

California Environmental Protection Agency



Air Resources Board

**PROCEDURE FOR DETERMINING THE COMPOSITION OF ELEMENTS IN
PARTICULATE MATTER FROM MOTOR VEHICLE EXHAUST BY ENERGY
DISPERSIVE X-RAY FLUORESCENCE (EDXRF) SPECTROSCOPY**

**SOP MV-AEROSOL-156
Version 1.1**

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Aerosol Analysis and Methods Evaluation Section
Chemical Analysis & Emissions Research Branch
Emissions Compliance, Automotive Regulations and Science Division

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1. Introduction

This document describes a non-destructive procedure using the Energy Dispersive X-Ray Fluorescence (EDXRF) spectroscopy to determine the composition of elements in particulate matter collected on Polytetrafluoroethylene (PTFE) membrane filters. These elements when irradiated by X-rays emit fluorescence X-rays that are characteristic for each element. The intensity of emitted fluorescence energy is proportional to the surface concentration of each element (in units of $\mu\text{g}/\text{cm}^2$) and is used for their quantification.

In the method the background (the same filter type) X-ray spectrum is subtracted from that of the sample spectrum. The net intensity is proportional to the concentration of the corresponding element collected on the filter.

2. Interferences and Limitations

- 2.1. This procedure is capable of quantitative analysis of the non-volatile elements with atomic numbers 11 (sodium) through 92 (uranium). The target elements are listed in Table 1. The vacuum condition in EDXRF during sample analysis causes some loss of elements associated with volatile and semi-volatile compounds. For those elements, the accurate quantification cannot be achieved.
- 2.2. EDXRF method does not distinguish oxidation states; therefore only total elemental concentrations are quantified.
- 2.3. EDXRF spectral interferences cannot be avoided. The Epsilon 5 system uses secondary polarizing targets to minimize the effect of spectral overlapping.
- 2.4. Particulate matter is assumed to be deposited uniformly on the filter. The elements in the particulate matter which are not uniformly deposited over the whole collection area cannot be accurately quantified.
- 2.5. The procedure can only apply to PTFE filters. Different type of filter media may exhibit severe background interference.

3. Safety

- 3.1. EDXRF instrument generates X-rays. The instrument has a built-in radiation shielding and safety interlock system with X-ray safety certifications. In addition, a Geiger counter is used to monitor any radiation leak.

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- 3.2. The EDXRF instrument uses liquid nitrogen to keep the X-ray detector at low temperature. The instrument's liquid nitrogen reservoir is refilled at least once a week. Liquid nitrogen is a cryogenic hazard and causes severe burns on contact with skin, eyes, or lungs. Wear protective gear (cryogenic gloves, safety glasses, lab coat) when handling liquid nitrogen (Reference: Occupational Safety and Health Administration).
- 3.3. Liquid nitrogen vapor displaces air while boiling off the liquid, and is an asphyxiation hazard. Keep the laboratory doors open when filling the liquid nitrogen reservoir.
- 3.4. For general laboratory safety procedures, consult the Chemical Hygiene Plan. Material Safety Data Sheets (MSDS) are available in the laboratory.

4. Equipment and Supplies

- 4.1. The PANalytical Epsilon 5 High Performance EDXRF Spectrometer is used for the quantitative analysis of elements. This consists of the following instrument components:
 - 4.1.1 X-ray Tube: A scandium/tungsten (Sc/W) dual anode X-ray tube, with gadolinium (Gd) side window,
 - 4.1.2 HV Generator: 600 Watt maximum power, output voltage range 25 - 100kV adjustable with steps of 1kV, output mA range 0.5-24mA adjustable with 0.1mV, with internal water cooling.
 - 4.1.3 A 3-dimensional polarized optical path with automated nine polarizing secondary targets: These polarizing secondary targets and their corresponding measuring conditions used for exciting target elements are listed in Table 2.
 - 4.1.4 X-ray Detector: A germanium (Ge) detector with beryllium (Be) window cooled by liquid nitrogen.
 - 4.1.5 Sample chamber equipped with automated controls: The chamber is in a vacuum environment during sample analysis.
 - 4.1.6 Computer system is running on Windows XP with PANalytical Epsilon 5 application software version 2.0K / ICSW 2.9.
- 4.2 Laboratory supplies and other Equipment:
 - 4.2.1 Step up transformer.
 - 4.2.2 Liquid nitrogen source with pressure regulator at 0-50 psi.

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- 4.2.3 Cryogenic gloves, lab coat, safety glasses.
- 4.2.4 Latex gloves, disposable, class 100 powder free.
- 4.2.5 Stainless steel forceps with flat wide tips for transferring filters.
- 4.2.6 Solid sample holders (part# 9430 050 01221) and sample holder inserts, for 50mm filters (part# 9430 050 11501)

5. Standards

5.1. Elemental Calibration standards:

- 5.1.1 These standards are thin vapor-deposited films of ultra-pure non-interfering elemental materials deposited on Nuclepore[®] polycarbonate aerosol membrane.
- 5.1.2 The calibration standard concentrations of the target elements are listed in Table 1.
- 5.1.3 Standards can be purchased from Micromatter, Inc. (4004 Westbrook Mall, Vancouver, BC, V6T 2A3) or from nanoXRF UHV Technologies, Inc. (450 South Freeway, Fort Worth, Texas 76104-3503).

5.2. Drift correction standard: FLX S13 (22/07/2011, 10, FLUXANA #D Elektronik).

6. Drift Correction

The X-ray tube and the detector degrade and the response of the other components can also change over time. The drift correction is conducted once a month using the drift correction standard, FLX S13.

7. Calibration

- 7.1 The target elements are calibrated according to their polarizing secondary targets and parameters listed in Table 2.
- 7.2 Calibration of all the elements is typically valid for one year.
- 7.3 Recalibration of any elements is performed when the quality control result of a particular element exceeds the limits, when the X-ray tube or the

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detector is replaced, or when there is a repair that can affect the calibration.

8. Sample Handling and Analysis

8.1 Sample Handling

8.1.1 Sample filters are submitted to the laboratory and stored in the freezer until analyzed.

8.1.2 Filter samples are manually inspected before analysis. If irregularities are found, a senior staff shall be consulted. Any irregularities are recorded in the logbook.

8.2 The analyst must be trained and familiar with the operation of the EDXRF system. Detailed operating manual/procedures are located in the EDXRF system "Help" program.

8.2.1 Create a sample list on the logbook and transfer the information to the "Sample Changer Measurement" window. Specify the number of repeats for each sample, and the sample rack position.

8.2.2 Carefully transfer the filter with a clean forceps (with the deposit side up) to the sample holder insert. Place the sample holder cup over the filter to complete the sample assembly. It is important that the deposit is not scraped, smudged or smeared when loading the filters.



Place the sample assembly in the sample tray with the filter facing down, according to the position on the sample list. Place the tray inside the sampling chamber. The samples are ready for analyses.



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- 8.3 A typical analytical sequence includes a blank filter for background correction, a QC standard at the beginning of the sample batch, a sample replicate for every 10 samples or less, and a QC standard at the end of the sample batch.
- 8.4 When the analyses are completed, load the filters back into the sample containers for storage.

9. Quality Control

9.1 Quality Control (QC) Standard: FLX S13

9.1.1 FLX S13 is analyzed before and after each set of samples. The limits are defined as follows:

Lower Control Limit (LCL) = mean value - 3 times the standard deviation
Lower Warning Limit (LWL) = mean value - 2 times the standard deviation
Upper Warning Limit (UWL) = mean value + 2 times the standard deviation
Upper Control Limit (UCL) = mean value + 3 times the standard deviation

9.1.2 The initial values for the control limits were calculated from the results of 20 analyses of the FLX S13. These control limits are shown in Table 3.

9.1.3 QC values outside the control limit are considered as a “QC failure.” If any of the QC values fall between the control and warning limits, it is considered a QC “warning”. If the second QC value falls within the warning limits, it is considered a QC failure. QC failure requires corrective actions such as recalibration of the elements.

9.2 Replicate sample analysis

9.2.1 At least ten percent of the samples are randomly selected for replicate analysis. The relative percent difference (RPD) between the pair of analyses is calculated for each element above the reporting limit as follows:

$$RPD = \frac{|\text{Sample Conc.} - \text{Replicate Conc.}|}{\text{Average Conc. of Both Analyses}} \times 100$$

9.2.2 The limit on the allowable RPD is established based on the average concentration of the replicate runs, as shown in the following table:

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Average Measurement for Replicate Runs	Allowable RPD (%)
1 to <3 times RL	= or <60%
3 to 5 times RL	= or <30%
Greater than 5 times RL	= or <10%

- 9.2.3 If the RPD of any of the target elements is greater than the allowable limit, the samples within the batch are re-analyzed.

10 Reporting Limit

- 10.1 Data reporting for the elements is based on the significant figures of the calibration standards listed in Table 1.
- 10.2 The reporting limit (RL) is based on 26 filters analyzed on September 28, 2012. RL is equal to the mean plus 3 times the standard deviation. The RL will be re-evaluated when more data are available.
- 10.3 Sampling area of 11.34 cm² is used to convert the reporting limit from surface concentration to mass for each element for a 47mm PTFE filter. The reporting limits are listed in Table 4.
- 10.4 Any element with mass detected below the reporting limit will be reported as <RL.

11 Data Handling

- 11.1 Confirm that all QC criteria are met before reporting data. Otherwise, make corrections and re-analyze samples.
- 11.2 Data analysis is processed by the Epsilon 5 software.
- 11.3 Export the report generated by the Epsilon 5 software to an Excel file. Back up data periodically.
- 11.4 Raw data in µg/cm² from Epsilon 5 is transferred to the SLB LIMS, where it is converted to µg/filter before reporting.

12 Reference standard

Standard Reference Material (SRM) 2783 from National Institute of Standards and Technology (NIST) is analyzed once a quarter. SRM 2783 is deposited on a polycarbonate membrane filter. A blank polycarbonate membrane filter (from NIST) is analyzed for background correction. Table 5 shows the NIST certified

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concentrations values and ARB values.

13 Maintenance

- 13.1 It is important that the Epsilon 5 system stays ON (Epsilon 5, computer and Epsilon 5 software). If the system is shut down for more than 2 hours, a maintenance call might be needed.
- 13.2 The XRF detector requires routine calibration and continuous supply of liquid nitrogen. The detector energy calibration is valid for 160 hours according to manufacturer. Fill the liquid nitrogen reservoir once a week. Calibrate the detector energy during the refilling of the liquid nitrogen.
- 13.3 Check the yellow light on top of the Epsilon 5 EDXRF. If the light is OFF, it indicates that the X-ray tube is not functioning. Check the software diagnostic messages and call for service if necessary.

14. Registration of the X-Ray Tube Radiation

The renewal of the registration of the X-Ray tube radiation is required annually. Use the Radiation Machine Registration (RH2261) form and mail with payment to the California Department of Public Health Radiologic Health Branch, MS 7610, Registration Unit P.O. Box 997414 Sacramento, CA 95899-7414

15. References

- 15.1 U.S. Environmental Protection Agency, June 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
- 15.2 ARB SOP MLD 034, January 2006: *Standard Operating Procedure for the Determination of Elemental Concentrations in Ambient Air by Energy-Dispersive X-ray Fluorescence (XRF) Spectroscopy*
- 15.3 Epsilon 5 software Help manual: PANalytical, Incorporated, 117 Flanders Road, Westborough, MA 01581
- 15.4 California Code of Regulations (CCR), title 17, section 30108
<http://www.cdph.ca.gov/certlic/radquip/Pages/RadiologicEquipment.aspx>
- 15.5 Occupational Safety and Health Guidelines for Nitrogen

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<http://www.osha.gov/SLTC/healthguidelines/nitrogen/recognition.html>

- 15.6 SLB Chemical Hygiene Plan, in draft, submitted to ARB safety officer for review and approval, December 2012.

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16. Revision Record

Revision	Date	Responsible Person	Description of Change	Status
	January 2013	Luzviminda Salazar	Initial release	Version 1.0
1	August 2014	Erin Shields	Change the SOP name from SOP No. MLD 156 to SOP MV-AEROSOL-156 due to Division and Branch name change	Version 1.1

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Table 1 Target elements and the corresponding calibration standard concentration (Conc. uncertainty \pm 5%)

Target Element 1	Conc. ($\mu\text{g}/\text{cm}^2$)	Target Element 2	Conc. ($\mu\text{g}/\text{cm}^2$)	Serial Number of Standards
sodium	6.02	chlorine	9.28	34063 NaCl
magnesium	7.26	fluorine	11.3	34064 MgF_2
aluminum	22.2			34065 Al metal
aluminum	51.8			12906 Al metal
silicon	11.0	oxide	6.28	34066 SiO
phosphorous	6.80	gallium	15.3	34067 GaP
sulfur	5.94	copper	11.8	34068 CuS_x
potassium	6.90	chlorine	7.61	34069 KCl
calcium	8.11	fluorine	7.69	34070 CaF_2
scandium	8.20	fluorine	10.4	34071 ScF_3
titanium	17.7			34072 Ti metal
vanadium	20.8			34073 V metal
chromium	17.6			34074 Cr metal
manganese	18.7			34075 Mn metal
iron	14.8			34076 Fe metal
iron	49.4			12907 Fe metal
cobalt	15.7			34077 Co metal
nickel	17.0			34078 Ni metal
copper	16.9			34079 Cu metal
zinc	5.93	tellurium	11.6	34080 ZnTe
germanium	17.3			34081 Ge metal
selenium	25.6			30482 Se metal
cesium	12.2	bromine	7.36	34083 CsBr
rubidium	7.69	iodine	11.4	34084 RbI
strontium	11.9	fluorine	5.14	34085 SrF_2
yttrium	13.5	fluorine	8.67	34086 YF_3
molybdenum	11.5	oxide	5.74	34087 MoO_3
rhodium	14.9			34088 Rh metal
palladium	17.6			34089 Pd metal
silver	19.6			34090 Ag metal
cadmium	10.7	selenium	7.55	34091 CdSe
indium	18.7			34092 In metal
tin	15.5			34093 Sn metal
antimony	16.4			34094 Sb metal
tellurium	18.0			34095 Te metal
barium	13.0	fluorine	1.80	34096 BaF_2
lanthanum	15.2	fluorine	6.23	34097 LaF_3
cerium	13.9	fluorine	5.67	34098 CeF_3
thallium	16.4	chlorine	2.85	34099 TlCl
lead	19.5			34100 Pb metal
bismuth	16.5			34101 Bi metal
platinum	17.4			12908 Pt metal
zirconium	11.5	fluorine	9.57	12909 ZrF_4

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Table 2 Nine polarizing secondary targets, the measuring conditions and the corresponding elements of interest

No.	Polarizing Secondary Target (Elemental composition)	Measuring Conditions				Element of interest
		kV	mA	Measured time (seconds)	Condition Name	
1	aluminum (Al)	25	24	500	Mg	Na and Mg
2	calcium fluoride (CaF ₂)	40	15	600	Si-K	Al, Si, P, S, Cl, K and for optimization of Si, P, S, and K
3	iron (Fe)	75	8	400	Ti-Cr	Ca, Sc, Ti, V, Cr,
4	germanium (Ge)	75	8	400	Cu-Zn	Mn, Fe, Co, Ni, Cu, Zn,
5	zirconium (Zr)	100	6	400	Rb_Re-Tl	Ga, Ge, Se, Br, Rb, Pt, Tl, Pb and Bi
6	molybdenum (Mo)	100	6	400	Sr-Y_Pb-U	Sr, Y, U and for optimization of Rb, Y, Tl, Pb, Bi and U
7	silver (Ag)	100	6	400	Mo-Tc	Mo, Pb, Rh and for optimization of Mo
8	cerium oxide (Ce ₂ O ₃)	100	6	400	I	for optimization of Iodine (I)
9	Barkla target aluminum oxide (Al ₂ O ₃)	100	6	500	Xe-La	Sr, Y, Zr, Mo, Rh, Pd, Ag, Cd, In, Sn, Te, I, Cs, Ba, La and Ce

Table 3 Quality control limits for selected elements

Element in concentration	Mean	One standard deviation	LCL	LWL	UWL	UCL
sulfur	1.22	0.03	1.12	1.26	1.29	1.32
chromium	10.1	0.03	9.98	10.0	10.1	10.2
iron	16.0	0.04	15.9	15.9	16.1	16.1
copper	32.5	0.1	32.2	32.3	32.6	32.7
lead	281	2	275	277	287	289

Concentration in µg/cm²

Lower Control Limit (LCL) = mean value - 3 times the standard deviation

Lower Warning Limit (LWL) = mean value - 2 times the standard deviation

Upper Warning Limit (UWL) = mean value + 2 times the standard deviation

Upper Control Limit (UCL) = mean value + 3 times the standard deviation

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Table 4 Reporting limit for the elements analyzed by EDXRF

Element	Reporting Limit (mean + 3xSTDEV ^a)	
	(µg/cm ²)	(µg/filter ^b)
magnesium	0.0530	0.601
aluminum	0.200	2.26
silicon	0.0207	0.235
phosphorus	0.0063	0.0714
sulfur	0.0012	0.0136
chlorine	0.105	1.19
potassium	0.0109	0.124
calcium	0.0042	0.0476
scandium	0.0339	0.384
titanium	0.0061	0.0692
vanadium	0.0010	0.0113
chromium	0.0087	0.0987
manganese	0.0048	0.0544
iron	0.0138	0.156
cobalt	0.0024	0.0272
nickel	0.0025	0.0284
copper	0.0045	0.0510
zinc	0.0064	0.0726
gallium	0.0086	0.0975
germanium	0.0063	0.0714
selenium	0.0575	0.652
bromine	0.0045	0.0510
rubidium	0.0021	0.0238
strontium	0.0050	0.0567
yttrium	0.0044	0.0499
molybdenum	0.0419	0.475
rhodium	0.0171	0.194
palladium	0.0293	0.332
silver	0.0321	0.364
cadmium	0.0240	0.272
indium	0.0261	0.296
tin	0.0185	0.210
antimony	0.0234	0.265
tellurium	0.0636	0.721
iodine	0.0864	0.980
cesium	0.0720	0.816
barium	0.0819	0.929
lanthanum	0.0861	0.976
cerium	0.108	1.23
thallium	0.0057	0.0646
lead	0.0081	0.0919
bismuth	0.0127	0.144
platinum	0.0087	0.0987
zirconium	0.0075	0.0851

a: STDEV: The standard deviation of the elemental concentration on 26 blank 47mm PTFE filters

b: The sampling area of 11.34 cm² is used for calculating the RL for the elements.

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Table 5 Certified mass loading values of selected elements in NIST SRM 2783 for EDXRF

Element	NIST Certified Conc. (ng)	NIST Conc. 95% uncertainty values (ng)	ARB Conc. (ng)
Aluminum	23210	± 530	23306
Potassium	5280	± 520	4671
Calcium	13200	± 1700	12948
Titanium	1490	± 240	1683
Chromium	135	± 25	165
Manganese	320	± 12	390
Iron	26500	± 1600	25597
Nickel	68	± 12	62
Copper	404	± 42	345
Zinc	1790	± 130	1902
Antimony	71.8*	± 2.6	<RL
Barium	335*	± 50	<RL
Lead	317	±54	336

* Elements with concentrations below reporting limits