Synchrotron XRF

RP – DRAFT –v1

ELEMENTAL ANALYSIS OF AMBIENT AIR PARTICUALATE SAMPLES COLLECTED ON DRUM IMPACTOR SUBSTRATES USING Synchrotron-XRF

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1. PURPOSE AND APPLICABILITY

This research protocol (RP) contains the protocol for performing multi elemental analysis of Rotating Drum Impactor (RDI) samples by synchrotron XRF using the Lawrence Berkeley National Laboratory's synchrotron in Berkeley. Research Protocols are subject to change. Every addition to this RP will be added as an Appendix during this study.

2. DEFINITIONS OF TERMS

RM: Reference material (RM) is a material or substance suitable for use in verifying the validity of the method.

CRM: Certified Reference Material, i.e., material whose analyses are accompanied by a certificate from the vendor, which contains an uncertainty statement at a stated level of confidence, and for which the analytical methodology and calibration is traceable to NIST or other excepted standards.

SRM: Standard Reference Material. Material whose analysis is certified by a certifying body such as the National Bureau of Standards and Technology (NIST). The certificate of analysis is accompanied by an uncertainty statement at a stated level of confidence.

Analyte: The component of a sample that is under investigation whose concentration is sought.

Accuracy: The degree to which the results obtained agree with the true values.

Precision: The degree to which there is agreement between measurements made on the same sample with same measurement system.

3 EQUIPMENT

Synchrotron Radiation Beam XRF system:
Synchrotron XRF is accomplished by irradiating samples with highly-focused polarized high-energy, highly intense, polychromatic light from a synchrotron light source. The system is composed of a remote positioning sample holder, solid-state X-ray detector, and ion chambers for measuring beam intensity. Measurements may be made in air or in vacuum.

ACCESSORIES

1. Non-metallic substrate holders

2. Thin-film calibration standards for elements to be detected
3. Plastic containers for holding substrates and calibration standards

OTHER MATERIALS

None

4. PROCEDURES

4.1 Mounting Samples

Samples are mounted by taping them to the substrate holders using Scotch or similar tape applied only at the edges of the substrate. This is to be done in a clean area, free from settling dust and preferably in a class 100 clean laminar-flow clean hood.

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4.2 Calibrations

1. Calibration standards for each element to be quantitatively determined should be run at least once on the system to determine analytical sensitivities.
2. Thereafter, calibrations using a few of the thin-film standards should be run during each analytical sequence (generally an 8 or 12-hr period) to check the calibration curve and beam intensities.

4.3 S-XRF OPERATIONS

The synchrotron is operated by personnel employed by the Lawrence Berkeley National Laboratory. S-XRF operators operate a beam stop to permit safe loading of samples, and control the remote positioning sample holder and data acquisition via computer control. S-XRF personnel also load and unload samples and calibration standards and run data analysis software.

Analysis Procedure

1. Set beam-stop to safe position
2. turn off beam alignment camera (ccd camera is degraded by visible light spectrum)
3. Check operation of x-ray detector, ion chamber, and remote positioning device
4. Check detector coolant level
5. Load fluorescent target for beam positioning, close safety surround door
6. Set beam stop to beam-on position
7. Switch on beam positioning camera
8. Observe beam position and mark on crt display using water soluble marker.
9. Center beam as necessary by moving sample positioning assembly as follow
    i) switch off beam and camera

ii) move sample positioning assembly
iii) switch on beam and camera
iv) observe new beam position, mark and repeat from step i, as needed.

10. switch-off beam and camera, Load sample or multi element standard ,
11. switch –on beam and camera, start data aquisition

To shut down:

1. Save files
2. switch off beam and camera
3. remove sample or standard

5. INSTRUMENT MAINTENANCE

The synchrotron beam-line is maintained and operated by LBL personnel. Malfunction of the X-Ray detector and sample positioning components should be reported to the principle investigator.

6. HEALTH AND SAFTY WARNING

1. Synchrotron and scattered X-ray radiation are ionizing emissions. Only approved and adequately-trained personnel may operate the XRF system. All LBL health and safety procedures must be understood and followed.
2. Do not switch on the beam shutter when personnel are left in the XRF detection enclosure.
3. Do not investigate other synchrotron experiments without the appropriate clearance and, as required, escort.
4. Samples and standards as well as sample positioning and X-ray detector components due not acquire residual radiation.

7. DATA QUALITY ASSURANCE

1. Thin-film calibration standards are analyzed during all analytical sequences.

2. Each analytical result shall be accompanied by a measure of its uncertainty, the datum or method DL, and the appropriate data quality flag (NARSTO convention).

3. The precision of the analytical results will be expressed in terms of one relative standard deviation (RSD) derived from counting statistics of samples and standards, ion-detector measurements, and the quality of “fits” to elemental calibration curves, as applicable. The reported accuracy of these results shall be assessed via analyses of SRM determinations (see below).

4. Because much of the RDI derived data will be used in a comparative sense (i.e., to determine size distribution spectra and to derive multivariate correlations), measurement precision, not accuracy, is the more appropriate uncertainty parameter. Thus, the analytical uncertainty reported for each analysis value will be the total precision of the measurement as derived from the instrument precision and standard deviation of substrate blank analyses. Specifically, the reported uncertainty is defined as twice the root mean square of the sum of the standard deviations of the substrate blank and instrumental uncertainty.

5. Blind SRM materials dispersed onto substrates as samples will be submitted for analysis during each analytical period. Results of these analyses will define the estimate of method accuracy. Method accuracy figures will be reported as meta data.

8. DATA QUALITY OBJECTIVES

S-XRF is capable of determining most of the elements between Na and Pb. However, certain elements (Pd, Ag, Cd, Sn, Sb, I, Ba, La – and other rare earths) are not accurately determined on a routine basis due to spectral interferences. Hg determinations require special precautions which are beyond the scope of the planned routine measurement protocol.

Instrument uncertainties (one standard deviation, relative), i.e., those derived from X-ray counting statistics of samples and standards, are expected to lie between 3 and 10% for all elements determined in samples where the collection volume exceeds 7.2 m^3. Uncertainties after blank corrections are expected to lie between 5 and 25%. A total of 75% of the analytical values determined for analytes on their respective peak impactor stages should lie above twice the root mean square of the sum of the standard deviations of the substrate blank and instrumental uncertainty when collection volumes exceed 7.2 m^3

Detection limits estimated for S-XRF of RDI samples (7.2 m^3 volume) are listed in Table 1.

Table 1. Detection Limit Estimates for S-XRF at the Berkeley Synchrotron

Element	DL, ng/m^3	Element	DL, ng/m^3
Na	3.35	Ni	0.027
Mg	2.01	Cu	0.027
Al	1.34	Zn	0.027
Si	0.67	Ga	0.020
P	0.27	Ge	0.020
S	0.20	As	0.020
Cl	0.13	Se	0.020
K	0.07	Br	0.034
Ca	0.05	Rb	0.040

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Ti	0.034	Sr	0.054
V	0.034	Y	N/A
Cr	0.034	Zr	0.07
Mn	0.034	Mo	0.10
Fe	0.034	Hg	0.13
Co	N/A	Pb	0.20

9. STATISTICAL CONTROL

Control charts will be developed in which test sample uncertainties will be monitored.