SECTION 12

LABORATORY SAMPLE PREPARATION AND ANALYTICAL METHODS

This section describes the steps to be taken by analytical laboratories to prepare for monitoring events, and the procedures laboratories will use for stormwater sample analyses. The following topics are discussed:

KEY TOPICS

- **Laboratory Selection and Contracting**
- **Pre-Sampling Preparations**
- **Sample Storage and Handling Prior to Analysis**
- **Reporting Limit Requirements**
- **Analytical Methods**
- **Laboratory Data Package Deliverables**

➤ LABORATORY SELECTION AND CONTRACTING

Important considerations in selecting an analytical laboratory include location, performance, ability to meet analytical reporting limits (RLs), and experience with the type of samples that will be generated by the monitoring program. The various analytical needs of the monitoring program may warrant the selection of multiple laboratories.

Selecting a laboratory in close proximity to the study area is important for convenience, logistical support, and analysis of constituents with very short holding times (such as coliform bacteria). A local laboratory can provide sample bottles, supplies, and equipment on short notice, and can quickly make arrangements for sample preservation and analysis that may need to be performed within a short holding time, at night or on weekends. If the latter is anticipated, the laboratory contract should provide for off-hours sample handling and analysis by the laboratory.

The laboratory should have a proven record of performance with the particular types of analysis to be conducted for the project. Ideally, the laboratory will have demonstrated experience conducting the analysis in a comparable sample matrix.

Department of Health Services (DHS) certification is required for Caltrans analytical work. However, in certain cases it may be difficult to contract for all required analyses with DHS-certified laboratories. In such cases, alternative arrangements may be made provided that the exception is documented and approved by the Caltrans task order manager. For example, if constituent reporting limits cannot be adequately achieved by

certified laboratories, a research level laboratory with a proven ability to perform the needed analysis can be used with approval from the Caltrans task order manager. Such laboratories may include out-of-state commercial laboratories or university/research laboratories with demonstrated expertise in EPA-sponsored research or method development programs.

It is important to ensure that the selected laboratory is able to meet the RLs derived for the project (Table 12-1), or alternatively, that the lab is able to reliably report constituent concentrations above their RL based on site-specific historical data. It is often necessary to utilize more than one analytical laboratory to meet the prescribed RLs. If one laboratory is unable to meet the project RLs for certain constituents, it may be necessary to ship those samples to other laboratories that can meet the project RLs. If multiple laboratories are selected, it is suggested that the monitoring program manager contract directly with all labs to allow for increased quality control and better response. This will require the monitoring program manager to package and ship samples to the appropriate laboratories. If multi-bottle sample compositing (i.e., combining multiple composite samples to create one representative sample) is necessary, the monitoring program manager should coordinate with the local laboratory to composite samples prior to shipping when possible. See ***Section 10*** for multi-bottle compositing and sample delivery information.

Finally, it is necessary that laboratories be made contractually accountable to meet all Caltrans' data quality acceptability limits or objectives (DQOs) and project specifications. This is discussed in more detail later in this section.

➤ PRE-SAMPLING PREPARATIONS

The analytical laboratory will be involved in a number of activities prior to the actual analysis of stormwater samples, including:

- Determination of key laboratory performance requirements (e.g., maximum reporting limits, turnaround times, report formats) for analytical services contract.
- Review and comment on the data quality evaluation plan (DQEP), QC sample schedule, and QC sample volumes. This overall package is sometimes referred to as the QA/QC plan.
- Providing sampling team with clean sample containers and blank water.
- Coordination with sampling team prior to each anticipated storm sampling event.

Determination of Laboratory Performance Criteria

The analytical laboratory must analyze the stormwater samples using methods that will achieve Caltrans' DQOs for the project (see ***Section 2***). The contract for analytical services should specify laboratory performance criteria designed to ensure that the project DQOs will be met. The contract should specify the following:

- Analytical reporting limits
- ✔ Holding times
- ✔ Types and frequency of QA/QC analyses
- ✔ Quality control performance limits
- ✔ Sample turnaround times
- ✔ Electronic and hard copy report formats
- ✔ Corrective action procedures

In addition, the contract with the laboratory should specify that at least 90% of the sample results must meet the QA/QC criteria and be deemed usable for the project.

Laboratory Input to Project QA/QC Plan

The contract laboratory should review and provide input to the QA/QC plan for each Caltrans stormwater monitoring project. This input will help ensure that the QA/QC plan specifies the correct sample containers, sample volumes, holding times, analytical methods, reporting limits, and the correct points of contact for communications between field and laboratory personnel. In addition, the laboratory should be involved early in the process so they can provide feedback on methods and performance standards during the planning phase.

Sample Containers, Blank Water

Each analytical method has specific requirements with regard to the type of sample container (e.g., plastic, glass, Teflon, amber glass), the size of the container, and the number of containers. Table 12-1 shows the appropriate sample containers for the analytical methods recommended for the Caltrans stormwater monitoring program. As noted above, the analytical laboratory should review the QA/QC plan for each Caltrans stormwater monitoring project to ensure that the plan specifies the appropriate sample containers, volumes, and preservatives. As discussed in ***Section 10***, sampling personnel will need to request the appropriate containers from the laboratory prior to each sampling event. The containers needed for a given project will vary depending on the constituents to be analyzed, the sample collection procedure, and the DQOs. For example, stormwater monitoring programs often include composite samples, wherein subsamples

collected during a storm event may be combined in one or more large containers. After the composite sample has been delivered to the laboratory, water is transferred from the composite sample containers into the individual containers required for each analysis, and the individual samples are then filtered and/or preserved as required.

If a given project calls for collection of composite samples, the field personnel must obtain the appropriate composite sample containers from the laboratory; however, the field personnel do not need the individual containers required for each analysis. The composite sample bottle container must be large enough to provide sufficient volume of sample for all of the individual constituents to be analyzed. The container type should be compatible with all of the constituents to be analyzed. Although plastic and Teflon are the preferred container materials for metals, borosilicate glass is the most common material for composite sample containers because it is also compatible with organic constituents and is more cost effective than Teflon. However, bottle contamination issues should always be assessed with blank samples, regardless of the bottle material (see ***Section 11***).

For stormwater projects that specify collection of grab samples, field personnel must obtain the appropriate pre-cleaned bottles from the laboratory prior to the sampling event.

Some projects may require use of "ultra-clean" techniques (USEPA, 1996) in order to meet the project DQOs. Such techniques may entail use of special cleaning procedures for the sample containers, which should be specified in the contract for analytical services and the QA/QC plan for the project, to ensure that the containers obtained from the laboratory have been cleaned in accordance with the EPA guidance. ***Appendix E*** describes these cleaning procedures in detail.

Sample volumes necessary for the requested analyses should be confirmed with the laboratory prior to sample collection, including sufficient sample volumes for the required laboratory QA/QC analysis. As discussed in ***Section 11***, laboratory QC samples that make use of sample water provided by the field crew include splits (laboratory duplicates), matrix spikes, and matrix spike duplicates. Additional sample water will also be required for field duplicate QC samples, as discussed in ***Section 11***.

If field blanks are to be collected, the laboratory also will need to provide sufficient quantities of blank water and appropriate containers (see ***Section 11***). The blank water supplied by the laboratory should be the same as the water used for equipment cleaning.

Laboratory Coordination Prior to a Sampling Event

It is important for the task manager to notify the laboratory of an anticipated storm sampling event so that the laboratory can prepare for possible off-hour sample delivery, and to set up for any analyses with short holding times. The laboratory contact should

be notified regarding the number of samples anticipated, approximate date and time of sampling (if known), and when sample containers, blank water or ice chests will be required.

In addition, the laboratory should be made aware of specific project requirements such as required laboratory performance objectives, required QC samples, and reporting requirements.

➤ SAMPLE STORAGE AND HANDLING PRIOR TO ANALYSIS

To minimize the chance of sample contamination and unreliable analytical results, special measures must be taken during the storage and handling of samples prior to analysis. For example, samples must be collected and stored in the appropriate containers and preserved. If composite samples are collected, sample splitting must be conducted to properly store and preserve the samples. In addition, some analytical methods require filtration of the sample prior to analysis. Finally, samples must be analyzed within established holding times to ensure reliability of the results. Each of these measures is discussed in more detail below.

Composite Splitting

As mentioned above, if composite sampling procedures are used, the samples must be split prior to analysis. It is recommended that composite sample splitting be conducted by the analytical laboratory or in another similarly controlled environment to minimize the chance of contamination. Clean techniques should be used when handling and splitting the composite sample. ***Section 10*** explains the sample splitting procedures in detail.

Sample Filtration

Sample filtration is required when collecting samples for dissolved metals determinations. It is recommended that filtration for metals be conducted by the analytical laboratory to reduce the potential for contamination in the field, especially during storm conditions. USEPA specifies the use of a 0.45 μm, 15 mm diameter or larger, tortuous-path capsule filter or equivalent (USEPA, 1996). To minimize dissolved/suspended phase partitioning of metals from the time of sample collection to the time of analysis, it is essential that the laboratory perform the sample filtration promptly. The field crew should therefore specify “filter for dissolved metals immediately upon receipt” on the sample chain-of-custody form, and coordinate this activity with the laboratory in advance.

Sample Preservation

Chemical preservatives are added to the samples for certain analyses to prolong the stability of the constituents during storage. Table 12-1 lists the required sample preservatives for various types of analytical constituents. If composite sampling procedures are used, no preservatives are added to the composite container, because no single chemical preservative is suitable for all of the constituents to be analyzed. The laboratory must first divide the composite sample into the appropriate bottle for each analysis, and then add chemical preservatives as appropriate for each analysis. If grab sampling procedures are used (i.e., field personnel directly fill the containers required for each analysis), the laboratory should add the appropriate preservative to each sample container immediately upon receipt at the laboratory. Use of bottles pre-filled with preservative is not recommended, as this may increase logistical problems (e.g., field crews have to avoid loss of preservative when collecting samples).

Holding Times

Maximum acceptable holding times are method-specified for various analytical methods and analytes (see Table 12-1). The holding time starts when sample collection is complete and is counted until extraction/preparation or analysis of the sample. The time of collection of the final sample aliquot is considered the "sample collection time" for determining sample holding time for composite samples that represent less than 24 hours of flow (APHA, *et al.*, 1998). If the composite sample collection period exceeds 24-hours, the composite sample bottle(s) should be replaced at or prior to the end of each 24-hour period. For constituents with short holding times, such as 48-hours or less, composite sample volume should be removed from each 24-hour composite for analysis as necessary to comply with holding time requirements. If a sample is not analyzed within the designated holding times, the analytical results may be suspect (see ***Section 13***). Thus, it is important that the laboratories meet all specified holding times and make every effort to prepare and analyze the samples as soon as possible after they are received. Prompt analysis also allows the laboratory time to review the data and, if analytical problems are found, re-analyze the affected samples.

Table 12-1 lists the maximum acceptable analytical holding times for a comprehensive list of constituents potentially monitored in Caltrans projects. Some of these holding times are short and will require the laboratory to immediately handle the sample once received. For example, the fecal coliform test must be started within 8 hours of sample collection. Similarly, BOD_5 or nitrite analyses must be performed within 24 and 48 hours, respectively, after sample collection. Holding times may be a factor affecting allowable sampling times if the laboratory has not agreed to work evenings or weekends.

To minimize the risk of exceeding the holding times, stormwater samples must be transferred to the analytical laboratory as soon as possible after sampling is complete.

Moreover, the laboratory should be notified before the sampling begins so that it can prepare to analyze the samples immediately upon receipt.

➤ REPORTING LIMIT REQUIREMENTS

Table 12-1 lists the reporting limits for the comprehensive list of analytical constituents potentially monitored in Caltrans projects. The reporting limit is the minimum concentration at which the analytical laboratory can reliably report detectable values. This operational definition does not distinguish between the type of reporting limit, but relies on the laboratory's historical practice of reporting and a thorough review of laboratory practice and performance. Definitions of specific types of reporting limits (MDL, PQL, ML, etc.) can be found in the glossary to this document. The reporting limits in Table 12-1 are provided as a guide for monitoring projects that do not have historical data sets for reference.

It is important to ensure that the RLs derived for the project are low enough to provide useful results. For example, if the analytical results are to be compared with water quality objectives (WQOs) every effort should be made to ensure that the RLs are lower. Therefore, the selected analytical methods should provide RLs at or below the criteria against which the stormwater samples are to be compared.

RLs are often specific to a given type of sample matrix. The RL for a given sample may be elevated due to the presence of interfering compounds. For example, RLs for metals in salt water are generally five to ten times higher than RLs for fresh water (when using the same method), due to salt interference with the atomic absorption instrument.

➤ ANALYTICAL METHODS

This section discusses the analytical methods that should be used to meet the reporting limits and other DQOs for the project (***Section 2*** describes how project DQOs are developed). As discussed in ***Section 4***, analytical constituents are selected based on regulatory and legal requirements, water quality objectives, historical data, and other considerations.

For some constituents, alternative analytical methodologies may be used to meet the data quality objectives for reporting limits and control limits of QC samples. Also, methods are being updated and new methods developed for different analytical parameters. In selecting the analytical method to be used, the following questions should be addressed:

- ✔ Does the method conform to any legal or regulatory requirements for the monitoring program?

- ✔ Does the method allow the required reporting limits to be easily obtained on stormwater samples?
- ✔ Does the method have the same or more stringent control limits for QA/QC samples?
- ✔ Will the data provided by the method be comparable to historical data collected at the station?
- ✔ Is the method recognized as "standard" so that the data collected at a station can be compared to other stations?
- ✔ Is the laboratory proficient with the method? Do they have historical data to show proficiency?

The recommended analytical methods for conventional, nutrient, metal, organic and bacteriological constituents are discussed below and are shown in Table 12-1. All of these methods are described either in "Standard Methods for the Examination of Water and Wastewater, 20th Edition" (APHA, *et al*., 1998) or in the listed EPA method. A complete list of the constituents in each EPA method is included in the Data Reporting Protocols (see ***Appendix H***) and also available on CD-ROM (Methods and Guidance for Analysis of Water – EPA 821-C-99-004). The 8000 series analyses (modified soils methods) can be downloaded from the Internet at "http://www.epa.gov/SW-846/8xxx.htm". The approved methods should be referenced for more detailed sampling and analytical information.

Conventional Parameters

Typical conventional parameters analyzed by the laboratory include hardness, total dissolved solids (TDS), total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and turbidity. Specific conductance, temperature, and pH are measured and recorded in the field using appropriate field instruments when each sample is collected.

Total hardness, expressed as the concentration of calcium carbonate, is a titrimetric-colorimetric method of sequestering the calcium and magnesium ions in the stormwater sample, as described by EPA Method 130.2. Total dissolved solids (also described as filterable residue), described in EPA Method 160.1, is measured by evaporating the filtrate from a previously filtered stormwater sample and weighing the remaining solids. TSS is measured by filtering the stormwater sample and recording the increase in filter weight, as described by EPA Method 160.2. The recommended RLs for these methods are listed in Table 12-1.

BOD measures the dissolved oxygen consumed by microbial life in the stormwater sample using a probe or bottle technique, as currently described by Standard Method 5210B. COD measures the amount of oxygen required by a strong chemical oxidizing

agent to oxidize the organic matter in a sample. COD is measured using EPA Method 410.1. Turbidity is a measure of how much light a stormwater sample will scatter; highly turbid (cloudy) samples will scatter more light than clear samples. The measurement of turbidity is accomplished using EPA Method 180.1.

Nutrients

Typical nutrient constituents analyzed include nitrite (as N), nitrate (as N), ammonia (as N), total Kjeldahl nitrogen (TKN), total phosphorus, and orthophosphate. Nitrite and nitrate are determined in stormwater samples using EPA Method 300.0 (ion chromatography) and are expressed as the concentration of nitrogen. Ammonia is measured with an ion-specific electrode described in Method 350.3 and expressed as the concentration of nitrogen. TKN is typically measured using EPA Method 351.3, in which ammonia is determined after distillation by titrimetric, colorimetric, or potentiometric procedures. Phosphorus is measured in all forms (total, dissolved, and soluble reactive phosphorus) by a colorimetric procedure described in EPA Method 365.2.

Metals

Metals analysis typically includes the total recoverable and dissolved fractions. If composite sampling procedures are used, the laboratory will filter an aliquot of the stormwater sample for analysis of the dissolved metals and add preservatives to both the total and dissolved subsamples.

There are several methods available for metals analysis. The EPA methods commonly in use are inductively coupled plasma (ICP), graphite furnace atomic absorption (GF-AA), and inductively coupled plasma mass spectrometry (ICP-MS). These methods may be used individually or in concert to meet the DQOs of the project.

Analysis should be performed for metals using (except mercury; see below) GF-AA (EPA method 200.9) or ICP-MS (EPA method 200.8). The GF-AA and ICP-MS methods have significantly lower reporting limits for most metals compared to the ICP, although the GF-AA and ICP-MS methods are more expensive that the ICP method. Caltrans stormwater samples should not be analyzed using ICP procedures currently described by EPA Method 200.7, because ICP reporting limits for several metals are often higher than their water quality criteria. However, many laboratories prefer to analyze the samples first using ICP to ensure that the metals concentrations are not too high for the more sensitive GF-AA or ICP-MS equipment.

EPA recently developed a new ICP-MS series (Method 1638) for metals analyses designed to yield very low reporting limits by using class 100 clean room practices and clean technique sampling. This method should be used if the reporting limits using EPA Method 200.8 are not sufficiently low enough to provide regular and reliable detection.

The recommended method for mercury analysis is cold vapor atomic fluorescence spectrometry (CVAFS, EPA Method 1631).

Organics

Total petroleum hydrocarbon (TPH) analyses for Caltrans monitoring projects will typically focus on gasoline, diesel, and motor oil hydrocarbons. Gasoline is in the carbon range between 5 and 10 carbons (C5 and C10) and requires volatile organic sampling techniques (grab sampled into VOA collection bottles with no headspace). The diesel range is typically considered from C12 to C24 and motor oil is approximately C24 to C36 or higher. EPA Method 8015 modified/extended is recommended for analysis of Caltrans' stormwater samples, because it distinguishes between the types of hydrocarbons present in the sample, and there is no concern of non-petroleum interferences. EPA Method 8015 mod/ext. also provides additional confidence in sample results because of the additional quality control/quality assurance procedures included with the method. Caltrans should specify to the analytical laboratory that the samples should be analyzed by EPA Method 8015 mod/ext. and quantified for the hydrocarbon range(s) of interest. The laboratory should review the chromatograms to ensure that the summary report of analytical results actually represents hydrocarbons which show a gas chromatographic trace similar to hydrocarbons range(s) of interest. The gas chromatograms for the samples, QC samples, and standards can be requested in the data package.

Measurement of total oil and grease is accomplished using EPA Method 1664 and should also be included if the expected concentrations are above the reporting limit noted in Table 12-1. EPA method 413.1 uses freon as the carrier gas. Freon is no longer readily available and it is likewise difficult to find laboratories that can cost-effectively perform the analysis using this method.

Additional organic constituents that may be analyzed include polynuclear aromatic hydrocarbons (PAHs), pesticides, and solvents. PAHs can be measured using a gas chromatography/mass spectrometry method such as EPA Method 625 (for semi- and non-volatile organics). However, this method is prone to matrix interferences and elevated reporting limits. EPA Method 8310, which was also developed for water samples, detects the most toxic PAHs. The high selectivity of the detectors used for Method 8310 eliminates most matrix interferences and allows for very low reporting limits.

Analysis for the organophosphorus pesticides diazinon and chlorpyrifos should be performed according to EPA Method 8141 (organophosphorus compounds by gas chromatograph) or by enzyme-linked immunosorbant assay (ELISA) analysis.

Solvents may be occasionally detected in stormwater runoff from maintenance/vehicle service locations (LWA, 1996). Although the majority of these constituents are volatile

organic compounds (which readily evaporate and are not expected to be found in stormwater runoff), their inclusion in Caltrans stormwater monitoring efforts may be important for characterization of runoff from maintenance yards. The best methods for analysis of solvent-related constituents are EPA Methods 601 and 602.

Fecal and Total Coliform Bacteria

Bacteriological constituents for analysis include fecal and total *coliform.* These analyses are typically performed using Standard Methods 9221B and 9221E, respectively, although other methods are available. This constituent has a short recommended holding time for analysis. Standard Methods specifies that these samples must be delivered to the laboratory within 6 hours of sampling and analysis begun by the laboratory within 2 hours of delivery (APHA, *et. al.*, 1998). This is interpreted as a maximum total holding time of eight hours prior to initiating analysis. Samples that do not meet holding time specifications should be qualified as described in ***Section 13***.

➤ LABORATORY DATA PACKAGE DELIVERABLES

As a part of the laboratory contract, the data package that will be delivered to Caltrans and the timing of its delivery (turn around time) should be defined. The data package should be delivered in hard copy and electronic copy (on diskette).

The hard copy data package should include a narrative that outlines any problems, corrections, anomalies, and conclusions, as well as completed chain of custody documentation. A summary of the following QA/QC elements must be in the data package: sample extract and analysis dates, results of method blanks, summary of analytical accuracy (matrix spike compound recoveries, blank spike compound recoveries, surrogate compound recoveries), summary of analytical precision (comparison of laboratory split results and matrix spike duplicate results, expressed as relative percent difference), and reporting limits. Because the laboratory must keep the backup documentation (raw data) for all data packages, raw data (often called Contract Laboratory Program (CLP) data packages) should not be requested. However, for all total petroleum hydrocarbon analyses, the gas chromatograms of station samples, QC samples, blanks, and standards should be requested, as described above.

In addition to the hard copy, an electronic copy of the data can be requested from the laboratory. The electronic copy includes all the information found in the hard copy data package, with the exception of TPH chromatograms. Data reporting and the standardized electronic format for Caltrans data submittals are discussed in ***Section 14***.

Common turn around times for laboratory data packages are two to three weeks for faxed data and three weeks to thirty days for hard copy and electronic copy. Receiving the faxed data quickly allows an early data review to identify any problems that may be

corrected through sample re-extraction or re-analysis. The hard copy data package should undergo data review as described in ***Section 13***.

Table 12-1. Analytical Constituent Method Specifications and Recommended Reporting Limits

Analyte	*Method Type*	*EPA Method Number [a]*	*Holding Time [b]*	*Container Type*	*Preservation*	*Reporting Limit/ Resolution*	*Units*
Conventionals							
BOD	probe	SM 5210B	24 hours [c]	glass or PE	4°C	3	mg/L
COD	titrimetric; calorimetric	410.1; 410.4	28 days	glass or PE	4°C and H_2SO_4 to pH<2	10	mg/L
Conductivity	conductivity meter	SM 2510	28 days	glass or PE	4°C; filter if hold time > 24 hours	±1[d]	µmho/cm
Hardness	titrimetric; colorimetric; calculation	130.2; 130.1; SM 2340B	6 months	glass or PE	4°C and HNO_3 or H_2SO4 to pH<2	2	mg/L
pH	electrometric	150.1	15 minutes	glass or PE	none	±0.1 [d,e]	std.units
Temperature	thermometer; thermistor; thermophone	SM 2550	15 minutes	glass or PE	none	±0.1[d]	°C
TOC; DOC	oxidation or combustion	415.1	28 days	glass or PE[f]	4°C and HCl or H_2SO_4 to pH<2 [g]	1	mg/L
TDS	dried filtrate weight	160.1	7 days	glass or PE	4°C	1	mg/L
TSS	dried filter weight	160.2	7 days	glass or PE	4°C	1	mg/L
Turbidity	nephelometric	180.1	48 hours	glass or PE	4°C	±0.05[d]	NTU
Nutrients							
NH_3-N	titrimetric; potentiometric	350.2; 350.3	28 days	glass or PE	4°C and H_2SO_4 to pH<2	0.1	mg/L
NO_3-N	ion chromatography	300.0	48 hours	glass or PE	4°C	0.1	mg/L
NO_2-N	ion chromatography	300.0	48 hours	glass or PE	4°C	0.1	mg/L
NO_3/NO_2-N	colorimetric	353.2	28 days	glass or PE	4°C and H_2SO_4 to pH<2	0.1	mg/L
P	colorimetric	365.2	28 days	glass or PE	4°C and H_2SO_4 to pH<2	0.03	mg/L
Ortho-P, dissolved	colorimetric	365.2; 365.3	48 hours	glass or PE	4°C; filter immediately	0.03	mg/L
TKN	titrimetric; colorimetric; potentiometric	351.3	28 days	glass or PE	4°C and H_2SO_4 to pH<2	0.1	mg/L
Metals							
Ag	GF-AA [h]; ICP-MS	272.2; 200.8 [j]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	0.2	µg/L
Al	GF-AA [h]; ICP-MS	200.9; 200.8 [k]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	25	µg/L
Cd	GF-AA [h]; ICP-MS	213.2; 200.8[j]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	0.2	µg/L
Cr	GF-AA [h]; ICP-MS	218.2; 200.8[j]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	1	µg/L
Cu	GF-AA [h]; ICP-MS	220.2; 200.8[j]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	1	µg/L
Ni	GF-AA [h]; ICP-MS	249.2; 200.8[j]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	2	µg/L
Pb	GF-AA [h]; ICP-MS	239.2; 200.8[j]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	1	µg/L
Zn	GF-AA [h]; ICP-MS	289.2; 200.8[j]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	5	µg/L
As	GH-AA; ICP-MS [l]	206.3; 200.8 [k]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	1	µg/L
Fe	GF-AA; colorimetric	200.9; SM 3500-Fe B	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	25	µg/L
Se	GF-AA [h]; GH-AA	270.3; 1639[m]	filter for dissolved fraction and preserve within 48 hours; 6 months to analysis	Teflon, PE, or borosilicate glass	4°C and HNO_3 to pH<2 [g]	2	µg/L
Hg	CV-AFS	1631	filter for dissolved fraction and preserve within 48 hours; 28 days	Teflon or glass	4°C and 5 mL/L of pretested 12N HCl or 5 mL/L BrCl solution [g]	0.5	ng/L

Table 12-1. Analytical Constituent Method Specifications and Recommended Reporting Limits (continued)

Analyte	*Method Type*	*EPA Method Number*	*Holding Time*	*Container Type*	*Preservation*	*Reporting Limit*	*Units*
Total Petroleum Hydrocarbons							
TPH (gasoline)	GC	8015b	14 days	VOA	4°C	50	µg/L
TPH (diesel)			extract - 7 days; analyze - 40 days	wide -mouth glass			
TPH (motor oil)							
Oil & Grease	gravimetric (HEM/SGT)	1664 [n]	28 days		4°C and HCl or H_2SO_4 to pH<2	5	mg/L
Pesticides and Herbicides [o]							
Glyphosate	HPLC	547	14 days	amber glass	4°C; sodium thiosulfate in the presence of chlorine	5	µg/L
OP Pesticides (esp. diazinon and chlorpyrifos)	GC; ELISA [p]	8141; ELISA [p]	extract - 7 days; analyze - 40 days			0.05 [p]	
OC Pesticides	GC	8081 [q]				0.05 -1.0	
Chlorinated Herbicides		8151 [r]				0.1-1.0 (Triclopyr)	
Carbamate Pesticides		8321 [s]				0.07 - 3.5	
Miscellaneous Organic Constituents [o]							
Base/Neutral and Acid Extractables [t]	GC-MS	625SIM	extract - 7 days; analyze - 40 days	amber glass	4°C; sodium thiosulfate in presence of chlorine	0.05 to 0.25	µg/L
PAHs	HPLC-UV; fluorescence	8310				0.05	µg/L
Purgeables	GC-MS	624	14 days	VOA		0.5 - 50	µg/L
Purgeable Halocarbons	GC	601					
Purgeable Aromatics		602			4°C; sodium thiosulfate in presence of chlorine; HCl to pH =2		
Miscellaneous Constituents							
Cyanide	titrimetric; spectrophotometric	335.2	14 days	PE or glass	4°C; sodium hydroxide to pH=12	3	µg/L
Bacteriological							
Fecal Coliform	multi-tube fermentation	SM 9221E	8 hours [u]	sterile glass or plastic	4°C; sodium thiosulfate in presence of chlorine	2 min., 2E6 max.	MPN/100 mL
Total Coliform		SM 9221B					

Notes for Table 12-1

•List of acronyms can be found at the end of the glossary.

•The 18th edition of Standard Methods for the Examination of Water and Wastewater is the current legally-adopted version in the Code of Federal Regulations (CFR). However, the 20th edition provides additional guidance on certain key items. For this reason the 20th edition is referenced in this table as the best available guidance.

• All EPA 1600 series methods require equipment handling, bottle preparation, sample collection (grab or composite) and sample handling according to EPA method 1669 protocols.

[a] Equivalent Standard Method can be substituted.

[b] Holding time specified in EPA guidance or referenced in Standard Method for equivalent method.

[c] The legally-adopted CFR (§136.3, Table II) specifies a holding time of 48 hours. Standard Methods 20th Edition requires a 6-hour holding time except when the sampling location is distant from the laboratory, in which case 24 hours is the maximum holding time. For composite samples, the start time for the holding time is the end of the compositing period. The total composite time is limited to 24 hours. For the purposes of this manual, the 24-hour holding time from the end of the compositing period is assumed because stormwater samples are usually not collected in close proximity to the laboratory. The method also specifies that storage time and conditions should be stated along with the results on the lab report when the holding time exceeds 6 hours.

[d] Refers to the instrument resolution.

[e] Also report temperature at time of measurement.

[f] Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

[g] Filter dissolved samples before preservation.

[h] Where GF-AA is specified, method 200.9 is an acceptable alternative, except for zinc.

[i] Not used.

[j] EPA method 1638 is an additional available "clean-technique" ICP-MS method that can be used for this constituent. EPA method approval is in process.

[k] EPA method 1620 is an additional method that can be used for this constituent. EPA method approval is in process.

[l] ICP-MS is prone to precision problems due to ionic interferences. ICP-MS is an acceptable method only if the sample matrix poses no significant interference problems. Hydride generation-atomic fluorescence spectroscopy (HG-AFS) can be used to achieve lower RLs if the project permits the use of an analytical technique that has not been officially approved.

[m] EPA method 1639 is a "clean-technique" GF-AA method. EPA method approval is in process.

[n] Use of EPA Method 1664 for hexane extractable material with silica gel treatment (HEM/SGT) is designed to measure "non-polar material" and is the preferred analytical technique for Caltrans-related oil & grease analysis.

[o] See Appendix H or the EPA method for a complete list of constituents.

[p] For diazinon and chlorpyrifos.

[q] Must request special extraction and analysis for Oxadiazon.

[r] Must request special extraction and analysis for Triclopyr.

[s] Must request special extraction and analysis for Oryzalin.

[t] EPA method 625 modified with SIM detection, or with other techniques/modifications providing equivalent performance. Includes PAHs, phthalates, phenols, etc.

[u] The 8 hour hold time includes the 2 hour delivery and 6 hour set-up time allowances described in Standard Methods 20th edition. All efforts should be made to analyze samples within 6 hours of sampling to conform with the currently adopted edition of Standard Methods.