

California Environmental Protection Agency



SOP MLD 034

**STANDARD OPERATING PROCEDURE FOR THE
DETERMINATION OF ELEMENTAL
CONCENTRATIONS IN AMBIENT AIR BY ENERGY-
DISPERSIVE X-RAY FLUORESCENT (XRF)
SPECTROSCOPY**

Northern Laboratory Branch
Monitoring and Laboratory Division

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Table of Contents

1.0	SCOPE	1
2.0	SUMMARY OF METHOD.....	1
3.0	SAFETY	1
4.0	INTERFERENCES	2
5.0	EQUIPMENT AND SUPPLIES.....	2
6.0	SAMPLE ANALYSIS.....	4
7.0	DATA ANALYSIS.....	6
8.0	QUALITY CONTROL	7
9.0	MAINTENANCE	9
10.0	REFERENCES	10

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1.0 SCOPE

This document describes a non-destructive method for the determination of concentrations of elements in air particulates. All non-volatile elements with atomic numbers from 11 to 92 may be detected by the Air Resources Board's current XRF instrument. The XRF method does not distinguish oxidation states; hence only total elemental concentrations are measured.

2.0 SUMMARY OF METHOD

- 2.1 A sample of air is drawn through thin Teflon[®] membrane filters over a period of twenty-four hours. The sampled volume is about 17 m³ for low-volume total suspended particulate or "total-metal" samples and about 10 m³ for PM_{2.5} samples.
- 2.2 The suspended particles collected by the filters are placed under vacuum in the XRF spectrometer and irradiated with x-rays of various energies. These (primary) x-rays generate fluorescent x-rays, which have characteristic energies for each element in the sample. The fluorescent x-rays, along with primary x-rays scattered from the sample, are individually detected and converted to electrical pulses. These electrical pulses are stored and utilized. Net counts of the characteristic fluorescent x-rays are assumed proportional to elemental surface concentrations (i.e., surface densities in units of µg/cm²). The sample is assumed to be distributed uniformly on the filter.

3.0 SAFETY

- 3.1 The XRF instrument generates X-rays. Exposure to X-rays is injurious to health. The instrument has built-in radiation shielding and safety interlock switches to prevent accidental exposure to X-rays. These safety devices must not be tampered with. Keep the door to the XRF Lab locked when unoccupied and X-rays are being produced.
- 3.2 The X-ray tube exit window and X-ray detector entrance window are made of extremely thin beryllium foil. The windows are extremely fragile and brittle and beryllium is an extremely toxic element. Do not contact the foil

under any circumstances. Use caution when working in the vicinity of the beryllium windows. Open and close the sample chamber cover slowly and carefully. Rapid pressure changes can rupture the windows. If a beryllium window is ruptured, proceed as follows:

- 3.2.1 Do not touch, breathe, or swallow any particles. Do not allow particles to contact skin or clothing.
 - 3.2.2 Using tweezers or the adhesive side of masking tape, collect any broken pieces and particles and place them in a sealed, unbreakable container.
 - 3.2.3 Call a qualified service engineer for additional advice on containment, cleanup, and disposal procedures.
- 3.3 The XRF instrument uses liquid nitrogen (LN) to maintain the detector at low temperatures. The instrument LN dewar must be filled twice per week. LN is a cryogenic hazard and can cause severe burns on contact with skin, eyes, or lungs. Do not allow skin contact with the liquid and do not breathe vapors boiling off the liquid. Wear protective gear (cryogenic gloves, face shield, lab coat) when handling LN. Handle dewars very carefully. LN is also an asphyxiation hazard because nitrogen vapors displace air while boiling off the liquid. Keep the door to the XRF Lab open while handling LN.

4.0 INTERFERENCES

Spectral interferences known as peak overlaps occur when the XRF detector is unable to resolve peaks that are very close to each other. To correct for peak overlaps and obtain accurate peak intensities, an XML peak-fitting method is employed. In this method, a library of pure reference spectra is generated for all elements determined by the method. Then sample spectrum deconvolution is performed by multiple, linear least squares fitting of the reference spectra to the sample spectrum. Additionally, digital filtering of spectra is used to correct for background interferences before the XML treatment is performed. These methods give accurate, net peak, X-ray intensities, which are necessary to accurately determine concentrations of each analyte element.

5.0 EQUIPMENT AND SUPPLIES

- 5.1 Thermo QuanX-EC XRF Spectrometer with the following configuration.
 - 5.1.1 X-ray Tube: 50 kV, 50 watt, rhodium target, end window emission.

- 5.1.2 X-ray Generator: Voltage range, 4-50 kV in 1 kV steps. Current range, 0 to 1.98 mA in 0.02 mA steps, 50 watts maximum.
- 5.1.3 Beam Filters: Automated 8-position beam filter wheel with an open position for direct excitation and 7 transmission filters as indicated in the following table.

Filter Material	Thickness (mm)
Cellulose	-
Aluminum	0.13
Palladium	0.025
Palladium	0.05
Palladium	0.125
Copper	0.377
Copper	0.63

- 5.1.4 X-ray Detector: LN cooled, high resolution, lithium-drifted silicon, 30 mm² area, 8 μm beryllium window, and 8 liter dewar.
- 5.1.5 Sample chamber with automated control of air or vacuum environment and the following:
 - 5.1.5.1 Automated 10-position sample tray with sample spinning capability.
 - 5.1.5.2 Sample cups with spinning capability and ability to accommodate either 37 mm or 47 mm diameter filters.
 - 5.1.5.3 Retaining rings, 31 mm I.D. and 47 mm O.D., for holding filters in sample cups.
- 5.2 Edwards RV 8 vacuum pump for evacuating the spectrometer sample chamber.
- 5.3 Printer, personal computer system with Wintrace™ XRF applications software.
- 5.4 Liquid nitrogen pressurized cylinder with 22 psi pressure relief valve.
- 5.5 NALGENE 4 Liter polyethylene dewar flask for transferring LN.
- 5.6 Cryogenic gloves, face shield, lab coat.

- 5.7 Pure copper calibration disk for daily energy calibration of detector.
- 5.8 Calibration and quality control standards that are thin vapor-deposited films of elements and compounds purchased from Micromatter Co., Deer Harbor, WA.
- 5.9 High purity reference standards used in peak overlap corrections.

6.0 SAMPLE ANALYSIS

- 6.1 Determine samples that require XRF analysis by running a query in LIMS.
- 6.2 Organize samples by type in batches of ten or less.
- 6.3 Generate a Method Tray List for a sample batch. The XRF computer desktop has shortcuts to method tray lists for the different types of filters.
 - 6.3.1 Double click on the appropriate desktop icon for the type of filters to be analyzed. A Method Tray List appears similar to the figure below.

Method Tray List					
	Sample	Method file	Position	Tray	Count
	PFS Barcode	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATION	1	1	1
*					

Ready NUM

- 6.3.2 Click in the cell under “Sample” and enter the first sample ID by reading the barcode on the cover of the sample container.
- 6.3.3 Press <Tab> four times to advance to the cell for the next sample and read its barcode as above.
- 6.3.4 Continue as above until all samples in the batch are entered on the Method Tray List.
- 6.3.5 Following the entry for the last sample in the batch, enter a replicate sample for quality control by typing the ID from the sample in position 1 followed by “A” and pressing <Tab> five times. Make sure that the replicate sample has a 2 in the Tray column.

6.3.6 An example of a properly completed method tray list resembles the figure below.

Method Tray List					
	Sample	Method file	Position	Tray	Count
	PFS01451	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	1	1	1
	PFS01432	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	2	1	1
	PFS01440	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	3	1	1
	PFS01436	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	4	1	1
	PFS01434	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	5	1	1
	PFS01435	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	6	1	1
	PFS01431	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	7	1	1
	PFS01452	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	8	1	1
	PFS01439	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	9	1	1
	PFS01441	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	10	1	1
	PFS01451A	C:\Documents and Settings\Engineer\My Documents\Methods\PM25 SPECIATI	1	2	1
*					

6.4 Load filters into the sample tray according to the positions listed on the method tray list.

6.4.1 Slowly and carefully raise the sample chamber cover.

6.4.2 Remove the cover of a filter container and carefully align an inverted XRF sample holder directly over the filter.

6.4.3 Invert the filter container and the filter should fall into place in the sample holder face-side down.

6.4.4 Place the sample holder with the filter into the appropriate position on the sample tray and place a retaining ring on the filter.

6.4.5 Continue to load samples until entire batch is loaded.

6.4.6 Slowly and carefully lower the sample chamber cover.

6.5 Record filter positions in logbook.

6.6 Click the Start Acquisition icon to begin analysis.

6.7 Spectra is automatically acquired and saved in the method file associated with the filter type. After acquisition is complete for Tray 1, a dialog box prompts to ensure that Tray 2 is in place. Click OK and acquisition continues for a replicate sample.

6.8 After acquisition for the replicate sample is complete, an analysis report is displayed in the Acquisition Manager window.

6.9 Close Acquisition Manager and transfer the samples back to containers.

7.0 DATA ANALYSIS

7.1 Data analysis is automatically performed and results are imported into the method file associated with the type of filter analyzed. Further processing of results is necessary prior to transferring data into LIMS.

7.2 Generate a comma separated value (CSV) file for each batch of samples analyzed.

7.2.1 Start the Method Explorer program from the Windows Start Menu and open the method file of the filter type for which data transfer is required.

7.2.2 Expand the "Sample Lists" item in the Method Contents Tree and sample analysis dates and times appear.

7.2.3 Double-click on the appropriate analysis date and "Analysis Results" appears.

7.2.4 Click on Analysis Results and a results table appears. Click on the "Concentration" tab at the bottom of the display. A table appears similar to the following figure.

Sample List: AM-10/05/05 01:06 PM

	Al	Si	P	S	Cl	K	Ca	Ti	
PFS01275	38.445	107.891	6.827	393.278	12.476	37.213	43.325	4.925	
PFS01276	41.647	126.980	0.560	304.300	9.163	69.975	31.030	6.331	
PFS01277	28.009	71.811	0.000	529.637	456.624	76.552	56.784	3.578	
PFS01278	46.414	131.192	2.529	277.712	164.492	53.729	44.378	4.203	
PFS01280	76.181	197.980	4.473	373.262	20.647	84.681	58.094	7.254	
PFS01279	38.166	106.963	0.000	224.550	17.560	65.473	20.932	3.791	
PFS01283	38.277	62.433	0.000	377.189	18.960	42.601	25.496	5.517	
PFS01285	23.375	67.285	1.095	389.558	101.331	35.264	34.389	4.432	
PFS01286	59.365	179.020	2.577	266.903	19.707	70.051	39.290	5.104	
PFS01287	63.280	137.208	2.984	416.023	27.107	54.424	48.659	5.461	
PFS01275A	36.998	106.978	5.454	391.831	20.730	35.863	44.218	4.837	

Peak Intensity Background Intensity **Concentrations** Normalized Concentrations Uncertainties Chi-Squared Analysis Messages

- 7.2.5 Click in the cell directly above the first sample ID and the table becomes highlighted in black.
- 7.2.6 Press <Ctrl+C> to copy the table to the clipboard.
- 7.2.7 Start Excel and press <Ctrl+V> to paste the table to Excel. Make sure that QC standard results are also copied to the Excel worksheet. A properly completed worksheet resembles the figure below.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	ChAl5327	37.478												
2	ChFe11311	44.33												
3	ChPb4475	42.051												
4	ChSr5345	42.519												
5														
6	PFS01273	19.887	56.606	5.235	554.107	34.351	76.071	23.293	4.094	0	0.465	0.698	35.108	0.577
7	PFS01274	50.677	131.661	1.959	378.055	52.481	50.172	46.602	6.034	0.283	0.923	2.46	67.539	0.417
8	PFS01268	175.831	469.028	11.733	192.077	33.897	110.087	219.967	14.093	0.519	1.115	3.111	147.048	1.716
9	PFS01270	72.862	171.073	12.13	260.864	32.175	93.656	66.679	7.968	1.584	0.584	3.1	120.88	1.416
10	PFS01281	17.038	44.01	0	198.076	53.096	28.565	23.476	1.485	0	0.591	1.052	48.632	0.389
11	PFS01273	24.802	55.354	5.061	556.372	28.944	77.148	23.671	2.997	0.59	0.754	0.797	36.998	0.497
12														

- 7.2.8 Save the Excel file as a *.csv file with the following formats: XPMMDYY.csv for PM2.5 Speciation and XTMMDDYY.csv for Total Metals, where MMDDYY is the month, day, and year the sample batch analysis started.

- 7.3 Copy the CSV file generated in 7.2.8 to the To_LIMS Folder on the C: drive.
- 7.4 Log on to IDM LimsLink and start a new worksheet for the appropriate method. Use the CSV file prefix for naming the worksheet.
- 7.5 Review the results, add replicate and QC samples to LIMS, then send results to LIMS.

8.0 QUALITY CONTROL

- 8.1 Calibrate the instrument using standards that are thin vapor-deposited films of elements and compounds purchased from Micromatter Co. For most elements, use two standards and a blank. Perform linear regression analysis on intensity (counts per second) versus elemental loading ($\mu\text{g}/\text{cm}^2$) and calculate correlation coefficients. Correlation coefficients must be 0.98 or better for all elements. Complete instrument calibration is

required annually, after instrument repair, or if a control standard result falls outside control limits. Calibrate the instrument using the standards that are listed in the following table:

ID	Element	ug/cm2	ID	Element	ug/cm2
Al 14372	Al	39.8	Ni 4459	Ni	39.0
Al 12891	Al	43.2	CuS 10608	Cu	41.6
SiO 14373	Si	28.6	CuS 10609	Cu	42.7
SiO 10607	Si	31.7	ZnTe 4461	Zn	12.7
GaP 15368	P	15.4	ZnTe 4460	Zn	12.9
CuS 10608	S	13.1	GaAs 15371	As	33.8
CuS 10609	S	14.1	Se 9807	Se	46.4
NaCl 15369	Cl	28.2	Se 9808	Se	47.1
KI 6044	K	11.6	CsBr 15372	Br	17.4
KI 6045	K	12.3	RbI 15373	Rb	19.2
CaF2 15370	Ca	24.0	SrF2 15374	Sr	34.1
Ti 4449	Ti	24.2	YF3 15375	Y	27.7
Ti 9804	Ti	40.3	MoO3 5338	Mo	32.4
V 3312	V	19.6	MoO3 5337	Mo	33.3
V 4451	V	47.8	Sn 9813	Sn	41.8
Cr 3313	Cr	25.0	Sn 9814	Sn	47.4
Cr 4452	Cr	42.7	Sb 5347	Sb	43.4
Mn 4455	Mn	39.1	Sb 5348	Sb	46.2
Mn 4454	Mn	53.9	BaF2 3316	Ba	17.7
Fe 4457	Fe	38.4	BaF2 9816	Ba	36.4
Fe 10613	Fe	51.7	HgAg 15376	Hg	20.6
Co 3509	Co	32.4	Pb 3317	Pb	18.8
Co 5334	Co	48.3	Pb 11315	Pb	49.2
Ni 3315	Ni	20.2	-	-	-

- 8.2 The limit of detection (LOD) for each element must be verified annually. The LOD is calculated using the x-ray counts in a blank spectrum. The counts in a blank spectrum for a given element are divided by the analysis time of the blank spectrum, then multiplied by the time of the given analysis condition. The square root of the resulting number (bkg. cts) is taken and multiplied by three to obtain the number of counts corresponding to the elemental LOD. This number is then converted to $\mu\text{g}/\text{m}^3$ using the appropriate elemental calibration factor C, sample area, sample volume, and analysis time:

$$\text{LOD} = 3(\text{bkg. cts})^{1/2} * \text{C} * (\text{sample area}) / ((\text{m}^3) * (\text{time}))$$

- 8.3 Perform daily energy calibration of the spectrometer to ensure that detected X-rays appear at the correct energy.
 - 8.3.1 Place the copper calibration disk in position 10 of the sample tray.
 - 8.3.2 Start the Acquisition Manager program from the Windows Start Menu.
 - 8.3.3 Click Acquire > Energy Calibration to start the process.
 - 8.3.4 Calibration is performed automatically and an energy calibration report is displayed. The error should be less than 4eV.
 - 8.3.5 Save the report in the Reports folder and close Acquisition Manager.
- 8.4 Analyze control standards before and after every sample batch.
 - 8.4.1 Double click on the QC Standards.mtl desktop icon.
 - 8.4.2 Load the QC standards into the sample tray using the positions listed on the method tray list.
 - 8.4.3 Click the Start Acquisition icon to begin analysis.
 - 8.4.4 After acquisition for the control standards is complete, an analysis report is displayed in the Acquisition Manager window.
 - 8.4.5 Review the control standard results to ensure that they are within the established Control Limits. If a result is not within limits, then the control standard must be reanalyzed. If a second result is also not within limits, analysis must be stopped and the problem investigated.
 - 8.4.6 Close Acquisition Manager.
- 8.5 Analyze at least one replicate sample in every sample batch.

9.0 MAINTENANCE

- 9.1 The XRF detector requires a continuous supply of LN. Fill the instrument LN dewar twice a week. The LN level must be maintained whether or not the system is in use. The dewar is located under the left side access cover of the instrument.

- 9.1.1 Keep the door to the XRF Lab open during the filling process.
- 9.1.2 Wear cryogenic gloves, face shield, and lab coat while transferring LN.
- 9.1.3 Place the 4 Liter dewar flask under the transfer hose of the LN pressurized cylinder. Slowly open the liquid valve on the cylinder and transfer enough LN to fill 4 Liter dewar about $\frac{3}{4}$ full. Place cover on dewar flask.
- 9.1.4 Open access cover on left side of instrument and place cardboard shield over opening to protect detector electronics during LN filling.
- 9.1.5 Remove cap of instrument dewar and place a funnel into the neck of the dewar.
- 9.1.6 Slowly and carefully pour LN into the funnel until the level reaches the bottom of the dewar neck.
- 9.1.7 Wipe condensation off of dewar cap and replace cap on instrument dewar.
- 9.1.8 Record LN fill in logbook. Allow 1 to 3 hours for the detector to stabilize before operating instrument.
- 9.2 Check the vacuum pump oil level monthly. The oil level should be in the middle of the sight glass. If the oil appears dark brown or has a burnt smell, it should be replaced using the same type of oil. It is important to use only pure hydrocarbon oil in the vacuum pump (NO oil containing silicones, which would contaminate the system with silicon).
- 9.3 The QuanX system is covered under a maintenance agreement. For service, repair, or technical support contact Thermo at 1-800-495-3839. Our system identification number is 136247.

10.0 REFERENCES

Thermo Electron Corporation, *QuanX-EC Operator's Manual*, WinTrace Software Version 3.0, Revision A.

Thermo Electron Corporation, *QuanX-EC Technical Manual*, Revision B.

U.S. Environmental Protection Agency, 1999. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, Compendium Method IO-3.3, *Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy*, EPA/625/R-96/010a, Office of Research and Development.

U.S. Environmental Protection Agency, 2001. *Guidance for Preparing Standard Operating Procedures (SOPs) (QA/G-6)*, EPA/240/B-01/004, Office of Environmental Education.