MEMORANDUM

DEPARTMENT OF ENVIRONMENTAL QUALITY WATER OPERATIONS

SUBJECT: Guid

Guidance Memo No. 98-2011

Inspection Checklists for Analyses of Mercury by Cold Vapor and Metals

TO:

Regional Directors

FROM:

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DATE:

November 4, 1998

COPIES:

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SUMMARY: These documents are checklists that outline appropriate sample collection and preservation; equipment; sample preparation; analyses; and data keeping for performing the analyses of Mercury by a cold vapor method and Metals using Atomic Absorption (AA) or Inductively Coupled Plasma (ICP). These checklists, when applicable, should be included with the final DEQ - Water Division Laboratory Inspection Report. Questions or comments regarding this topic can be directed to Betsy Ziomek at (804) 698-4181.

DISCLAIMER

This document provides technical and procedural guidance to the inspection staff to evaluate laboratories producing data related to permit compliance. This document is guidance only. It does not establish a binding norm and is not finally determinative of the issues addressed. Agency decision in any particular case will be made by applying the State Water Control Law and the implementation regulations on the basis of site specific facts.

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ANALYST:	1			VPDES NO	1	
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Parameter: Metals Checklist 10/98

	Checklist 10/98		
METHO	OD OF ANALYSIS		
	EPA 200 Series (See individual element method no. in 40 CFR Part 136)		
	EPA 200.7 Revision 4.4, 1994		
	EPA 200.9 Revision 2.2, 1994		
	18th Edition of Standard Methods 3000 Series		
			1
	SAMPLE COLLECTION AND PRESERVATION	Y	N
1	Are all glassware and plasticware acid washed with detergent and tap water, rinsed with 1:1 HNO ₃ , tap water, 1:1 HCl, tap water, and final DI water rinse? If not, were blanks run to ensure acceptability of procedure and materials?		
<u>2</u>	Are samples for total and total recoverable metals unfiltered and preserved with HNO ₃ to a pH of <2? If samples are not preserved in the field, after acidification in the lab are they held for 16 hours before beginning digestion?		
<u>3</u>	Are samples for dissolved metals filtered through a 0.45 μ membrane filter immediately after collection and preserved immediately after filtration with HNO ₃ to a pH of <2?		
4)	For dissolved metals, were the filtration apparatus and filter rinsed with 50-100 mLs of sample and the filtrate discarded prior to filtering the aliquot to be preserved as the dissolved metals sample?		
	SAMPLE PREP		
<u>1</u>	Are all glassware and plasticware acid washed with detergent and tap water, rinsed with 1:1 HNO ₃ , tap water, 1:1 HCl, tap water, and final DI water rinse? If not, were blanks run to ensure acceptability of procedure and materials?		
2)	Is the area where metal samples are prepared sufficiently clean to produce data that meet the data quality objectives?		
<u>3</u>	Are only trace element or equivalent grade reagents used for AA and ICP analysis?	ļ	
4)	Are reagents being dated and initialed on the container upon receipt and when opened?		
<u>5</u>	DISSOLVED METALS a. For dissolved metals being analyzed using AA without digestion were all of the following true for Methods 202, 204, 206, etc.? (FR July 1, 1997, footnote 4) COD was low (<20 μg/L) Visibly transparent with turbidity of ≤ 1 NTU Colorless with no perceptible odor Consisted of one liquid phase free of particulate or suspended matter after acidification		
	 b. For methods 200.7 and 200.9 was the following procedure carried out? (11.1.1) 1. ≥20 mL of filtered, acidified sample added to polypropylene centrifuge tube 2. Add (1 + 1) nitric acid to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO₃ to a 20 mL aliquot of sample) Allowance for acid dilution should be made in the calculations! 3. Cap tube and mix 		
	 For Standard Methods, was sample digested if a precipate formed after acidification? 		
6)	Are digestion fumes removed by a fume hood or evacuation equipment?		
<u>7</u>)	Is a digestion log being maintained with the following information recorded?	1	

a) Date, time, method, and analyst performing digestion.

		Υ	N
	b) Sample ID number with beginning and final volumes.		
	c) pH of sample taken just prior to digestion. NOTE: If pH is > 2, add HNO₃ and hold sample for 16 hrs. Repeat step until verified to be pH ≤ 2.		
	d) Reagents and volume of each one used.		
	e) ID of digestion container used.		
	f) Samples used for quality control properly identified [blanks, laboratory control samples (LCS), spikes, and duplicates]		
	g) Conc., volume, and source of spiking solution used.		
	DIGESTION METHODS		
1)	"Less Vigorous" Digestion for Total Metals by FLAA and Sb using GFAA (Preferred method: FR July 1, 1997, footnote 4) Smaller initial sample volumes may be used with acid volumes being adjusted accordingly. (200 series)		
	a) Began with 100 mL of sample?		
	b) Added 5 mL of 1:1 HCI?		
	c) Volume reduced to 15-20 mL without boiling or going to dryness?		
	d) Insoluble materials removed by settling, filtration or centrifugation?		
	e) Diluted volume with DI water?		
2)	"Less Vigorous" Digestion for Total Metals by GFAA Excluding As, Se, and Sb (<u>Preferred method</u> : FR July 1, 1997, footnote 4) (200 series)		
	a) As above with HCI_OMITTED?		
3)	"Vigorous" Digestion for Total Metals by FLAANOT for Sb and Sn; insoluble oxides result! Procedure recommended only for samples with very high conc. of organic materials or for colorimetric procedures: FR July 1, 1997, footnote 4. Smaller initial sample volumes may be used with acid volumes being adjusted accordingly. (200 series)		
	a) Began with 100 mL of sample?		
	b) Added 3 mL conc HNO ₃ ?		
	c) Evaporated to near dryness without boiling or baking sample?		
	d) Cooled and added 3 mL conc HNO ₃ ?		
	e) Covered and refluxed, adding acid until digestion was complete (no additional color change)?		
	f) Added 5 mL 1:1 HCl ?		
	g) Warmed to dissolve precipitates or residues?		
	h) Insoluble materials removed by settling, filtration or centrifugation?		
	I) Diluted to volume with DI water?		
4)	"Vigorous" Digestion for Total Metals by GFAAexcluding Sn, Sb, As, & Se (FR July 1, 1997, recommends this procedure only for samples with very high amounts of organic materials or for colorimetric procedures.) (200 series)		:
	As Above with HCl omitted: substituted HNO ₃ for 0.5% final volume?		
5)	Digestion for As and Se by GFAA. Smaller initial sample volumes may be used with acid volumes being adjusted accordingly (As 206.2; Se 270.2)		
	a) Began with 100 mL of sample?		

		Υ	<u>N</u>
	b) Added 1 mL HNO ₃ ?		
	c) Added 2 mL 30% H ₂ O ₂ ?		
	d) Reduced volume to slightly less than 50 mL without boiling?		
	e) Insoluble materials removed by settling, filtration or centrifugation?		
	f) Diluted to volume with DI water?		
	g) Is appropriate matrix modifier being used?		
6)	Digestion for methods 200.7 and 200.9. Smaller initial sample volumes may be used with acid volumes being adjusted accordingly: (11.2)		
	Samples having <1% undissolved solids. a) Began with 100 mL acidified sample?		
	b) Added 2 mL (1+1) $\rm HNO_3$ and 1.0 mL $\rm HCl$?		
	c) Volume reduced to 15-20 mL on hot plate <u>without boiling</u> and temperature no higher than 85°C?		
	d) Covered beaker with watch glass and gently refluxed sample for 30 mins.?		
	e) Transferred sample to 50 mL volumetric flask and brought to volume?		
	f) Allowed sample to settle prior to analysis?	_	
	Samples having >1% undissolved solids: a) Calculated percent solids using a drying temperature of 60°C?		
	b) Placed 1.0 \pm 0.01 g of dried, sieved and ground sample in beaker?		
	c) Added 4 mL of (1+1) HNO $_3$ and 10 mL of (1+4) HCl ?		
	d) Covered with watch glass and gently heated and refluxed for 30 mins.?		
	e) Transferred extract to 100 mL volumetric flask and diluted to volume?		
7)	Digestion for SM 3030E (Smaller initial sample volumes may be used with acid volumes being adjusted accordingly): a) Began with 100 mL acidified sample?		
	b) Added 5 mL of conc. HNO ₃ and a few boiling beads?		
	c) Brought to slow boil and reduced volume to 10-20 mL?		
	d) Continued heating and adding conc. HNO ₃ until digestion was complete?		
	e) Filtered if necessary and transferred to 100 mL volumetric flask and diluted to volume?	paracementaria alta	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
	ANALYTICAL EQUIPMENT		
1)	Is the area where metal samples are prepared sufficiently clean to produce data that meet the data quality objectives?		
2)	If micro pipettes are used, are the critical volumes checked quarterly for accuracy and precision?	···	
3)	Are micro pipette tips metal free? (Yellow may have Cd and Cr; Blue may have Cu)		
4)	Are instrument responses electronically recorded either by strip chart or computer?		
5)	Is instrument allowed an appropriate warm-up time? Suggested times are HCL=5-10 min, EDL=30-60 min, and ICP 30-60 min.		
	AA Spectrophotometer		
<u>6)</u>	Does the spectrophotometer cover the wavelength range desired (suggested range of 190-880 nm)?		

		Υ	N
<u>7)</u>	Is the set-up (wavelength, slit width, burner or furnace head, and gasses) as recommended by the manufacturer?		
<u>8)</u>	Is background correction being used? If not, are samples close to or above the regulatory limit reanalyzed with a nonabsorbing line to assess background contribution?		
<u>9)</u>	Is autosampler being used for GFAA (furnace)?		
10)	Is a mixture of hydrogen and argon gas supply used for analysis? Required for 200.9 (2.2)		
	ICP-AES		
<u>11)</u>	Is instrument computer controlled and capable of performing background correction?		
<u>12)</u>	Can background be measured adjacent to analyte lines during analysis in a position free from spectral interference?		
13)	Is high purity (99.99%) argon gas supply used for analysis?	229 CM C 0. 8 (00)	50004 600 Julio 20000
	ANALYSIS General		
1)	Are reagent and standard solutions that have been prepared on site, dated and initialed by the analyst? NOTE: It is recommended that a log be maintained with the lot numbers of the chemicals used in each preparation.		
<u>2)</u>	Are stock standards within expiration dates?		
<u>3)</u>	Are Class A volumetric flasks used for preparing standards?		
4)	Are working calibration standards prepared by diluting stock metals solutions at the time of analysis for AA?		
<u>5)</u>	Are calibration standards and blanks matrix matched to samples? (Identical conc of all acids used in digestion are in the standards and blanks.)		
6)	Are a minimum of 2 replicates of each sample, blank, check sample, etc. read?		
7)	Has instrument detection limit been established?	\$2\$	80.200.200.000000
	AA (FLAA and GFAA)		
<u>8)</u>	Has initial demonstration of performance been completed?		
	a) Have quality control samples (QCS) - from different external source than standards- been analyzed with recovery of 90-110% of stated value?		
	b) Have method detection limits (MDL) been determined for each method and element? NOTE: MDL's must be determined annually.		
8)	Is instrument stability determined prior to calibration by analyzing a standard solution with 20X conc of IDL a minimum of 5 times with resulting RSD of <5%? (200.9, 11.4.3)		
<u>9)</u>	Does the calibration curve consist of a blank and at least 3 standards and have a calibration coefficient of \geq 0.995?		
<u>10)</u>	Is instrument performance check (made from same source as standards) and calibration blank analyzed immediately after calibration (ICV), after every 10th sample (CCV), and at end of sample run (CCV)? Recoveries must be within 95-105% for ICV (200.9); 90-110% for ICV (other methods); 90-110% for CCV (all methods).		
<u>11)</u>	Is a quality control sample (QCS)from different external source than standardsanalyzed to verify each calibration? Recovery within 90-110%.		
<u>12)</u>	Is a laboratory reagent blank (LRB) analyzed with each batch of 20 or fewer samples of the same matrix?		
<u>13)</u>	Is a laboratory fortified blank (LFB) analyzed with each batch of samples with a spike recovery of 85-115%?		

		Υ	N
14)	Have control limits been established using LFB data? (Suggested but not required)		
15)	Are a minimum of 10% of samples being spiked prior to digestion?		
	a) is recovery within 70-130%?		
	b) If recovery is <70% or >130%, is a post digestion spike analyzed with recovery of 85-115%?		
	c) If post digestion spike recovery is not within 85-115% is method of standard additions carried out?		
16)	Are duplicate samples being analyzed at rate of 10% with RPD \leq 20%? (RPD's are valid only for values > 5X CRDL.)		
17)	Are sample analyte conc > 90% of the highest standard diluted and reanalyzed? NOTE: This isn't required <u>if</u> the linear dynamic range (LDR) has been established demonstrating linearity well beyond the highest standard.	elignet sedures avecte	(8storo postorokop o
	ICP		
18)	Are all acids of trace metal grade or equivalent?		
<u>19)</u>	Has initial demonstration of performance been completed?		
	a) Has the upper limit of the linear dynamic range (LDR) been established for each method and element?		
	b) Have quality control samples (QCS) - from different external source than standards- been analyzed with recovery 95-105% of stated value?		
	c) Have method detection limits (MDL) been determined for each method and element? NOTE: MDL's must be determined annually.		
<u>20)</u>	Have spectral interferences been documented? (This must be done initially and then annually thereafter.)		
21)	Have instrument detection limits been established for each element?		
<u>22)</u>	Is instrument calibrated according to manufacturer's instructions?		
23)	Are standards checked either against a <u>freshly</u> prepared QCS (from different external source than standards), or by comparing counts/intensity and repreping when change occurs?		
<u>24)</u>	Is the highest calibration standard analyzed daily before beginning the sample run? Recovery must be within 95-105%?		
<u>25)</u>	Is a quality control sample (QCS) from different external source than standards analyzed daily with a recovery of 95-105% to verify calibration? QCS solution should be ≥1 mg/L, except silver, which must be 0.5 mg/L for solution stability.		
<u>26)</u>	Is the interference check sample analyzed at the beginning, end, and at periodic intervals throughout the run?		
<u>27)</u>	ls a calibration blank used to flush the system after each solution (standards, samples, check solutions) is analyzed?		
<u>28)</u>	Is an instrument performance check (made from same source as standards and in midrange of curve) and calibration blank analyzed immediately after calibration (ICV), after every 10th sample (CCV), and at end of sample run (CCV)? Recoveries must be within 95-105% for ICV; 90-110% for CCV.		
<u>29)</u>	Is a laboratory reagent blank (LRB) analyzed with each batch of 20 or fewer samples of the same matrix?		
<u>30)</u>	Is a laboratory fortified blank (LFB) analyzed with each batch of samples with a spike recovery of 85-115%?		
31)	Have control limits been established using LFB data? (Suggested but not required)		
<u>32)</u>	Are a minimum of 10% of samples being spiked prior to digestion?		

a) Is recovery within 70-130%?	
b) If recovery is outside of 70-130% range, is a post digestion spike analyzed with recovery of 85-115%, and a 1:4 dilution analyzed having agreement of 90-110% of the original determination?	
Are duplicate samples being analyzed at rate of 10% with RPD ≤ 20%? (RPD's are valid <u>only</u> for values >5X the CRDL.)	

DATA KEEPING

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- 1) Are the permit levels met by the analytical technique chosen?
- 2) Does raw data have analyst's initials, analysis time and date recorded?

Are sample analyte concs > 90% of the LDR diluted and reanalyzed?

- 3) Are all sample concentrations bracketed by standards?
- 3) Are all raw data retained for at least 3 years?
- 4) Is there a QA/QC plan available which includes a 'Corrective Actions' section?

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PROBLEMS:				

RATING:	SAT	ISFACTORY	SATISFACTORY W/QUALIFICATI	ONS	UNSATIS	SFACTORY

ANALYST:	VPDES NO	

Parameter: Mercury by Cold Vapor Checklist 9/98

i	METH	OD OF ANALYSIS
		EPA 245.1-2 Revision 3.0
		18th Edition of Standard Methods 3112B

	18th Edition of Standard Methods 3112B		
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	SAMPLE COLLECTION AND PRESERVATION	<u>Y</u>	N
1)	Are all glassware and plasticware acid washed with detergent and tap water, rinsed with 1:1 HNO ₃ , tap water, 1:1 HCl, tap water, and final DI water rinse? If not, were blanks run to ensure acceptability of procedure and materials?		
<u>2)</u>	Are samples for total mercury (Hg) unfiltered and preserved with HNO_3 in the field to a pH of <2?		<u> </u>
<u>3)</u>	Are samples for dissolved Hg filtered through a 0.45 μ membrane filter immediately after collection and preserved immediately after filtration with HNO $_3$ to a pH of <2?		
4)	For dissolved Hg, were the filtration apparatus and filter rinsed with 50-100 mLs of sample and the filtrate discarded prior to filtering the aliquot to be preserved as the dissolved Hg sample?		
	EQUIPMENT		
1)	Is either an AA spectrometer with a Hg lamp or a commercial mercury system used for analysis?		ļ
2)	Are instrument responses electronically recorded either by strip chart or computer?		ļ
3)	Is instrument allowed an appropriate warm up time?		<u> </u>
<u>4)</u>	Is the absorption cell of approximately 1" OD by 4½" long with quartz windows cemented to both ends? (245.1)		
<u>5)</u>	Is the aeration tube used in sample bottles made of straight glass ending with frit of coarse porosity? (245.1)		
6)	If micro pipettes are used, are the critical volumes checked quarterly for accuracy and precision?	0.0000000000000000000000000000000000000	0. 2004-1-12-20-20-00-00-0
	SAMPLE PREP		
<u>1)</u>	Are all glassware and plasticware acid washed with detergent and tap water, rinsed with 1:1 HNO ₃ , tap water, 1:1 HCI, tap water, and final DI water rinse? If not, were blanks run to ensure acceptability of procedure and materials?		
2)	Is the area where Hg samples are prepared and analyzed free from dust and other sources of possible Hg contamination, such as noncompatible analyses (COD and TKN) and uncovered fluorescent light bulbs?		
<u>3)</u>	Are all reagents of low Hg content (may need trace metal grade)? Solid reagents should not exceed 0.05 ppm of Hg.		
4)	Are reagents being dated and initialed on the container upon receipt and when opened?		
5)	Are reagent and standard solutions that have been prepared on site, dated and initialed by the analyst? NOTE: It is recommended that a log be maintained with the lot numbers of the chemicals used in each preparation.		
6)	Are digestion fumes removed by a fume hood or evacuation equipment?		
7)	Is a digestion log being maintained with the following information recorded?		
	a) Date, time, method, and analyst performing digestion.		
	b) Sample ID number with beginning volume.		

		Y	N
	c) pH of sample taken just prior to digestion. NOTE: If pH is > 2, add HNO $_3$ and hold sample for 16 hrs. until verified to be pH $_\leq$ 2.		
	d) Reagents and volume of each one used.		
	e) ID of digestion container used.		
	 f) Samples used for quality control are properly identified [blanks, laboratory control samples (LCS), spikes, and duplicates] 		
	g) Conc., volume, and source of spiking solution used.		
<u>8)</u>	Are stock standards within expiration dates?		
<u>9)</u>	Is Hg standard prepared fresh each day of use (v/v= 0.15% HNO ₃)?		
<u>10)</u>	Are calibration standards and check samples prepared by transferring aliquots of the working solution to Hg bottles and diluting to a final volume of 100 mLs?		
<u>11)</u>	Are 100 mLs of sample, or an aliquot diluted to 100 mLs, transferred to Hg bottles?		
<u>12)</u>	Are the following digestion reagents added to standards, blanks, samples, and quality control samples?		
	a) 5 mL conc H₂SO₄		
	b) 2.5 mL conc HNO ₃		
	c) 15 mLs potassium permanganate (KMnO₄). If necessary, add additional amounts of KMnO₄ until a purple color persists for 15 min.		
	d) 8 mL potassium persulfate (K ₂ S ₂ O ₂)		
<u>13)</u>	Are samples heated in a covered hot water bath maintained at 95°C for 2 hrs? (NOTE: Timing should begin when the temp reaches 95°C.)		
<u>14)</u>	Are samples allowed to reach room temperature prior to beginning analysis?		
<u>15)</u>	Are ≥6 mL of hydroxylamine solution added per bottle to reduce excess permanganate?	NORTH (NEW PROPERTY AND INC.)	90995575 5009582
	<u>ANALYSIS</u>		
1)	Has initial demonstration of performance been completed?		
	a) Has a quality control sample been analyzed with recovery ± 10% of stated value?		
	b) Has the method detection limit (MDL) been determined? Must be done annually.		
2)	Are Hg bottle solutions aerated after addition of hydroxylamine solution?		
<u>3)</u>	Are 5 mL of stannous solution added and <u>immediately</u> attached to the aeration tube? (245.1). For automated systems, are manufacturer's instructions followed? (245.2)		
<u>4)</u>	Is the absorbance allowed to reach a maximum height prior to taking a reading?		
<u>5)</u>	Is the system purged and the recorder allowed to return to minimum value prior to reading the next bottle?		
<u>6)</u>	Are Hg vapors vented or passed through a trapping solution or through activated charcoal?		
<u>7)</u>	Does the calibration curve consist of a blank and at least 3 standards and have a calibration coefficient of \geq 0.995?		
<u>8)</u>	Is an instrument performance check (made from same source as standards) and calibration blank analyzed immediately after calibration (ICV), after every 10th sample (CCV), and at end of sample run (CCV)? Recoveries must be within \pm 5% for ICV and \pm 10% for CCV.		

		Υ	N
<u>9)</u>	Is a quality control sample(QCS) made from outside source different from standards, analyzed to verify each calibration? Recovery within ± 10%.		
<u>10)</u>	Is a laboratory fortified blank (LFB) analyzed with each batch of samples with a spike recovery of \pm 15%?		
11)	Have control limits been established using LFB data? (Suggested but not required)	<u></u>	
<u>12)</u>	Are a minimum of 10% of samples being spiked prior to digestion?	ļ	
	a) Is recovery within 70-130% (245); 85-115% (3112B)?	ļ	
	b) If recovery is outside the acceptable range, and the laboratory performance is shown to be in control, are the results flagged as being suspect due to matrix effects?		
13)	Are duplicate samples being analyzed at rate of 10% with RPD \leq 20%? (RPD's are valid only for values > 5X the CRDL.)		
14)	Are sample analyte conc > the highest standard diluted and reanalyzed?	<u> </u>	
<u>15</u>)	Are reported sample values bracketed by standards? (Values below the lowest standard must be reported as <.)	All at the reduced lead and	i edulu 5 v quedepii s
	DATA KEEPING		
<u>1</u>)	Does raw data have analyst's initials, analysis time and date recorded?		
<u>2)</u>	Are all raw data retained for at least 3 years?		
3)	Is there a QA/QC plan available which includes a 'Corrective Actions' section?		

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PROBLEMS:			 	

RATING:	SATISFACTORY	SATISFACTORY W/QUALIFICATIONS	UNSATISFACTORY