STANDARD OPERATING PROCEDURE (S.O.P.) FOR METALS ANALYSIS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

S.O.P. MLD 005, REVISION 6.1

October 2007

California Air Resources Board
Monitoring and Laboratory Division

Northern Laboratory Branch
Inorganics Laboratory Section

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1. SCOPE

1.1 This document details the analysis of lead (Pb) and chromium (Cr) by atomic absorption (AA) spectrophotometry.

1.2 This method is currently used for determining the concentration of dilute-acid-soluble Pb collected on Total Suspended Particulate (TSP) glass micro-fiber filters. This method is also used to determine the total Cr concentration of source emission samples collected in 0.1 Normal (N) sodium bicarbonate ($NaHCO_3$).

1.3 The TSP filter extraction procedure is also suitable for analysis of dilute-acid soluble arsenic (As), beryllium (Be), and cadmium (Cd).

1.4 The TSP filter extraction procedure is technically suitable for dilute-acid-soluble Cr. However, use caution when interpreting Cr data from TSP samples because the glass micro-fiber filters used for sampling contain an inherent Cr artifact of approximately 1 to 5 micrograms (μg) of Cr per an entire filter, sized 8"x10".

1.5 This method specifies the use of graphite furnace atomic absorption (GFAA) spectrophotometry. Flame atomic absorption (Flame-AA) is an acceptable alternative for analysis of samples with concentrations expected in the parts-per-million (ppm) range or higher.

1.6 The TSP filters are pre-inspected, mailed out, post-inspected, and logged into the laboratory database in the Balance Room (Refer to SOP MLD016 for these procedures).

2. SUMMARY OF METHOD

2.1 Pb from TSP Filters (hereafter referred to as Pb-TSP):

TSP samples are collected over a 24-hour period by exposing a glass micro-fiber filter, sized 8" x 10", to an ambient airflow of approximately 1600 cubic meters (m^3). A section, sized 1 ¾" by 4 ½", is cut from this exposed filter. Metals deposited on this section are extracted by dilute nitric acid using sonication with heating. The extraction solution is vacuum filtered, bottled, and stored at room temperature until Pb analysis by GFAA.

2.2 Total Cr from Source Testing Emissions (hereafter referred to as Cr-Total):

Emission samples are collected at the source using “Method 425, Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources,” July 1997. An aliquot of the refrigerated $NaHCO_3$ sample solution is acidified using ultra pure grade nitric acid, degassed by manual agitation via pipette, and analyzed for total Cr by GFAA.

3. APPARATUS AND MATERIALS

3.1 Atomic Absorption Spectrophotometer (Perkin-Elmer Model 800, hereafter referred to as PE800); graphite furnace with transversely heated graphite atomization (THGA) and Zeeman-effect background correction; flame burner with deuterium arc background correction; furnace sampler (AS-800); a printer and a computer for data handling; and the PE800 control and data collection software (PE WIN-Lab 32, Version 8.0).

3.2 Graphite tubes with integrated platforms; graphite contacts; and graphite extraction tip.

3.3 Hollow cathode lamps (HCL) for Pb, Cr, and Be. Electrodeless discharge lamps (EDL) for As and Cd.

3.4 Ultrasonic bath with heating capability to 69^{o}C; built-in timer.

3.5 Centrifuge vials, polypropylene, 50 milliliter (ml), with screw-top caps for extraction or sample storage.

3.6 Dispensing bottles: amber-tinted glass: 1 liter (l), equipped with an adjustable, volumetric dispensing unit with 30 ml capacity; 4 l, equipped with an adjustable, volumetric dispensing unit with 25 ml capacity.

3.7 Sample storage bottles, polypropylene, 60 ml, with screw-top caps.

3.8 Cutting board with ruled edges; scissors, stainless steel, long edge.

3.9 Filtration membranes, 47 millimeter (mm) in diameter, 0.45 micrometers (μm) pores, non-cellulose composition; magnetic filter funnel, metal-free, 300 ml capacity, for use with 47 mm filtration membranes; glass enclosed vacuum filtration chamber.

3.10 Sampler cups, metal-free, suitable sizes for PE800.

3.11 Pipettes with metal-free disposable tips, 10 to 2500 microliter (μl) capacity.

3.12 Disposable laboratory wipes; self-adhesive labels; waterproof ink pen.

3.13 Furnace cooling system capable of maintaining a 2.5 liter/minute (l/min) flow.

3.14 Labconco SteamScrubber dishwasher with de-ionized water rinse.

3.15 Laboratory Information Management System (LIMS).

4. CHEMICALS AND REAGENTS

4.1 Nitric acid, HNO_3, concentrated. For Pb-TSP analysis: trace-pure spectrometric grade. For Cr-Total analysis: ultra-pure spectrophotometric grade. For glassware and equipment cleaning: reagent grade.

4.2 Standards, NIST traceable material, 10 to 100 microgram per milliliter (μg/ml) stock, in 2% HNO_3, from two separate sources or manufacturing lots; diluted stock solutions for calibrating standards and controls.

4.3 Matrix modifier, magnesium and phosphate in dilute HNO_3, AA grade.

4.4 Compressed air with inlet filter for particulate, oil, and water.

4.5 Argon gas, 99.99% purity, for GFAA. Acetylene gas, Grade 5, for Flame-AA.

4.6 $NaHCO_3$, solid, 95% purity or better.

4.7 Alconox detergent.

4.8 ASTM Type I water with resistivity equal to 16.5 megaohms-centimeter or better (nanopure water) purified by a Barnstead Nanopure water system.

5. INTERFERENCES FROM REAGENTS AND SAMPLING MEDIA

5.1 Glass micro-fiber filters are inherently contaminated with metals, such as aluminum (Al), nickel (Ni), copper (Cu), and Cr. The level of contamination for each element varies slightly by the filter manufacturing lot. For example, approximately 1 to 5 μg of Cr are contained per an entire filter, sized 8”x10”.

5.2 All reagents and standards must be free of interfering levels of the analytes of interest before sample extraction or analysis. If levels of sampling media are elevated and cannot be compensated for in the analysis reagent blank, yet are acceptable to the client for a particular project, the analyst should insure that the concentration levels are noted and, if needed, the interfering level subtracted from the final results. Assays from the product supplier may be adequate to initially determine interfering levels.

5.3 For Cr analysis of emission samples, use concentrated HNO_3 with an assay value for Cr of less than 100 parts-per-trillion (ppt).

6. INTERFERENCES FROM SAMPLE PREPARATION

6.1 Failure to degas the acidified $NaHCO_3$ sample solutions during sample preparation will produce inaccurate Cr results.

6.1.1 To check that the degassing procedure is adequate, analyze a blank sample spiked with a concentration near 2 times the instrument detection limit. A negative reading indicates incomplete degassing.

6.2 Never return unused chemicals, such as solid $NaHCO_3$, to the original container.

6.3 Contamination of samples can occur from failure to clean the cutting board and scissors. Wipe both thoroughly with a dry laboratory wipe prior to each use.

6.4 Use glassware and vials of a known quality and cleanliness.

6.5 Use only nanopure water for sample/standard preparation. The canister-deionized water available on tap at some lab sinks may have elemental contamination that is equal to regular tap water.

6.6 Always rinse the end of the nanopure water delivery tube with clean nanopure water prior to every use.

6.7 Blank (unexposed) filter pieces used for Quality Control (QC) blanks must be stored carefully to avoid contamination. Place filter pieces in a glassine enclosure, and store away from the filter cutting area.

7. INTERFERENCES FROM SPECTROPHOTOMETER

7.1 Atomic absorption is susceptible to chemical, ionization, matrix, and background interferences.

7.2 The GFAA analytical technique for Pb analysis is well-developed, meaning the Perkin-Elmer instrument software and manual give clear descriptions and correction tactics (e.g., adjusting modifiers and temperature steps) to resolve the effects of any interferences.

7.3 For the GFAA analytical technique for Cr analysis of $NaHCO_3$ samples, the modifier and temperature steps recommended by Perkin-Elmer for dilute acid matrices do not apply.

7.4 If the graphite tube is in good condition, and the background is uncorrectable, consider replacing the contact rings.

7.5 Pay attention to the history of the matrix modifiers used. For example, Perkin-Elmer recommends the use of modifiers that contain palladium (Pd). Prolonged use of high concentrations of Pd-containing modifiers would forever contaminate the furnace components. This means that the PE800 instrument would no longer be viable for very sensitive Pd analysis.

8. LABORATORY INFORMATION MANAGEMENT SYSTEM (LIMS)

8.1 Consult the LIMS coordinator for information on the function and operating details of LIMS.

8.2 Data reporting using the current LIMS is available for both Pb and Cr.

8.3 For Pb-TSP analyses: Samples are logged into LIMS and assigned a LIMS number. Before beginning sample extraction, generate an extraction LIMS report. Prior to sample preparation, verify the assigned LIMS numbers.

8.4 For Cr-Total analyses: Samples are logged into LIMS after analyzing the samples. The analyst, rather than LIMS, assigns numbers for Cr-Total samples. Before beginning sample preparation, assign an individual sample identifier (i.e., Nozzle Rinses #1 05/01/04) to each sample. The identifiers must be entered into the PE800 software to initially track the Cr-Total sample within the lab. After the sample is analyzed using the PE800, the data should be electronically transferred into LIMS.

8.5 For both Pb and Cr analyses, the data transferred into LIMS includes the sample results, all corresponding quality control (QC), and extraction dates. After analysis, use the PE800 software to generate an exportable CSV file in order to transfer the data into LIMS.

9. SAMPLE BOTTLE CLEANING PROCEDURE

9.1 Wash all sample bottles and caps in the dishwasher with laboratory detergent, and then vigorously rinse with a 10% (volume/volume) nitric acid solution, followed by a triple rinse with nanopure water.

9.1.1 To prepare 1 l of 10% nitric acid, slowly add 100 ml of concentrated nitric acid (reagent grade) to a clean 1 l volumetric flask that already contains approximately 600 ml of nanopure water. Do not add the acid to an empty flask.

9.1.2 Measure the acid using a graduated cylinder specifically labeled for use with nitric acid. After slowly adding the acid, triple rinse the cylinder with nanopure water, dumping each of the rinses into the flask. Bring the flask to volume using a nanopure water squirt bottle.

9.1.3 Manually mix the acid solution before transferring the solution from the volumetric to the labeled dispensing bottle.

9.2 Dry the sample bottles in a tipped position to avoid contamination after cleaning.

9.3 Tap the excess water out of the caps before placing on a clean lab towel to dry. Lightly place a lab towel over the drying caps to prevent contamination.

9.4 Allow the bottles and caps to dry thoroughly before storing.

10. EXTRACTION REAGENT AND RINSE SOLUTION PREPARATION FOR Pb-TSP

10.1 The Filter Extraction Reagent is 0.50 N HNO_3.

10.1.1 Prepare the Filter Extraction Reagent by diluting 31.6 ml of concentrated nitric acid in a 1 l volumetric flask containing 600 ml of nanopure water.

10.1.2 Measure the acid using a graduated cylinder labeled for use with HNO_3. After slowly adding the acid, triple rinse the cylinder with nanopure water, dumping each of the rinses into the flask. Bring the flask to volume using a nanopure water squirt bottle.

10.1.3 After mixing, place the Filter Extraction Reagent in a washed, rinsed with 10% nitric acid, and triple nanopure water rinsed 1 l amber glass bottle equipped with a volumetric dispenser, set to deliver 20 ml aliquots.

10.2 The Filter Rinse Solution is 0.25 N HNO_3.

10.2.1 Prepare a 0.25 N nitric acid solution by diluting 15.8 ml of concentrated nitric acid in a 1 liter volumetric flask containing 600 ml of nanopure water.

10.2.2 Same as Section 10.1.2.

10.2.3 After mixing, place a portion of the Filter Rinse Solution in a marked polyethylene squirt bottle for easy use. Store the remainder in a properly sealed volumetric until use.

11. EXTRACTION SPIKE AND BLANK PREPARATION FOR Pb-TSP

11.1 Exposed filter spikes are used to verify efficiency of exposed filter extraction.

11.2 A filter spike is prepared by adding a tiny aliquot of known standard to a filter segment (1 ¾" by 4 ½") cut from an exposed filter (See Section 12).

11.2.1 Prepare and digest a spike with each batch of samples. A batch is 40 samples or less, including the unspiked exposed filter sample.

11.2.2 The final concentration of the spike should be 40 ng/ml Pb. Pipette 0.16 ml of a 10 μg/ml Pb stock standard onto a filter segment (a duplicate cut of the unspiked exposed sample).

11.2.3 To allow the spike time to dry, create the spike before cutting the other samples in the batch. Allow the spiked filter to dry under the hood for 3 to 4 hours, and then proceed through the extraction process described in Section 12.5 through 12.10.13.

11.3 Extraction blanks are prepared by cutting a 1 ¾" by 4 ½" section from an unexposed glass-microfiber filter. The blank should be taken through the extraction procedures listed in Section 12.5 through 12.10.13. One blank should be digested along with each batch of 40 samples or less listed on the extraction worklist.

12. SAMPLE PREPARATION PROCEDURE FOR Pb-TSP

12.1 Generate a LIMS extraction worklist for Pb-TSP and follow steps 12.4 through 12.10.13 for all samples including the blanks, duplicates, and spikes.

12.2 Label clean sample bottles or use new metal-free disposable centrifuge vials for all samples to be extracted (regular samples, duplicates, blanks, and spikes).

12.3 Use a fresh, dry Kimtowel to thoroughly clean all cutting apparatus prior to cutting. Place several opened, clean Kimtowels around the immediate cutting area to prevent contamination.

12.4 Place the filter exposed-side up on the cutting board. Use the cutting board scale as marked 1st cut, 2nd cut, and 3rd cut as a guide. Cut the filter in half along the lengthwise edge (10" side). Retain the portion without the factory-stamped number. Place the remaining filter portion, including the factory-stamped corner for identification purposes, back into the glassine enclosure. Make certain that the cut halves the exposed area, and not just the entire filter. (Note: The filter may not have been exposed symmetrically; cutting the filter in half may not always cut the exposed area in half.) Cut the retained filter half in half along the widthwise edge (8" side). Cut this halved portion in half again on the same edge (along the widthwise, 8" edge). The resulting product should be a section one-eighth in size of the original, exposed area of the filter and should measure 1 ¾" by 4 ½" as shown in Figure 12.4.

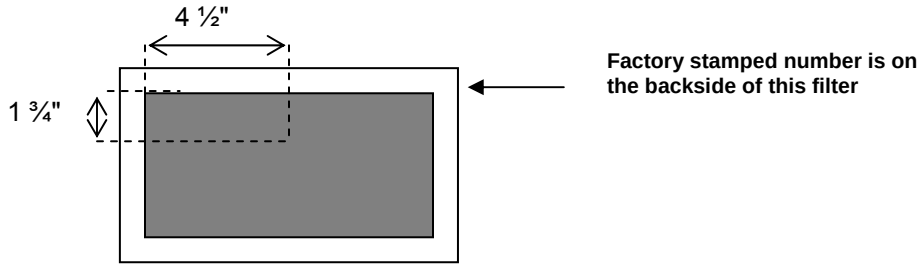

Figure 12.4, Exposed Filter Section.

12.4.1 Use the diagonal corners adjacent to the factory-stamped corner for cutting duplicate sample segments.

12.5 Cut the 1 ¾" by 4 ½" filter segment directly into the labeled extraction vial using the cut and fold technique depicted in Figure 12.5. Use long-edge scissors to cut the segment into smaller pieces.

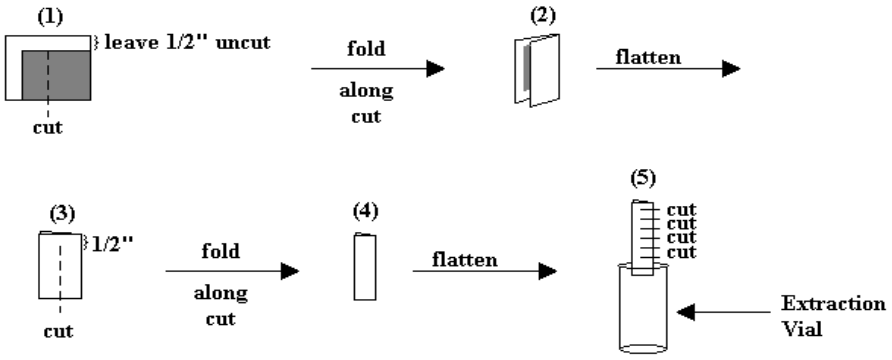

Figure 12.5, Cutting Filter Section.

12.6 Next, dispense a 20 ml aliquot of 0.50 N nitric acid (Filter Extraction Reagent) onto the cut filter pieces in the vial. Be certain the acid covers all the filter pieces. Seal the vial with a metal-free cap. Place each vial in a sonication rack.

12.7 Place the filled racks 2-3 cm apart in the sonication bath.

12.8 After the acid covered samples have sonicated at 60 ± 5 ^{o}C for 90 minutes, use a 4 liter bottle equipped with a dispensing unit to dispense a 20 ml aliquot of nanopure water into each sample vial, gently mix the capped solution, and then quickly return the sample to the sonicator. Sonicate an additional 90 minutes at 60 ± 5 ^{o}C. Each sample should sonicate for a total of 180 minutes at 60 ± 5 ^{o}C.

12.9 After the samples, the blank, and the spike have finished sonicating for the second time, allow the solutions to cool to room temperature and settle overnight (or for at least 6 hours) before vacuum filtering. The extraction solutions should then be vacuum filtered using the set-up in Figure 12.9.

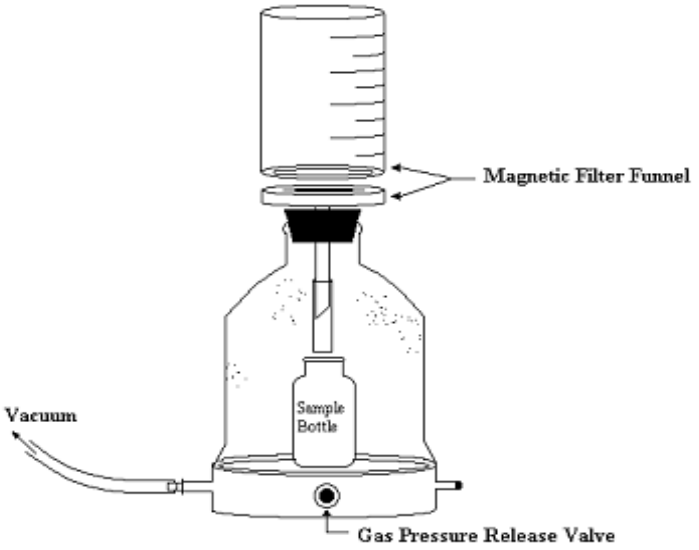

Figure 12.9, Vacuum Filtration Apparatus.

12.10 Repeat the following steps (12.10.1 through 12.10.13) for each sample listed on the extraction worklist, as well as the blank and spike.

12.10.1 Transfer the label from the vial directly to the individual sample bottle in which the filtrate will be stored.

12.10.2 Place a clean filtration membrane into the magnetic funnel assembly.

12.10.3 Place a waste container into the vacuum apparatus, positioned to collect fluid at the output tube of the magnetic funnel assembly.

12.10.4 Verify the vacuum assembly is properly setup.

12.10.5 Using a squirt bottle filled with the 0.25 N nitric acid (Filter Rinse Solution), thoroughly pre-moisten the membrane.

12.10.6 Vacuum the membrane as dry as possible, allowing the excess Filter Rinse Solution to vacuum off into the waste container. Discard this waste into the sink. Thoroughly rinse the sink with tap water.

12.10.7 Place a clean sample bottle below the output tube of the magnetic funnel.

12.10.8 Again, verify the vacuum assembly is properly setup.

12.10.9 Pour the sample extraction solution into the magnetic funnel. Let the vacuum pull the liquid through the membrane. Any filter fragments or large particles should remain above the membrane.

12.10.10 After almost all of the liquid has been pulled through, gently pull the gas pressure release valve several times to remove any remaining liquid, and then disconnect the apparatus carefully.

12.10.11 Carefully remove the filled sample bottle from the apparatus. Immediately seal the bottle with a clean, metal-free lid. Place the accumulating bottles in an upright position in a shallow, labeled box. The lead samples are stored at room temperature in a clean environment and are valid for 6 months.

12.10.12 Discard the used filtration membrane.

12.10.13 Rinse the magnetic funnel several times with nanopure water to remove any particles or residue. After rinsing the funnel, re-attach the funnel to the vacuum apparatus. Send an additional 50 ml aliquot of nanopure water through the magnetic funnel assembly without a membrane in place. Discard all rinse solutions, and reconnect the apparatus.

12.11 The extraction solutions are now ready to be analyzed by atomic absorption (See Section 14).

13. SAMPLE PREPARATION PROCEDURE FOR Cr-TOTAL

13.1 For each sample, blank, calibration standard, control, duplicate, and spike to be analyzed, prepare an acidified cup by placing 10 μl of ultra-pure nitric acid into a metal-free autosampler cup using an auto-pipette.

13.1.1 The Cr assay for the ultra-pure acid should be less than 100 ppt. Use good laboratory practices when handling the ultra-pure acid. Never pipette directly from the acid bottle. Never use suspect pipette tips.

13.1.2 This method is developed to acidify the reagent blank and calibration standards in small quantities, i.e., per autosampler cup. If these solutions are needed in bulk, use a volumetric flask to acidify the

$NaHCO_3$ reagent blank and calibration standards in bulk. Add 1 ml of ultra-pure acid per 100 ml of $NaHCO_3$ solution. Be cautious of the large amount of bubbles generated during preparation of bulk solutions: always mix solutions slowly, and vent volumetric flasks often to avoid caps popping off flasks. Vent flasks away from your body between mixing rolls.

13.2 Use an auto-pipette to dispense a 0.990 ml aliquot of each sample into an acidified cup. Bubbles will immediately be generated when the basic sample solution touches the drop of acid.

13.3 An electronic pipette set to the "MIX" mode works well for degassing. Mix the acidified sample gently, careful not to allow the bubbling to overflow the sampler cup. Continue mixing (degassing) each sample for 15 to 30 seconds prior to analysis. Degas the sample until you no longer generate any bubbles.

13.3.1 Use a fresh tip for each sample. Never introduce an acid-exposed tip into a sample collection jar.

13.4 The degassed samples are ready for GFAA analysis as described in Section 14.

14. GFAA ANALYSIS

14.1 Refer to Section 15 for the quality control measures required by this method. Historical quality control data can be found in the ILS Quarterly Quality Control Reports.

14.1.1 Use the appropriate instrument method and matrix modifier. Calibrate the instrument using a minimum of 3 standards; zero using a reagent blank. These solutions must be adjusted to match the matrices of the extracted samples as close as possible, i.e., standard solutions should be adjusted to 0.25 N HNO_3 and the chemical modifier should be added similarly to both the samples and standards.

14.1.2 Verify accuracy of the calibration with a non-standard control that falls within the calibration range: the result should be within the established limits (See Section 15.1) of the expected (target) value. If the control is out of range, the instrument may need adjusting prior to re-calibration, or the solutions may be invalid, requiring that a new set of standards and a new control be prepared. A check of a mid-range standard should be made every ten samples. If a standard check is greater than plus or minus 10% of the expected value, recalibrate and re-analyze samples back to the point where the calibration was known to be in control. The spike and blank should be treated as samples and should be analyzed along with the ambient filter samples.

14.2 GFAA Analysis Specifications

Table 14.2. GFAA Temperatures.

Analyte	Pyrolysis Temp. (°C)	Atomization Temp. (°C)
Cr	950	2500
Pb	850	1600

14.2.1 For all analyses, stop the argon gas flow during the atomization step; other steps require a continuous argon flow of 250 cubic feet per minute (ft^3/min). Ramp rate equals zero at this step for maximum power heating. An argon gas flow of 10 to 30 ft^3/min may be required during analysis of samples with high background interference.

14.2.2 For Pb, background correction is suggested. Do not use an argon purge.

14.2.3 For Cr, background correction is crucial. For Cr analysis of a $NaHCO_3$ matrix, the background is relatively high; however, do not use an argon purge. Use a maximum of 20 µl aliquots per analysis. Do not run more than a single sample injection per sample because of the likelihood of excessive salt buildup.

15. PERFORMANCE CRITERIA

15.1 Controls:

Control solutions for Pb and Cr are prepared by dilution of the stock control solution, based on the actual assay of the control material.

Controls should be analyzed immediately following calibration. For Pb or Cr analysis, the control value should fall within the acceptable upper and lower control limits, which are permanently set at ± 10% from the target value. If a control value is found to be outside the acceptable upper or lower control limits, adjustments to the instrument are made until re-calibration and re-analysis of the control yields a value that falls within the acceptable limits.

The control values should be plotted per day over time to illustrate value biases that might indicate: 1) a decline in the integrity of the calibration or control solutions, or 2) a problem with the pipettes or glassware. If plotted values are shown to be consistently biased near or outside the upper or lower warning limits, which are permanently set at ± 8% from the target value, the analyst should consider replacing the stock solutions, or checking the condition of the pipettes and glassware used.

15.2 Duplicates:

Every tenth sample should be analyzed in duplicate as a record of the method precision. The sample identification label for a duplicate should be marked with a "D_1" along with the sample number and the extraction date below it (i.e.

TP000001 D1 and 10/09/07). The Pb-TSP and Cr-Total duplicates should be extracted and prepared following the steps outlined in either Section 12 or 13.

If the percent difference of duplicate results is found to be greater than twenty percent and the mean of the two results is greater than the limit of quantitation (LOQ), then the analysis run should be evaluated by the analyst. The LOQ is defined as five times the LOD. If re-analyzing the duplicate samples gives similar results, no further action is needed.

For Pb-TSP, if a discrepancy is found between the first and second analysis, then the analysis set should be re-analyzed in total, and the separate runs compared; if these runs still do not compare, the entire set should be re-extracted and re-analyzed. If the discrepancy still occurs, consult the management on the course of action.

For Cr-Total source testing samples, if a discrepancy is found between the first and second analysis, then the analysis set should be re-analyzed; although continued discrepancy is unlikely, in the event it does occur, management and the client should be consulted for the data quality objectives for a given source testing project.

15.3 Blanks:

Results for TSP blanks must be less than two times the LOD for Pb. If greater, the sample preparation and analysis procedures should be reviewed to determine the extent and source of contamination. The analyst should determine whether the samples extracted along with the contaminated blank require re-extraction and analysis.

Pre-testing Protocol Blanks for Cr-Total source testing samples must be less than the LOD for Cr. See ARB Method 425 for a description of these samples. The analyst should contact the client for guidance in determining the response action to be taken when Cr-Total Pre-testing Protocol Blank results are found to be greater than the LOD.

15.4 Spikes:

The percent spike recovery (% R) for this method is calculated by:

$$\%R = \left[\frac{\text{Spiked result}}{(\text{Unspiked result} + \text{Spike added})} \right] * 100 \qquad \text{Equation 1}$$

where the results are in concentration units of ng/ml.

The spike results for Pb-TSP and Cr-Total should be within 80-120% recovery. If the limit is exceeded for any spike, the sample preparation and analysis procedures for the entire corresponding batch should be reviewed. In the event the analyst determines that the results are questionable, the samples should be re-analyzed. Validation of the results may require that a secondary sample segment or aliquot be analyzed. For Pb-TSP spikes, excessively loaded filter samples (samples concentrations greater than four times the spike added value)

or filter samples found to be less than the LOQ may exceed spike recovery limits without action. Cr-Total spikes may not exceed recovery limits. Re-analyze all samples associated with failed spike sample.

15.5 Limit of Detection (LOD):

The limit of detection for this method is calculated by:

$$LOD = T_{n-1,\alpha=0.99}(SD) \qquad \text{Equation 2}$$

where each term is expressed in concentration units, SD equals the standard deviation for seven replicate analyses and $T_{n-1,\alpha=0.99}$ equals 3.14, which correlates to a 99% confidence level and a SD estimate with a degree of freedom equal to n-1.The lowest standard should be within one to five times the estimated LOD.

15.5.1 Set the PE800 software to run the calibration through Y-zero.

Table 15.5.1. Published Limit of Detection

Analyte	ng/m^3 *	ng/ml
Pb-TSP	1	5
Cr-Total	---	1

*Assumes an air volume of 1600 m^3.

The following equation is used to convert from ng/ml to ng/m^3:

For Pb-TSP,

$$ng/m^3 = \frac{ng/ml \text{ x } (40\ ml)(8)}{1600\ m^3} \qquad \text{Equation 3}$$

where, 40 ml = total extraction volume, 8 = factor for total exposure area of filter (Note: extraction strip is 1/8 of exposure area of original filter), and 1600 m3 = air flow volume.

15.6 Characteristic Mass:

For GFAA analysis, the characteristic mass (m_o) is a value that represents the measured mass of the analyte that yields an absorbance reading of 0.0044. Each m_o value is specific to both the element and the sample matrix.

15.6.1 The m_o should be established for each element during the method development, and then checked during the daily calibration and prior to the analysis of samples. The m_o value for the lowest calibration standard must meet the criteria established for the method in use.

15.6.2 The PE800 software will calculate the m_o following each standard analysis. The analyst must determine whether the calculated value meets the method criteria.

15.6.2.1 The equation to calculate the m_o is:

$$m_o = \frac{(V)(C)(0.0044)}{A}$$ Equation 4

where the constant (0.0044) is unit specific for a sample aliquot volume (V) expressed in units of μl, C is the known sample concentration in units of μg/l, and A is the measured absorbance in units of absorbance-seconds.

15.6.3 For Pb-TSP analysis, the m_o for the lowest calibration standard should be within 24 to 36 picograms (pg)/ 0.0044 absorbance-seconds.

15.6.3.1 This assumes a 0.25 N HNO_3 matrix and the use of a platform-integrated tube with an end cap design.

15.6.4 For Cr-Total analysis, the m_o for the lowest calibration standard should be within 3.1 to 4.6 pg/ 0.0044 absorbance-seconds.

15.6.4.1 This assumes a 0.1 N $NaHCO_3$ matrix, acidified with 1% ultra-pure HNO_3, degassed of bubbles, and the use of a platform-integrated tube with an end cap design.

15.6.5 For GFAA method development of other analytes, start with a target value that is ± 20% of the Perkin Elmer (PE) expected value, assuming the matrix is 0.2 to 5% acid. For other matrices, the analyst should try to establish a viable criteria range prior to analyzing samples.

15.7 For Flame-AA, the characteristic concentration (m_c) of the low calibration standard should be determined for each element analyzed.

15.7.1 For Flame-AA method development, physically adjust the nebulizer spring and gas flows until the m_c value is within ± 20% of the PE expected value, assuming the matrix is 0.2 to 5% acid.

15.7.2 The equation for m_c is:

$$m_c = \frac{(C)(0.0044)}{A}$$ Equation 5

The constant used (0.0044) is unit specific for when C is the concentration of sample analyzed expressed in units of mg/l, and A is the determined absorbance in units of absorbance.

16. INSTRUMENT OPERATION

16.1 Follow the manufacturer's operation manual for a detailed description of programming and operation of the PE800 spectrophotometer, the computer, the control software, and the attached peripherals.

17. TROUBLESHOOTING

17.1 Consult the PE800 software for guidance in troubleshooting problems such as changes in the drying effectiveness or the peak shape.

17.2 The following are items to be aware of when operating the system. The information provided here is not intended to replace the operator's manual, but does include information not clearly or readily presented in the manual.

17.2.1 Lamp alignment. Computer controlled. Do not accept the computer alignment of lamps as faultless. If a lamp fails to reach a usable energy, the analyst may need to physically resituate the lamp as little as a millimeter nudge, or turn the entire system (including the computer) off-and-on several times in order to reset system.

17.2.2 Lamps, general. Allow ten minutes for a lamp to warm-up before beginning analysis. The selected line and slit width for the element of interest are manually entered. Consult the manual for sensitivity expectations of each available line for each element. Make a note of the starting energy of each new lamp. Changes in energy, a substantial drop or even an increase in energy are all indicative of lamp malfunctions, degradation, or alignment problems.

17.2.3 Burner head. Computer controlled. Positioning the burner at a 45-degree angle may be helpful for highly sensitive elements. The 10 cm head provides the best sensitivity for air-acetylene flames.

17.2.4 Injection tip alignment. Semi-computer controlled. It may take many attempts to properly position tip.

17.2.5 Nebulizer adjustment. Manually adjust/check the nebulizer whenever the aspirating chamber has been moved or whenever the characteristic concentration falls outside acceptable limits (Section 15.7). Consult operator's manual for proper adjustment of the internal spring system.

17.2.6 Gas flows. Computer controlled feature, although there is a manual override. In addition to determining the acetylene/air ratio that gives the maximum sensitivity, be aware of analyzing elements requiring a yellow-rich flame versus a lean-blue flame. Also, keep aware of the flows and the available tank pressures.

17.2.7 Impact bead versus flow spoiler. The impact bead improves sensitivity for solutions with low solids. Use the flow spoiler for solutions high in solids.

17.2.8 Deuterium lamp. A fluctuation in energy indicates possible deterioration. Call for PE service.

17.2.9 Platform and tube, general. The PE800 uses an end cap design, THGA graphite tube with integrated platform, which is suitable for all

elements using a platformed tube, as well as those typically volatilized directly off the wall of the tube. The cooling step is not recommended when using the THGA tube. Never use a platform-loose tube (L'vov or forked) with the PE800.

17.2.10 Drying/ pyrolysis/ atomization setup. Consult software for starting point estimates to develop proper temperatures and ramp times. Drying should be a smooth melt. Fine tuning of the initial pyrolysis and atomization settings can be obtained by plotting absorbance versus temperature to find the maximum absorbance.

17.2.11 Quartz windows. Clean with nanopure water or alcohol to remove dust build-up. If windows are splattered, the drying step needs to be adjusted. Be certain windows are dry before replacing.

17.2.12 Tube, replacement. Gently wipe the inside of the cylinders with a nanopure water moistened cotton swab before replacing tube. Replace the graphite tube when peak shape and/or absorbance readings deteriorate.

17.2.13 Matrix modifiers. Modifiers should be used to volatilize interferences prior to atomization of the analyte, and to increase the amount of analyte atomized. Significant differences in results can be found by altering components and concentrations of the modifiers. Plot modifier: standard ratios versus absorbance to determine maximum absorbance and minimum background.

17.2.14 Contact rings. If random peaks appear or drying times become insufficient, blow out and/or rinse with nanopure water the graphite cylinder to clear the inlet gas flow. If condition persists, change the contact rings.

17.2.15 Zeeman-effect magnet. Odd fluctuations in absorbance output may indicate a possible deterioration of the magnet. If unable to correct by changing the lamp position and/or source, call PE service.

18. INSTRUMENT MAINTENANCE

18.1 Routine GFAA maintenance:

- Clean quartz windows with lab wipe and alcohol.
- Check tube condition/ do a high temperature burn on new tubes.
- Wipe contact rings with DI moistened cotton swab before replacing tube.
- Check condition of contact rings.
- Check water flow inlet/outlet.
- Check argon tank pressure.
- Verify lamp energies are consistent.
- Check flushing system tubing for clogs or leaks.
- Check furnace alignment after instrument changeover.

18.2 Routine Flame-AA maintenance:

- Check condition of aspirator tubing before each use.
- Run a thin cardboard card, such as a business card, in burner slot to remove lodged materials before each use.
- Confirm “even” flame with visual inspection.
- Verify lamp energies are consistent.
- Check drainage tubing and drain reservoir level.
- Check burner alignment after instrument changeover.

19. HANDLING AND DISPOSAL OF CHEMICALS

19.1 The analyst is responsible for ensuring the responsible purchase and subsequent safe storage of all chemicals associated with this method.

19.2 The GFAA autosampler rinse solution is less than 0.05% acidified nanopure water and can be disposed of in the laboratory sink, followed by a minute of flushing with tap water.

19.3 Standard dilutions for non-hexavalent Cr and Pb that are in the parts-per-billion (ppb) range, which is the typical operating range of the GFAA, can be disposed of in the laboratory sink, followed by a minute of flushing with tap water.

19.4 Contact the Monitoring and Laboratory Division’s Hazardous Waste Coordinator for the proper disposal of stock standards for non-hexavalent Cr and Pb that are in excess of 1 ppm and any other chemicals.

20. ATOMIC ABSORPTION OPTICAL SYSTEM

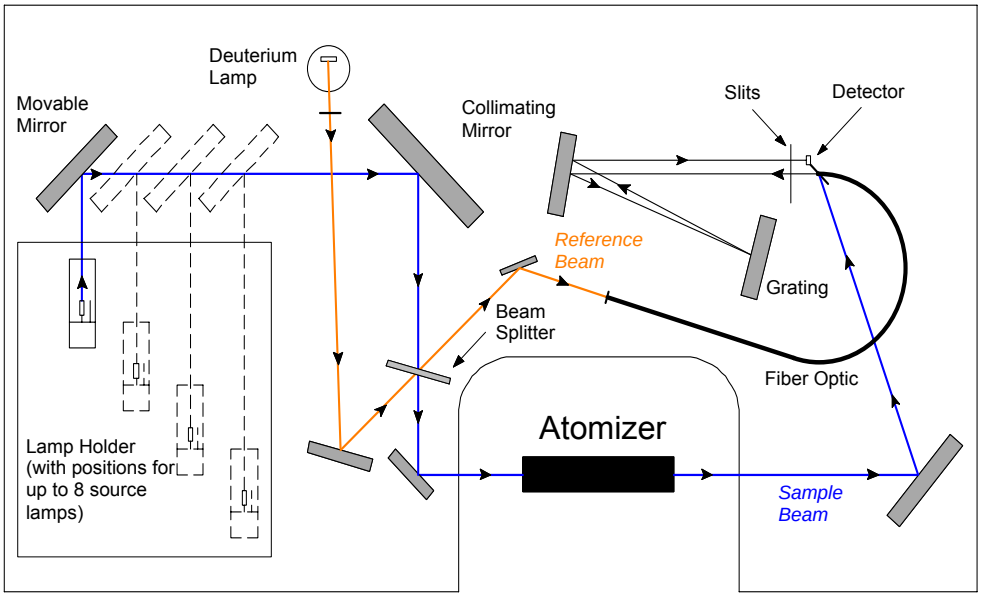

Figure 20. Atomic Absorption Optical System.

21. EXAMPLES OF INSTRUMENT OUTPUT

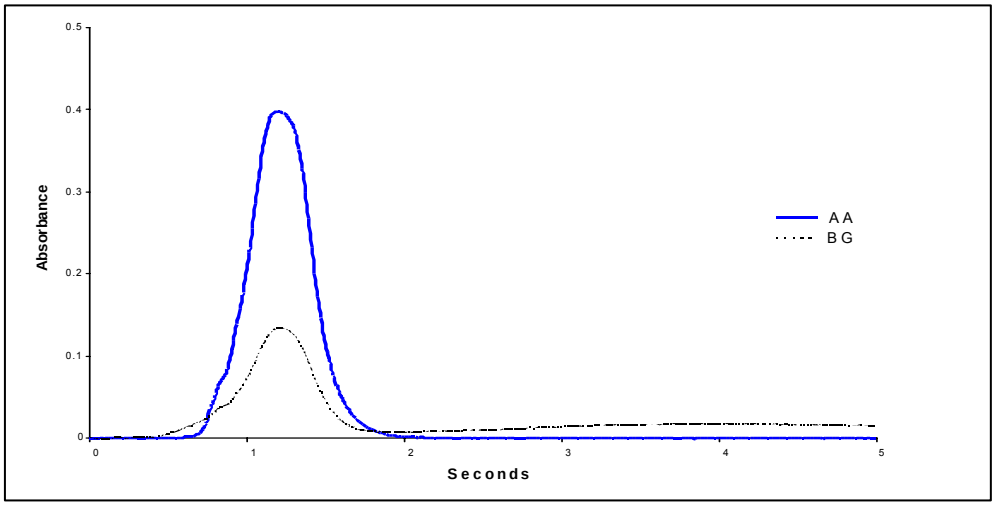

Figure 21.1. Spectra for Pb from TSP filter sample, with matrix modified and background corrected.

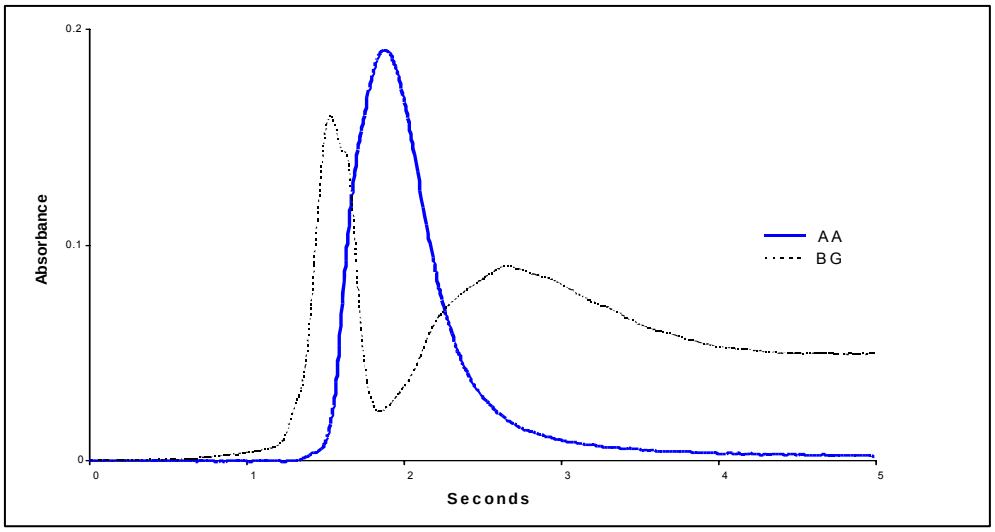

Figure 21.2. Spectra for Cr-Total collected in 0.1 N $NaHCO_3$, with matrix modified and background corrected.

22. REVISION HISTORY

METHOD	EFFECTIVE DATE	PRIMARY CHANGE(S) FROM PREVIOUS REVISION
NLB005, Preliminary Draft 2	10/28/85	Heavy metal determinations using flame; developed from EPA Method EM/SL/RTP-SOP-EMD-002 (10/83).
NLB005, Revision 3.2	09/18/88	Instrument changed from Varian 375 to PE 3030B, specific to Pb.
NLB005, Revision 4.0	06/01/92	Addition of As, Be, and Cd analyses by GFAA; amount of filter extracted increased by two.
MLD005, Revision 5.0	04/01/93	Instrument changed from PE 3030B to PE 5100PC; analyses of Pb changed from Flame-AA to GFAA.
MLD005, Revision 5.1	01/01/97	Control software and autosampler (AS-70 to AS-71) upgrades; general fine-tuning of procedures.
MLD005, Revision 5.2	07/01/98	Extraction apparatus upgrade (Section 11 of Rev 5.2); general fine tuning of procedure (Section 11 and Section 14, Subsection 14.5.2 of Rev 5.2); amount of filter extracted reduced by half (Sections 1 and 11 of Rev 5.2).
MLD005, Revision 6.0	10/16/03	Instrument changed from PE 5100PC to PE800; added specifics for Cr source testing sample analysis; removed specifics for As, Be, and Cd.
MLD005, Revision 6.1	5/15/07	Added statement referring to SOP MLD016 (Balance Room procedures for TSP filters). Corrected filter strip size.