute suspended matter. This is especially true for water supplies that receive only chlorination pretreatment. Once solubilized, the energy of the plasma is sufficient that all species in the nebulized droplets are desolvated, dissociated and raised to an energetic excited state for atomic emission spectrometric analysis.
- 2.2.3 Method 200.7 describes two acceptable sample preparation procedures for "total" element analyses. One is a vigorous nitric acid digestion (Section 9.3), while the other is a total recoverable acid solubilization procedure (Section 9.4). These procedures are essentially the same as those used for flame atomic absorption analysis, except the final acid concentration has been changed to match the ICP calibration standards. The total recoverable procedure is preferred for drinking water analyses because there is less chance of losses from volatilization, the formation of insoluble oxides or occlusion in precipitated silicates.
- 2.2.4 Data that are to be used for compliance monitoring should be reported with a known estimate of uncertainty. The uncertainty of the analysis should be determined at the critical MCL concentration and should be a precision of small enough variance to determine that the contaminant is either in-or-out of compliance. A guide for evaluating data to be reported can be described as data with sufficient precision at the MCL, that when two standard deviations are either added to or subtracted from the MCL concentration, the value is not changed by more than 10%. An example is As (MCL = 0.05 mg/L) where data reported with a precision of two standard deviations equal to less than 0.005 mg/L would be acceptable as shown in the preconcentration data of Table 2 with the interval values of 0.048 to 0.052 mg/L.
- 2.2.5 As indicated in Table 1, the MCLs for As and Pb are close to their estimated instrumental detection limits. A single analysis of these two elements using the total recoverable procedure 9.4 of Method 200.7 lacks the precision needed for compliance monitoring at their respective MCLs. As a consequence inaccurate determinations can result. Only with repeated analyses of the sample can an average value with acceptable precision be determined. The number of analyses required can be specified by the following equation:

$$n = \left(\frac{S_a}{S_x} \right)^2$$

where: n = the number of replicate analyses required,

S_a = the determined standard deviation of a single observation, and

S_x = the standard deviation deemed acceptable around the mean value for n determinations.

Using the preceding equation the number of repeated analyses required for the procedure 9.4 can be calculated from the direct analysis standard deviation data given in Table 2. For each element the listed determined standard deviation is S_a and the acceptable standard deviation is S_x. From the calculation the number (n) of repeated analyses required for As is 8, while for Pb the number is 6. (Note: From the standard deviation data listed for analysis after 4X concentration, the number for both elements is 1.)

2.2.6 The drinking water procedure that follows (5.1) is a modification of the total recoverable procedure 9.4 Method 200.7 that provides for improved precision and accuracy by concentrating the contaminants 4X prior to ICP analysis. With preconcentration the determination is made on a more reliable portion of the calibration curve. Also, since the variability over the narrow concentration range in question is nearly constant and does not change significantly by concentrating the sample 4X, the precision of the determination improves when the concentrated value is divided by 4 to calculate the analyte concentration in the original sample. Table 2 gives a comparison of precision and accuracy for the two elements As and Pb as determined by direct analysis and after preconcentration. The data for the direct analysis were determined from seven replicate analyses of a single unconcentrated aliquot while the preconcentration data were determined from the analysis of seven aliquots after preparation using the procedure described in 5.1. The percent recovery range data are the spread of the average percent recoveries from the seven replicate analyses determined on four separate days. The mean value is the average of the spread. The listed standard deviation is from the set of replicate analyses having the greatest variance.

3. INTERFERENCES

3.1 Concentration of surface, ground and drinking water supply samples can produce slight spectral and matrix interferences in ICP analysis. Reported effects have not been severe with the spectral

interference being an elevated shift in background intensity, while the matrix interference causes the signal intensity of some analytes to be reduced. In both cases the alkaline earth elements, calcium (Ca) and magnesium (Mg), are the primary interferences. For a complete description of interferences affecting ICP analysis see Section 5 of Method 200.7.

3.2 Spectral Interference

3.2.1 The technique of "off-the-line background correction adjacent to the wavelength peak," as required in Method 200.7, is usually adequate to compensate for shifts in background intensity. To test the spectral location selected for background correction, analyze analytically pure, single element Ca and Mg solutions of high concentration (>500 mg/L) and compare the data to the instrumental detection limit from acid blank determinations. If a value falls outside a confidence interval of ± 2 standard deviations around the instrumental detection limit, the wavelength should be spectrally scanned for selection of a different background location. If it is not feasible to change the background correction location, an interelement correction factor can sometimes be used. An example is the effect of Ca on the recommended wavelength for Pb (220.353 nm). A non-uniform background shift occurs on the low side of the wavelength peak; however, the location is not changed because of a possible severe spectral interference from Al on the high side of the wavelength peak. For the situation described only a very small correction factor (-0.00002) is required for the EMSL-Cincinnati instrument. When using interelement correction for this purpose, the correction should not be completed when the determined interferent concentration deviates from linearity by more than 10% or unless the equation used in standardization includes terms for non-linear calibration.

3.2.2 Although no significant interelement spectral line interferences have been reported from the alkali and alkaline-earth elements on the wavelengths specified for the contaminants listed in Table 1, the EMSL-Cincinnati instrument does experience a weak Mg interference at 0.037 nm below the recommended Zn wavelength (213.856 nm) read in the second order. To avoid a possible Mg spectral interference, background intensity should be read on the high side of the Zn wavelength peak. Another possible spectral interferent whose effect should be determined is that of Al on the recommended wavelengths for As, Mn and Pb. Also, care must be taken that spectrally interfering elements are not mixed in the same calibration standard unless the computer program provides for their correction during standardization.

3.3 Matrix Interference

- 3.3.1 As the dissolved solids in the solution to be nebulized increase to exceed a concentration of 1500 mg/L, a suppressive effect on the analyte signal can occur. The most noticeable effect has been observed on certain analytes where a characteristic ion line is the preferred wavelength for the analysis. To determine the presence of a suppressive interference because of concentrating the matrix, a second aliquot of the sample should be spiked with each element to a concentration above 10X its determined MDL (but not to exceed its MCL), concentrated and analyzed. Recoveries outside the interval of 90% to 110% of the expected value can be used to indicate the presence of a matrix interference.
- 3.3.2 At EMSL-Cincinnati, using a fixed crossflow nebulizer with the instrument conditions given in Section 4.2, it has been observed that high concentrations of Ca (>400 mg/L) can cause a 5% suppressive effect on the emission signal of certain analytes; Cd and Pb experience the greatest suppression. As the concentration of Ca increases, its suppressive effect becomes more pronounced. Also, Mg has an additive suppressive effect on Pb, and this combined effect must be recognized when considering matrix interferences.
- 3.3.3 When the concentration of a primary contaminant is determined to be 90% of its MCL or above, and the Ca concentration exceeds 400 mg/L (100 mg/L in the original sample concentrated 4X) or the combined Mg and Ca concentration equals 500 mg/L, a matrix matched calibration standard must be used. Otherwise the sample should be analyzed by the standard addition technique (see Section 10.6 of Method 200.7).

4. APPARATUS

- 4.1 In addition to the minimum requirements listed in Section 6 of Method 200.7, the use of mass flow controllers to regulate the argon flow rates, especially through the nebulizer, provide more exacting control and reproducible plasma conditions. Their use is highly recommended, but not required.
- 4.2 Operating conditions — Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. However, the following instrument conditions were used in conjunction with a fixed crossflow nebulizer in developing the analytical data contained in this appendix:

Operating Conditions

Forward rf power	1100 watts
Reflected rf power	< 5 watts
Viewing height above work coil	16 mm
Argon supply	Liquid Argon
Argon pressure	40 psi
Coolant argon flow rate	19 L min ⁻¹
Aerosol carrier argon flow rate	630 cc min ⁻¹
Auxilliary (plasma) argon flow rate	300 cc min ⁻¹
Sample uptake rate controlled to	1.2 mL min ⁻¹

5. SAMPLE PREPARATION

5.1 Transfer a 200 mL aliquot of a well mixed acid preserved sample to a Griffin beaker. Add 1.0 mL of (1+1) HNO₃ and 5.0 mL (1+1) HCL to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 20 mL making certain the sample does not boil. Allow the sample to cool, transfer to a 50 mL volumetric flask, dilute to the mark with deionized-distilled water and mix. The sample is now ready for analysis. If after preparation the sample contains particulate matter, an aliquot should be centrifuged or the sample allowed to settle by gravity before aspiration.

6. QUALITY CONTROL

6.1 Instrumental

6.1.1 For required instrumental quality control see Section 12 of Method 200.7.

6.1.2 (Optional) To monitor nebulizer performance and aerosol effects in the plasma, a surrogate spike of a noncontaminant element (Au) is added at a concentration of 2 mg/L (1 mL of 100 mg/L Au per 50 mL sample) to each sample after dissolution, but before final dilution. If the analyzed Au value is not within ±5% of the true value, either the nebulizer or torch has become partially clogged or a suppressive matrix effect has occurred. An analysis of the instrument check standard will indicate if shutdown and cleaning is required. (Note: EMSL-Cincinnati has been able to use the "high surge" argon flow when the mass flow controller is first opened, to flush clean the argon port of the nebulizer. This purging is usually done during the print-out of analytical data and has proven in almost all instances to restore calibration drift back to its original calibration.)

6.2 Method Detection Limit (Mandatory)

6.2.1 The MDL (2) must be determined for each contaminant using the described procedure in 5.1 with the instrument system configured in mode to be used for compliance monitoring. The determined MDL concentration must be no greater than 1/5 the element's respective MCL before the procedure and instrument system can be used for compliance monitoring of that particular contaminant. The MDL must be redetermined once a year and all data must be maintained on file.

6.3 Method (Mandatory)

6.3.1 The following method quality assurance represents 15% of the analyzed sample load for 20 samples.

6.3.2 A reagent blank as defined and described in 3.12 and 7.5.2 of Method 200.7 should be processed through the entire procedure with each group of samples. The analyzed value for each contaminant should be less than its determined MDL. If the analyzed value is greater than the MDL, contamination is suspected and succeeding analyses should be closely monitored for systematic errors. If the analyzed value exceeds the reporting limit, the analysis is considered to be out of control. The source of contamination should be determined, corrected and the samples reanalyzed.

6.3.3 To measure the precision of the analysis, one sample of every 20 is selected at random, spiked in duplicate and analyzed. The two aliquots are spiked with all 10 contaminants and processed through the entire procedure. The resulting spike concentration of each contaminant should be above 10X its determined MDL but not to exceed its MCL. The relative difference (RD) between the spiked duplicates for each contaminant is then compared to a previously established critical relative difference (CRD) determined from 15 prior spiked duplicate sample analyses of the same concentration. If the RD exceeds the CRD, the analysis is considered to be out of control. The RD between the spiked duplicates is determined by dividing their difference in concentration by their mean concentration. The CRD can be calculated using the following equation:

$$CRD = 3.27 \left[\frac{\sum_{i=1}^n \frac{R_i}{\bar{X}_i}}{n} \right]$$

where: R_i = is the calculated difference between the spiked duplicates in each set,

\bar{X}_i = is the mean value of the spiked duplicate set and

n = is the number (15) of spiked duplicate sets analyzed

6.3.4 To measure the accuracy of the analysis, percent recovery of the spike is determined. The analysis of the unspiked sample aliquot is subtracted from the mean concentration of the analyzed spiked duplicates. If the sample concentration is less than the spike concentration, and the percent recovery of the spike is outside an interval of 90% to 110% of the expected value, the analysis is considered to be out of control. If the spike recovery is acceptable, the determination is an indication of accuracy for the matrix spiked. Only, if all samples analyzed have a similar matrix, can the spike recovery be an indication of accuracy for all samples.

7. Procedure

- 7.1 See Section 10 of Method 200.7 for the recommended and required analytical operating procedures.
- 7.2 To eliminate possible memory carry-over from sample to sample, a washout time of at least 30 sec. between succeeding aspirations should be strictly observed.
- 7.3 To assure that the sample has reached equilibrium in the plasma, the sample should be aspirated for 15 sec. after reaching the plasma before beginning the integration of the background corrected emission signal.
- 7.4 The data provided in support of this appendix were determined using an average value of four, 4 sec. background corrected integration periods.

8. Calculations

- 8.1 All determined concentrations should be divided by four prior to reporting data.
- 8.2 Reagent blank concentrations less than the upper control limit of the MDL ($UCL = 2.2 \times MDL$) should not be subtracted from the samples.
- 8.3 All data should be rounded to the thousandth place and reported in mg/L up to three significant figures.
- 8.4 Sample concentrations less than the upper control limit of the MDL should be reported as "not detected". Data reported in this manner will have a confidence level of 95% certainty that false positives are not reported. (See footnote 2 of Table 1.)

9. Precision and Accuracy (Single laboratory, EMSL-Cincinnati)

- 9.1 Table 3 lists precision and accuracy data for seven aliquots of deionized distilled water spiked with each contaminant at a concentration near its reporting limit, concentrated 4X by the described procedure, and analyzed using a simultaneous ICP instrument.
- 9.2 Table 4 lists precision and accuracy data for verification of ICP analysis of drinking water. Seven aliquots of Cincinnati, Ohio tap water were spiked with each contaminant at its respective MCL, prepared by the described procedure, and analyzed using a simultaneous ICP instrument. Table 4 lists the spike value, the mean and percent recovery of spike after tap water blank subtraction, the standard deviation and the 95% confidence interval about the respective MCL.
- 9.3 Precision and accuracy data for seven aliquots of Cincinnati, Ohio tap water spiked to a concentration of 1/2 the MCL are listed in Table 5.
- 9.4 Table 6 lists the mean, standard deviation and percent recovery of a spike of each contaminant added to 12 separate ground water drinking supplies having concentrations of Ca and Mg ranging from 14 to 82 mg/L and from 0.7 to 20 mg/L, respectively. The spike concentration selected for each contaminant was a convenient value between its MCL and 10X its determined MDL. Any naturally occurring background levels subtracted were the average value of duplicate analyses of the unspiked sample.

10. References

1. Method 200.7 - Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes, EPA-600/4-79-020, revised 1984, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
- 2.- Glaser, J., Foerst, D., McKee, G., Quave, S., and Budde, W., "Trace Analyses for Wastewaters," Environmental Science and Technology, Vol. 15, No. 12, December 1981, pp 1426-1435.

TABLE 1. COMPARISON OF ICP DETECTION LIMITS, MG/L

Element	Maximum Contaminant Level	Estimated Detection Limit (1)	Method Detection Limit		EMSL-Cinti Reporting Limit(2)
			Procedure 9.4	Modified 4X Procedure	
<u>Primary</u>					
Silver (Ag)	0.05	0.007	0.0028	0.0013	0.004
Arsenic (As)	0.05	0.053	0.0157	0.0030	0.008
Barium (Ba)(3)	1	0.002	0.0013	0.0004	0.002
Cadmium (Cd)	0.010	0.003	0.0013	0.0006	0.002
Chromium (Cr)(3)	0.05	0.006	0.0031	0.0006	0.002
Lead (Pb)	0.05	0.042	0.0157	0.0046	0.011
<u>Secondary</u>					
Copper (Cu)	1	0.005	0.0028	0.0007	0.002
Iron (Fe)	0.3	0.006	0.0063	0.0037	0.009
Manganese (Mn)	0.05	0.002	0.0003	0.0002	0.001
Zinc (Zn)(3)	5	0.002	0.0019	0.0010	0.003

- (1) The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma - Atomic Emission Spectroscopy - Prominent Lines," EPA-600/4-79-017.
- (2) Method 200.7 states "data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures." The listed reporting limit for each element is an adjusted 95% upper control limit (UCL) of the corresponding 4X method detection limit. The reporting limit takes into account rounding errors and prevents false positive values below the upper control limit from inadvertently being reported (UCL = 2.2 X MDL).
- (3) The EMSL-Cincinnati instrument uses wavelengths for Ba (493.409 nm) and Cr (205.552 nm read in the 2nd order) that are different from those recommended in Method 200.7. Also, the Zn wavelength (213.856 nm) is read in the 2nd order.

TABLE 2. COMPARISON OF PRECISION AND ACCURACY
CONCENTRATION, MG/L

Element	MCL Spike	Percent Recovery		Determined Precision		Acceptable Precision	
		Range	Mean	Standard Deviation	95% Confidence Interval at MCL	Standard Deviation	± 10% Interval About the MCL
<u>Direct Analysis, Not Concentrated</u>							
As	0.05	84 - 108%	99%	± 0.007	0.036 - 0.064	± 0.0025	0.045 - 0.055
Pb	0.05	88 - 106%	100%	± 0.006	0.038 - 0.062	± 0.0025	0.045 - 0.055
<u>Preconcentrated 4X Before Analysis</u>							
As	0.05	98 - 102%	101%	± 0.001	0.048 - 0.052	± 0.0025	0.045 - 0.055
Pb	0.05	96 - 102%	99%	± 0.002	0.046 - 0.054	± 0.0025	0.045 - 0.055

TABLE 3. PRECISION AND ACCURACY DATA IN DEIONIZED DISTILLED WATER
FOR CONCENTRATIONS NEAR THE REPORTING LIMIT, MG/L

<u>Element</u>	<u>Reporting Limit</u>	<u>Spike Conc.</u>	<u>Mean (1)</u>	<u>Standard Deviation</u>	<u>Percent Recovery</u>
Ag	0.004	0.0020	0.0021	± 0.0002	105%
As	0.008	0.0100	0.0107	± 0.0012	107%
Ba	0.002	0.0025	0.0028	± 0.0002	108%
Cd	0.002	0.0025	0.0024	± 0.0002	96%
Cr	0.002	0.0025	0.0027	± 0.0002	108%
Cu	0.002	0.0020	0.0018	± 0.0002	90%
Fe	0.009	0.0160	0.0170	± 0.0006	107%
Mn	0.001	0.0025	0.0025	± 0.0001	100%
Pb	0.011	0.0100	0.0097	± 0.0013	97%
Zn	0.003	0.0040	0.0044	± 0.0006	110%

(1) The reported data are listed to the ten-thousandths place to correspond to the spike level used.

TABLE 4. DRINKING WATER PRECISION AND ACCURACY DATA CINCINNATI, OHIO TAP WATER CONCENTRATION, MG/L

<u>Element</u>	<u>MCL Spike</u>	<u>Average Recovery</u>		<u>Standard Deviation</u>	<u>95% Confidence Interval at MCL</u>
		<u>Mean (1)</u>	<u>Percent</u>		
Ag	0.05	0.0497	99%	± 0.001	0.048 - 0.052
As	0.05	0.0503	101%	± 0.001	0.048 - 0.052
Ba	1	0.978	98%	± 0.025	0.950 - 1.050
Cd	0.010	0.0097	97%	± 0.0002	0.0096 - 0.0104
Cr	0.05	0.0479	96%	± 0.001	0.048 - 0.052
Cu	1	1.01	101%	± 0.024	0.952 - 1.048
Fe	0.3	0.291	97%	± 0.006	0.288 - 0.312
Mn	0.05	0.0507	101%	± 0.001	0.048 - 0.052
Pb	0.05	0.0497	99%	± 0.002	0.046 - 0.054
Zn(2)	1	0.989	99%	± 0.019	0.962 - 1.038

(1) The mean concentrations listed to the ten-thousandth's place are recorded data before rounding. The data are presented in this manner to coincide with the reported percent recovery.

(2) The data listed for Zn are for a concentration 1/5 the MCL.

TABLE 5. DRINKING WATER PRECISION AND ACCURACY DATA CINCINNATI, OHIO TAP WATER CONCENTRATION, MG/L

<u>Element</u>	<u>Spike Conc. 1/2 MCL</u>	<u>Mean (1)</u>	<u>Standard Deviation</u>	<u>Percent Recovery</u>
Ag	0.025	0.0245	± 0.0004	98%
As	0.025	0.025	± 0.001	100%
Ba	0.500	0.490	± 0.010	98%
Cd	0.005	0.005	± 0.0001	100%
Cr	0.025	0.024	± 0.0003	96%
Cu	0.500	0.494	± 0.008	99%
Fe	0.150	0.147	± 0.002	98%
Mn	0.025	0.0245	± 0.0003	98%
Pb	0.025	0.025	± 0.001	100%
Zn(2)	0.500	0.495	± 0.004	99%

- (1) The mean concentrations listed to the ten-thousandth's place are recorded data before rounding. The data are presented in this manner to coincide with the reported percent recovery.
- (2) The data listed for Zn are for a concentration 1/10 the MCL.