TI 301A: LN2 Fills and Detector Calibrations

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1. PURPOSE AND APPLICABILITY

The purpose of this SOP is to describe the procedure used for the liquid nitrogen (LN2) fill, liquid nitrogen calibration, and detector calibration for the Epsilon 5 instruments.

2. SUMMARY OF THE METHOD

The Epsilon 5 instruments use liquid nitrogen to cool the PAN-32 Ge X-Ray Detector. Liquid nitrogen fills for each Epsilon are performed on a weekly basis. The liquid nitrogen level is calibrated automatically. Several hours after the LN2 fill is completed, detector calibration is performed for each instrument.

3. SAFETY

Liquid nitrogen should be handled with care in ventilated rooms. Wear a face shield or safety glasses, safety gloves, and a laboratory coat when performing liquid nitrogen fills. For more information, see section 3.3.3, “Liquid Nitrogen Handling,” in the Epsilon 5 EDXRF Spectrometer System User’s Guide, in addition to SOP 301, Attachment 1 on liquid nitrogen safety.

4. PERSONNEL QUALIFICATIONS

Only trained lab personnel designated by the laboratory manager may perform liquid nitrogen fills. A course offered on the UC Davis campus, “Safe Use of Cryogenic Liquids,” is recommended (http://safetyservices.ucdavis.edu/tr/cd/suoclcd).

5. EQUIPMENT AND SUPPLIES

- Liquid nitrogen tank
- Safety glasses/face shield
- Safety gloves
- Laboratory coat

6. PROCEDURE

6.1 Epsilon 5 LN2 Fill

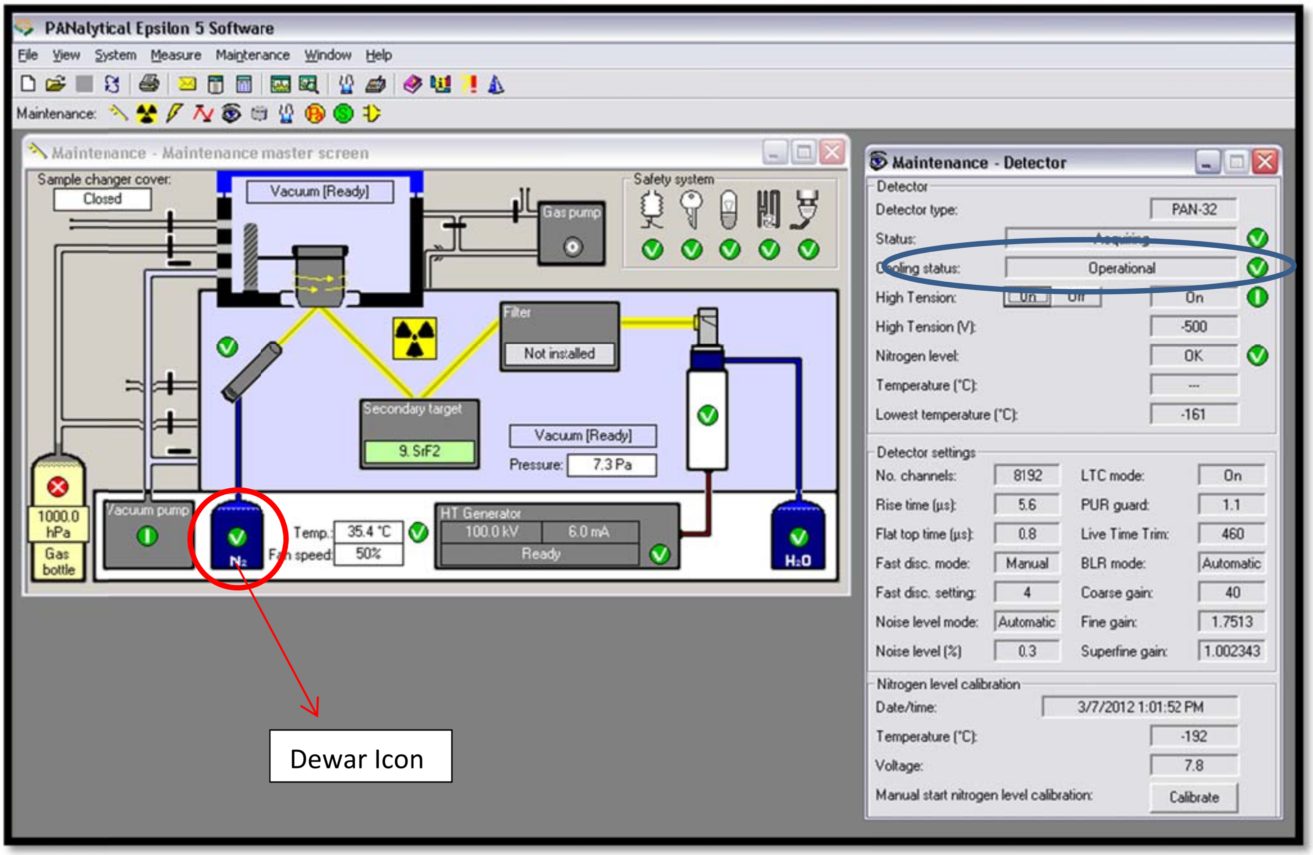
The detector in the Epsilon 5 should be filled on a weekly basis by staff that has been fully trained in the safety hazards of working with liquid nitrogen.

1. The Epsilon 5 has several potential “detector states” that are displayed on the Maintenance screen (circled in blue in Figure 1). These detector states include Pre-Operational, Operational, Long Grace, Short Grace, Filling Allowed, Cooling, and Forced Heat-Up. Ensure that the detector state is not in Forced Heat-Up prior to filling the detector with liquid nitrogen. Check this by clicking on the picture of the liquid nitrogen dewar (circled in red in Figure 1).
2. Open the LN2 fill access door on the right-hand side of the Epsilon 5.
3. Connect the fill tube to the detector fill line.
4. Insert the tube from the LN tank into the detector fill tube using the adapter.
5. Slowly open the valve on the LN tank while ensuring that the line from the LN tank into the detector fill tube does not come apart.
6. Note the time required to fill the detector and the temperature of the cabinet in the corresponding log book. Also create a new entry with the same information in the Microsoft Access log on the desktop.

6.2 Epsilon 5 Detector Calibration

Before starting the detector calibration, abort analysis. No sample can be running during detector calibration, as the Tungsten (W) underside of the vacuum seal is utilized to perform the measurements.

1. Click on the “System” drop-down menu, then “Detector Calibration.”
2. Select, “Calibrate All.”
3. When both the detector calibration and the liquid nitrogen calibration are complete, copy the screen by pressing “ALT+Print Scrn.”
4. On the desktop, there is a folder named “Detector and LN Calibrations.” Inside the folder is a document called Detector and LN Calibrations. Open it. Type the date and press “CNTRL+V” to paste the screen shot. Save and close the file.
5. On the Epsilon software, click on File, then Print. After making sure that the resulting data would be copied to the clipboard in a delimited format, click on OK. On the same folder, open an excel sheet called EpsilonName_ Detector and LN Calibrations. Paste the corresponding numbers at the bottom of the data set based on their respective setting. Review the graphs to make sure that visually there are no significant jumps or discrepancy with the values that the detector was calibrated from last week. Save and close the file.



Sample changer cover: Closed

Vacuum [Ready]

Filter: Not installed

Secondary target: 9. SrF2

Vacuum [Ready]

Pressure: 7.3 Pa

Gas bottle: 1000.0 hPa

Temp.: 35.4 °C

Fan speed: 50%

HT Generator: 100.0 kV 6.0 mA Ready

Detector

Detector type:	PAN-32
Status:	Acquiring
Cooling status:	Operational
High Tension:	On
High Tension (V):	-500
Nitrogen level:	OK
Temperature (°C):	---
Lowest temperature (°C):	-161

Detector settings

No. channels:	8192	LTC mode:	On
Rise time (µs):	5.6	PUR guard:	1.1
Flat top time (µs):	0.8	Live Time Trim:	460
Fast disc. mode:	Manual	BLR mode:	Automatic
Fast disc. setting:	4	Coarse gain:	40
Noise level mode:	Automatic	Fine gain:	1.7513
Noise level (%)	0.3	Superfine gain:	1.002343

Nitrogen level calibration

Date/time:	3/7/2012 1:01:52 PM
Temperature (°C):	-192
Voltage:	7.8
Manual start nitrogen level calibration:	Calibrate

Dewar Icon

Figure 1. Maintenance Master Screen.

6.3 Epsilon 5 Detector States

The different detector states which may be encountered by the user of Epsilon 5 during operation, will be briefly described. The user software displays the state in the detector status screen.

Filling allowed

The detector is 'warm'. Both the LN2 level sensor as well as the detector temperature are at room temperature for at least one hour. It is allowed to start filling with liquid nitrogen.

Cooling

After the N2 level sensor has detected more than 20 degrees temperature decrease due to filling the dewar, one has to wait for 6 hours before switching on the detector high tension in order to allow the crystal and the FET to cool down to -178ºC.

Pre-operational

The system is available for normal use. As the liquid nitrogen consumption is not yet constant it can warm up a little quicker than expected.

Operational

The system is available for normal use.

Short grace period

The system is available for normal use. Please refill as soon as possible. There are 75 hours (3 days) left to refill the dewar.

Long grace

The system is available for normal use. Please refill as soon as possible. There are 100 hours (4 days) left to refill the dewar.

Forced heat-up

The detector crystal has to be brought to room temperature. This can be done just waiting for the state ‘filling allowed’, which can be rather time consuming. Acceleration of this procedure can be achieved by blowing with dry air into the liquid nitrogen fill opening.

TI 301B: Tray file creation

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1. PURPOSE AND APPLICABILITY

The purpose of this standard operating procedure is to describe the process of generating tray files using SQL Server Management Studio. Tray files are a set of procedures that are used to queue samples to the Epsilon 5 software.

2. SUMMARY OF THE METHOD

Trayfiles are generated by executing stored procedures in SQL Server Management Studio. After tray file IDs have been assigned, the .XML files are created through a Tray file Writer Application. These .XML files are archived at the IMPROVE Sharepoint share, where they can be accessed when they are ready for use.

3. PRIVILEGES

The lab manager, spectroscopist, and designated lab technicians can generate tray files. Permissions to access and work with SQL Server Management Studio are granted by the IMPROVE Database Manager, or any member of the IMPROVE Software Development Team.

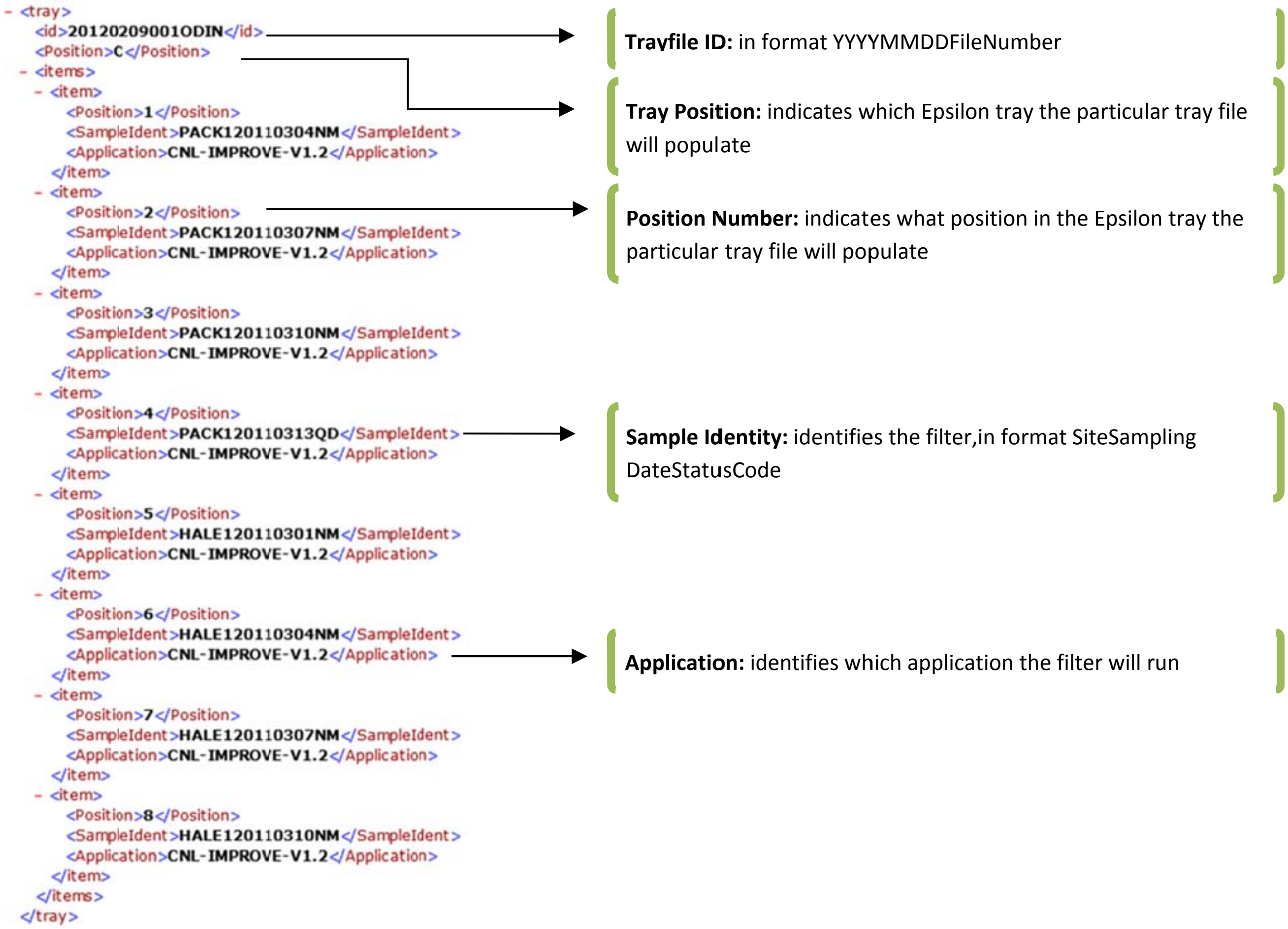
4. CAUTIONS

Pay close attention when making modifications to the tray files. The information in a tray file has to follow the format above precisely in order for the LIMS program to translate the file properly.

5. PROCEDURE

5.1 Trayfiles

Written in .XML format, tray files are used to queue samples to the Epsilon software. A diagram depicting the composition of a typical 8-position tray file is shown in Figure 1.



```
- <tray>
    <id>201202090010DIN</id>
    <Position>C</Position>
  - <items>
    - <item>
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        <SampleIdent>PACK120110304NM</SampleIdent>
        <Application>CNL-IMPROVE-V1.2</Application>
      </item>
    - <item>
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        <SampleIdent>PACK120110307NM</SampleIdent>
        <Application>CNL-IMPROVE-V1.2</Application>
      </item>
    - <item>
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        <Position>7</Position>
        <SampleIdent>HALE120110307NM</SampleIdent>
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      </item>
    - <item>
        <Position>8</Position>
        <SampleIdent>HALE120110310NM</SampleIdent>
        <Application>CNL-IMPROVE-V1.2</Application>
      </item>
    </items>
  </tray>
```

Trayfile ID: in format YYYYMMDDFileNumber

Tray Position: indicates which Epsilon tray the particular tray file will populate

Position Number: indicates what position in the Epsilon tray the particular tray file will populate

Sample Identity: identifies the filter,in format SiteSampling DateStatusCode

Application: identifies which application the filter will run

Figure 1. 8-position tray file.

5.2 Preparation before Generating Tray files

Contractor files should be updated (regenerated from logs) just before tray files are generated to assure that the most current statuses for all samples are applied. The hard copies of these files will be placed within each tray of samples for a visual check at the time of loading the samples into the Epsilons for analysis. For detailed instructions on how to update contractor files, please refer to TI 251 M.

Generally, a request for tray files will include the following information:

Epsilon Name: Quarter, Set Number, Contractor File Name, Sheet Number, First Filter in that Contractor File, Starting Tray Position **(Tray file format)**

An example is given below:

Thor: D10, Set 1, AContractor1, Sheet 1, ACAD1 1/3/2011, Tray A **(8-position)**

5.3 Writing tray files using SQL Server

Generating tray files using the SQL Server is the most convenient method. The person writing the tray file must have a terminal (PC or laptop) that has access to SQL Server Management Studio. Specific credentials are also necessary to access certain databases; if needed, contact the Software Development team for help.

5.3.1 Accessing SQL Server Management Studio

SQL Server Management Studio can be accessed in two ways:

1) From the Desktop, click on the Windows icon. Click on "All Programs." Then, go to Microsoft SQL Server 2008 R2 and click on SQL Server Management Studio.

2) From the Desktop, press Window+R. Write "ssms" in the run bar. Click on Run.

5.3.2 Running the Stored Procedure

1) Once SQL Server is open, make sure that the server name is 'cl-sql.' Click on "Connect."
2) Once the application is ready, make sure that the database on the top-left corner of the screen is on IMPROVE.XRFTrayfiles. Click on "New Query."
3) Type the following query using the format below:

   exec spCreateTrayFileSets TrayFileFormat, NumberofTrayfiletoGenerate, 'EPSILONNAME', 'FIRST_TRAY','QUARTER'

   An example would be: exec spCreateTrayFileSets 8, 50, 'Thor', 'A','C11'

4) Press F5, or click on 'Execute.'

5.3.3 Checking the Trayfile IDs

Once the query has been executed successfully, tray file IDs are checked through the SQL Server Database Management.

1) Open a new query in SQL Server. Input the text below:

```
SELECT [TrayFileID]
      ,[TrayID]
      ,[Position]
      ,[NumberOfFilters]
      ,[DeviceId]
  FROM [Improve.XRFTrayFiles].[dbo].[XRFTrayFile]
order by TrayFileID desc
```

NOTE: This query is also saved at: K:\XRF Tray File Creation Tool\SQLQuery_CheckingTrayfileID.sql.

2) Press F5, or Click Execute. Take note of the first and last tray file ID numbers that need to be generated and then minimize the window.

5.4 Using the Tray file Writer Application

1) Go to K:\XRF Tray File Creation Tool\ArchiveFiles and click on XRFTrayFileWriter.exe.
2) The program will ask for the first and last tray file IDs to generate.
   If tray files for multiple instruments need to be generated, the application can generate tray files for different instruments at the same time as long as the tray files are consecutively numbered. If they were consecutively numbered, enter the first tray file ID (smallest number) and the last tray

file ID (largest number). If the IDs are not consecutive, enter the series of tray file IDs separately.

3) The program will now ask for the directory that the generated files would be saved. It is advised to save a batch of trayfiles to a folder on one's desktop.
4) Once the application has completed the routine, close it. By now, all the .XML tray files should be generated and stored to the specified directory. There is no specific directory for the files generated by the application as the tray files would be archived in Sharepoint later.

5.5 Uploading the Tray files to Sharepoint

1) Open Internet Explorer, and go to http://cl-ds.ou.ad3.ucdavis.edu. Login to Sharepoint using Kerberos credentials. Make sure the domain name is "ad3." If it is not, add ad3\ in front of the username.
2) Under "Libraries" on the left hand side of the screen, find "Panalytical Tray Files" and click on it. At the top of the page, click on "Documents," which is under "Library Tools." Then, go to the "Upload Document" button. Click on it and select "Upload Multiple Documents."
3) Return to the directory where the generated tray files were saved earlier and select all of the files. Drag these files into the Sharepoint window. Once the files are uploaded, uncheck the box for "Add as a New Version to Existing Files." Then, click "OK."
4) After the files have been uploaded to Sharepoint, for organizational purposes, delete the original directory where files were files initially saved.

5.6 Updating the Properties on Sharepoint

1) While keeping Sharepoint open, re-open SQL Server Management Studio. Click on New Query and input the text below:

```
SELECT *
      , LEFT([Source],13) ContractorFile
      , RIGHT([source],9) ContractorSheet
      FROM (SELECT TOP 400 [TrayFileItemID]
            ,[TrayFileID]
            ,[Position]
            ,[SampleIdent]
            ,[Application]
            ,[Source]
            ,[SeasonalQuarter]
            ,[MonthlyQuarter]
            ,[Repeat]
      FROM [Improve.XRFTrayFiles].[dbo].[XRFTrayFileItem]
         ORDER BY TrayFileID desc)b
         WHERE Position = 1 ORDER BY trayfileid asc
```

NOTE: The query is also saved at: K:\XRF Tray File Creation Tool\SQLQuery_EdittingProperties.

2) Press F5, or click on ‘Execute.’
3) Go back to Sharepoint and click on “Library,” which is under “Library Tools.” Then click on “Data Sheet View.”
4) Return to the newly-generated “Results” table in SQL. Using copy and paste functions, fill in the newly downloaded tray files in Sharepoint with their respective properties.

TI 301C: Sample Changes for 8-Position Trays

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1. PURPOSE AND APPLICABILITY

The purpose of this SOP is to describe the process of loading and unloading samples using standard cups in 8-position trays in the Epsilon 5 EDXRF instruments.

2. SUMMARY OF THE METHOD

Tray files are transferred to the PANalytical sample changer software using a program called LIMS. Filters are transferred from Petri dishes into cups in the order designated by the corresponding tray file. The cups are placed into one of six 8-position trays (as designated by the tray file). The samples are queued in the software and the trays are placed into the Epsilon 5 sample changer compartment. After analysis is complete, trays are removed and filters are transferred back into labeled Petri dishes.

3. SAFETY

The Epsilon 5 produces X-rays which can be dangerous if appropriate precautions are not taken. Dosimeters must be worn during loading and unloading of samples.

4. PERSONNEL QUALIFICATIONS

The lab manager, spectroscopist, and designated lab technicians perform sample changes on the Epsilon 5 instruments. Dosimeters must be worn, so all training and instruction required by the University to receive dosimetry must be completed.

5. CAUTIONS

Once filters are placed into cups, they are completely unidentifiable beyond their positions in the tray. Be very attentive when transferring filters into cups, and be sure to place every filter in the correct tray as well as the proper position in the tray as designated by the tray file.

Similar caution must be taken when unloading filters from the cups. Ensure that the filters return to the proper labeled Petri dish.

Check the green “Free to Open” light on the control panel of the Epsilon 5 before opening the sample changer cover. Only open the cover if the button is illuminated.

Report any mishaps or unusual occurrences that happen during a sample change. If the Epsilon 5 generates an error message or has a software malfunction, note it in both the physical log book at the station as well as the Microsoft Access log on the desktop at the station. If a filter is dropped or appears unusual (hole, particles, uneven sampling, etc.), fill out a status adjustment form explaining the issue. No notes in electronic or physical log records are required.

6. EQUIPMENT AND SUPPLIES

- Filter mount cups
- Sample retaining cups
- 8-position sample trays (labeled A-F)
- 4-position sample tray (labeled S)
- Forceps
- Tray files
- Log books (physical and electronic)
- Petri dish holder

7. PROCEDURE

Because the Epsilon 5 instruments run 24 hours a day, seven days a week, trays must be unloaded before tray files can be uploaded and new filters can be loaded in trays. In order to stay consistent with how the procedure occurs in practice, the procedure section will begin with the unloading of filters.

7.1 Overview and General Definitions

The following picture outlines the terms given to each element that houses the samples:

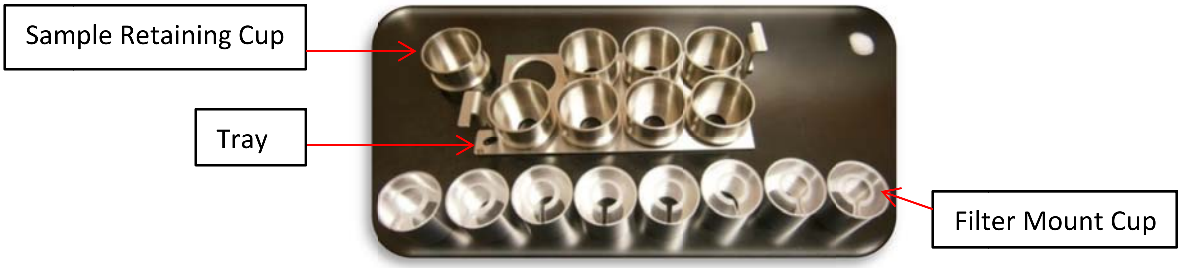


Figure 1. 8-position tray contents.

The Epsilon 5 sample changer compartment holds six 8-position sample trays labeled A-F. Positions in the tray are numbered #1-8. There is also one 4-position tray labeled S. The “S” tray house a Nuclepore blank, 1 or 2 multi-elemental reference filters, and a Teflon® blank. Each Epsilon 5 (Odin, Froya, and Thor) have an assigned “S” tray that is analyzed daily for monitoring sampling performance.

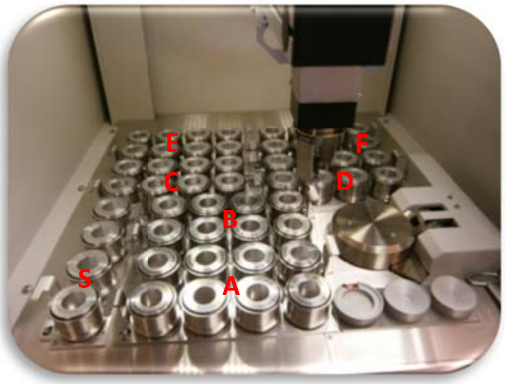


Figure 2. Sample changer compartment with trays.

The letter on each sample tray matches an etched letter on the surface of the sample changer. The trays are keyed to prevent them from being loaded backwards in the sample changer; this ensures samples #1-8 are in the proper order.

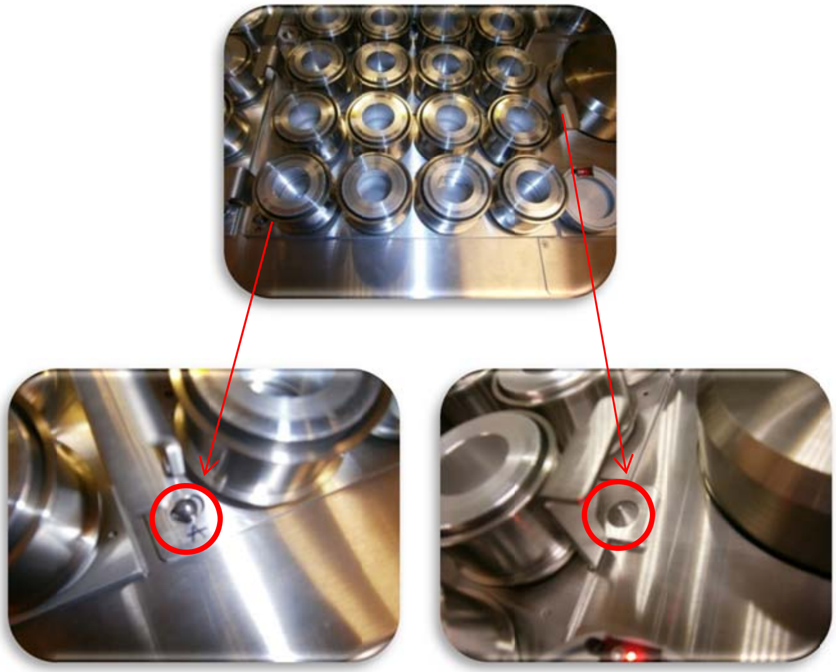


Figure 3. Tray keys

The Epsilon software displays the configuration of the trays in the compartment. The individual samples are color-coded. Examples are shown in the figure below:

- Orange/Gray: Not queued to be measured (Ex. E8)
- Yellow/Orange: Queued to be measured (Ex. F8, Tray A, Tray B)

- Green/Orange: Measured and okay (Ex. Trays S, C & D, E1-E7, F1-F6)
- Gray/Yellow: Currently analyzing (F7)

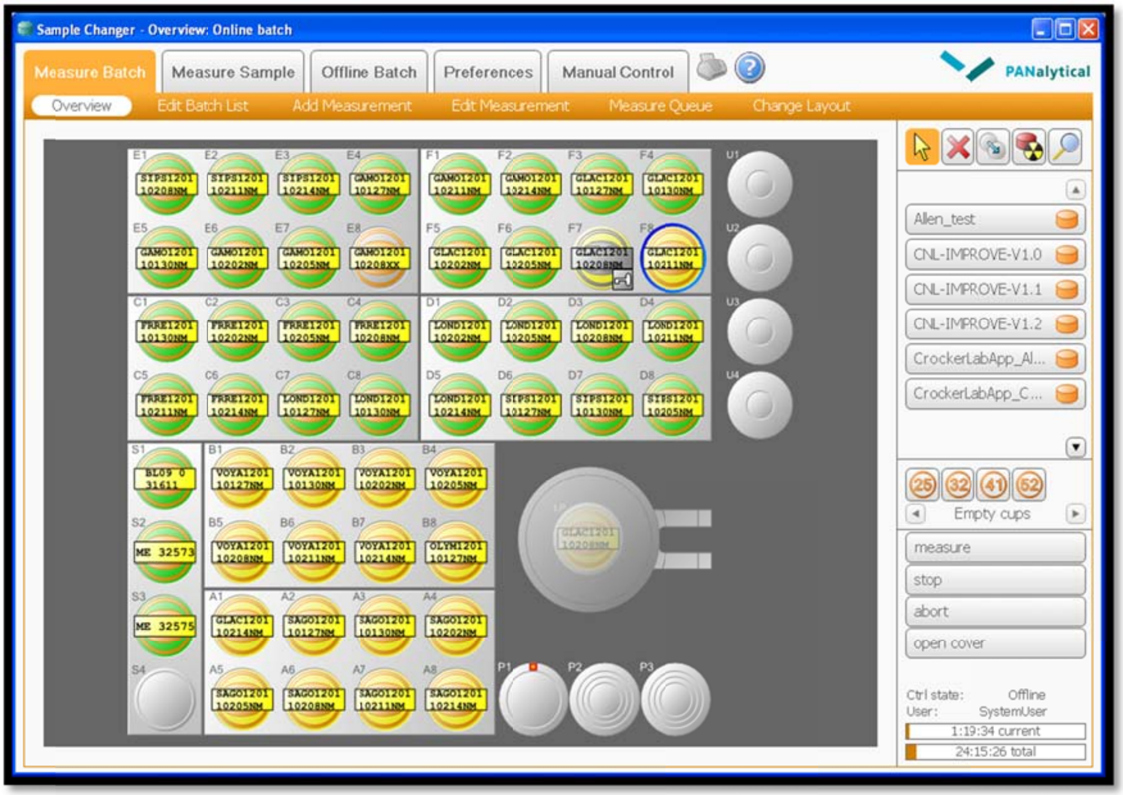


Figure 4. Color-coded samples.

The samples that are loaded in the sample changer compartment correspond with the empty Petri dishes located in the Petri dish holder. Each Petri dish holder is labeled with the instrument it is used with (Odin, Froya, or Thor). Each compartment is labeled with a letter that matches one of the trays (A-F, S). The top Petri dish in the stack in each compartment corresponds to the filter in Position 1 for that tray.

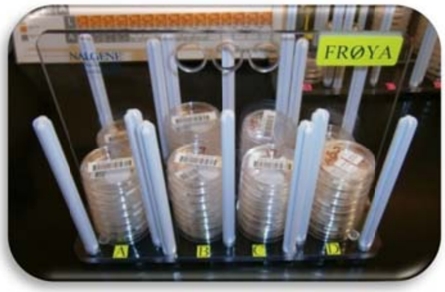


Figure 5. Petri dish holder

7.2 Procedure for Unloading Analyzed Samples

Sample changes can be made while the instrument is analyzing as long as the "Free to Open" light is illuminated.

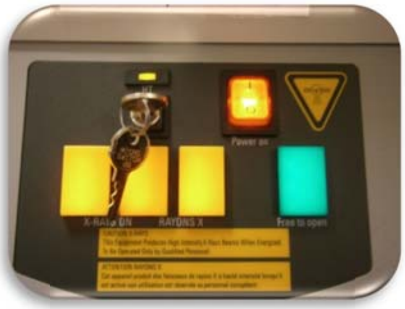


Figure 6. "Free to Open" light

1) Note which trays have completed analysis. They will be unloaded in alphabetical order, starting with the earliest letter.
2) After making sure that all 8 samples in the tray have been analyzed, open the sample changer cover and remove the first tray of filters. As a precautionary measure, perform sample changes for one instrument at a time.
3) Set the tray on the desk or sample handling table and close the sample changer cover.
4) Remove the Petri dishes in the corresponding compartment of the Petri dish holder. Typically, the top Petri dish will be flagged with a sticky tab to indicate that it is the first tray that needs to be unloaded. Line up the Petri dishes from left to right, starting with the top Petri dish. Make sure that the information in the sticker of the Petri dishes matches the filter identities on the screen.

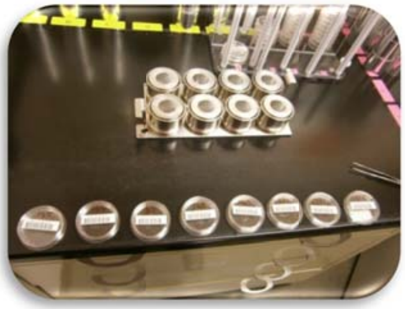


Figure 7. Layout of petri dishes

5) Pick up the sample retaining cup from position A1. Place one finger on the inner filter mounting cup for support, then turn the sampling cup upside down and line it above the first Petri dish.

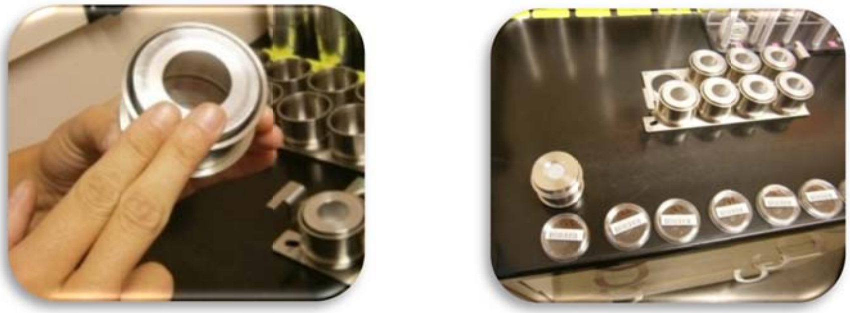


Figure 8. Sample retaining cup handling and positioning

6) Now, remove the sample retaining cup by lifting it up and off of the filter mounting cup. Pick up the filter by its outer support ring using forceps and place it in the Petri dish. Make sure the sample side remains face-up.

7) Place the Petri dish in its white Petri tray (located next to the Petri dish holder). Confirm that it is the correct tray by examining the filter inventory list included in the tray.

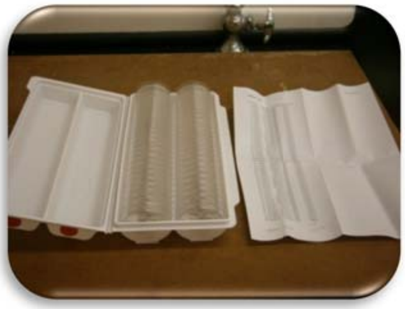


Figure 9. Petri tray and inventory list

8) Place the filter mount cup back into the retaining cup.
9) Repeat steps 5-8 for positions 2-8, and then for the rest of the completed trays except for the “S” tray. The “S” tray should not be unloaded during routine sample changes. See Section 7.8 below for instructions regarding the analysis the the “S” tray. Empty trays may be placed back into the sample changer compartment if necessary to keep them out of the way until loading occurs.
10) NOTE: Remember that for now, the Teflon® filters have no functional identifier of any kind. Therefore, it is extremely important to keep everything in the proper order while the filters are separated from their corresponding Petri dishes.

7.3 Removing the Analyzed Filters from the Queue

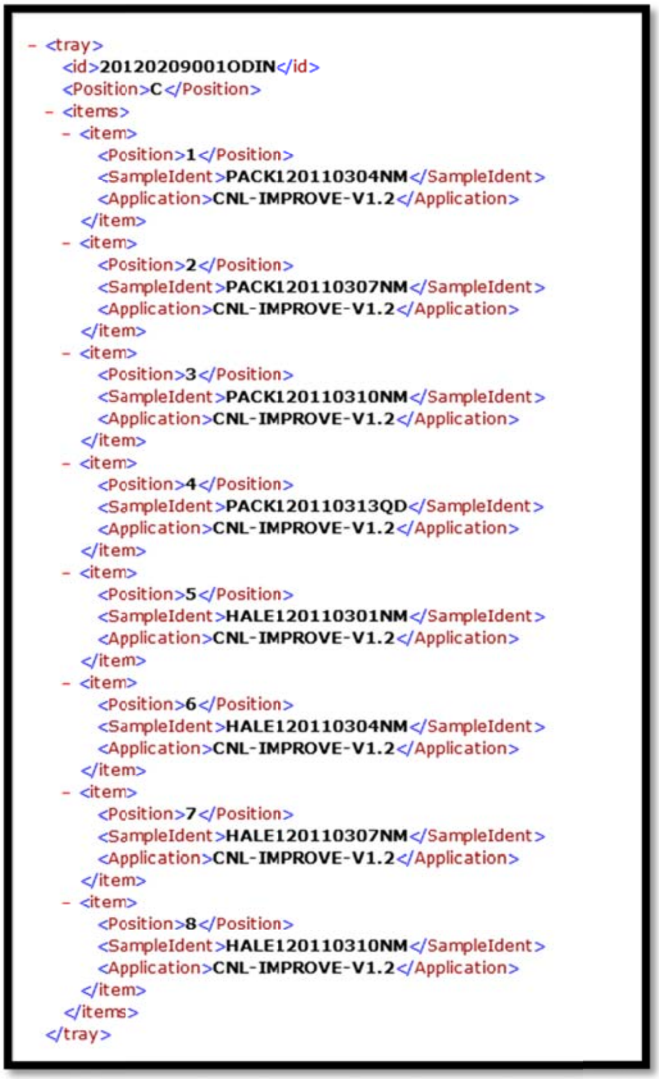
After removing the analyzed filters, they need to be deleted from the Epsilon queue. Towards the right side of the sample changer window, there is a ☒ symbol. Click on the symbol to activate the “Delete” function. Then, move the mouse over the middle of the picture of the completed tray and click once. This should delete the entire tray. It is also possible to delete one sample at a time by clicking on each position. Do not delete the S tray.

7.4 Weekly Check of the Designated Blank

On a weekly basis, the blank filter is checked before adding new samples to make sure that the filter is properly designated. Please see TI 301E QA_QC of XRF Analysis for more information.

7.5 Adding New Samples to the Queue with a Pre-Made Batch File

1) On the desktop of the Epsilon computer, there is a folder named “Tray files.” This folder contains pre-made bach files and a folder named “Queued.” If there are no batch files in “Tray files,” download them from Sharepoint. For instructions how to access pre-made tray files, refer to Section 8.1 in the Additional Checks/Procedures section.
2) There is one tray file for each tray. The naming format is YYYYMMDD(###) Instrument, where YYYYMMDD is the date the file was created, ### is the sequence number, and “Instrument” is the Epsilon the files are being created for. For example, 20120209001ODIN was created on 02/09/12 for Odin. The “001” means it is the first of the series created. This number is intended to be used so that if the files are sorted in ascending order, they will be in the correct loading order.
3) When the different tray files are sorted by name, the first file on the list will be the first file that needs to be loaded. Check the file by clicking on it. See figure 10 for an example.
4) Copy the necessary files to the folder called “Shortcut to LIMS.” Once the files have been copied over, move them from their current location in the “Trayfiles” folder to the “Queued” folder, so that the next user performing sample changes can easily find the files that they need.



```
- <tray>
    <id>20120209001ODIN</id>
    <Position>C</Position>
  - <items>
    - <item>
        <Position>1</Position>
        <SampleIdent>PACK120110304NM</SampleIdent>
        <Application>CNL-IMPROVE-V1.2</Application>
      </item>
    - <item>
        <Position>2</Position>
        <SampleIdent>PACK120110307NM</SampleIdent>
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    - <item>
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        <SampleIdent>PACK120110313QD</SampleIdent>
        <Application>CNL-IMPROVE-V1.2</Application>
      </item>
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        <Application>CNL-IMPROVE-V1.2</Application>
      </item>
    - <item>
        <Position>8</Position>
        <SampleIdent>HALE120110310NM</SampleIdent>
        <Application>CNL-IMPROVE-V1.2</Application>
      </item>
    </items>
  </tray>
```
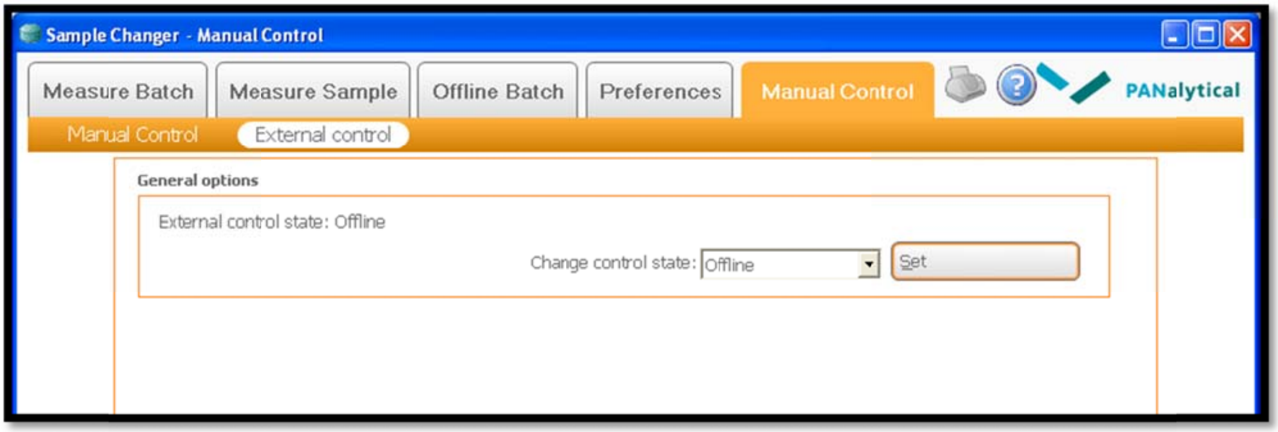

Figure 10. Sample tray file

5) Find the LIMS2UAI.exe icon on the desktop and double-click it.
6) A small window will appear. There will be red highlighted text saying “Offline” that will change to a green highlighted “remote.” Then, in the “Overview Screen” in the “Measure Batch” tab of the sample changer window, filters will begin to populate the trays. When all the trays are complete, close the LIMS window by clicking the “X” in the window. The files in the LIMS folder will now be gone.
7) Now, go to the “Manual Control” tab. Then click on “External Control.” Check to make sure that the External Control State is “Offline.” If not (and it

will usually not be), change it to “Offline” and click “Set.” If the status does not change after clicking the button, try setting it to “Local” and then “Offline.”



External control state: Offline

Change control state: Offline

Figure 11. “Manual Control” tab

7.6 Saving the New Queue

1) When all of the samples have been queued to be measured, save the queue (batch) by first clicking on the “Measure Batch” tab, then “Edit Batch List.”
2) A list of what was just loaded will appear. Sometimes, this takes a few seconds to display.
3) On the right hand side, click “Save As.”
4) When the “Save Batch” screen appears, the correct folder should already be displayed. The folder is on the desktop and is called “Batch Files.”
5) The format for saving batch files is “current_mmddyyyy.batch” (ex. current_09172011.batch).
6) After entering the name, click “Save.”

7.7 Loading New Samples into the Sample Chamber

1) Find the next white Petri tray with filters to be analyzed.
2) Line up the first eight filters on the table from left to right. Confirm that these filters match the corresponding tray file.
3) Remove the designated 8-position tray from the Epsilon and place it on the sample handling table.

4) Remove the mounting cups from the tray and place them directly behind the samples.
5) Open the first Petri dish and use the forceps to lift the filter by the outer support ring and place it on the mount. The sample side should be facing up.
6) Next, place the sample retaining cup over the top of the mounting cup. Tip the cup slightly and support the filter mount cup by applying gentle pressure on the bottom of the cup. Then, turn the assembly upside down and place it in the first position of the tray.
7) Continue with the rest of the samples, moving to position 2, then 3, etc., until all eight have been loaded. Double-check that the physically-loaded filters match the filters displayed on the "Overview" screen.
8) Stack the empty Petri dishes with the far-left Petri (for position 1) at the top of the stack. Place the Petri dishes in the appropriate compartment (A-F) of the Petri dish holder.
9) Look at the front panel display of the Epsilon. Make sure the green "Free to Open" light is lit. Then, open the sample changer cover.
10) Load the filled sample tray into the sample changer compartment with the letter written on the sample tray matching the etched letter in the sample changer.
11) Close the sample changer cover and repeat steps 2-10 for the remaining empty trays.
12) Add the newly populated filters to the analysis queue by clicking the ☢ symbol (in the "Overview" screen of the "Measure Batch" tab. Then, click on the newly-loaded trays. The samples will change from gray to yellow.

7.8 Analyzing the "S" Tray

The "S" tray is analyzed once every day. The current method is to add the "S" tray to run directly after the current tray being analyzed, and then continue with the A-F cycle. If the queue needs to be re-ordered for the "S" Tray to be analyzed, refer to Section 8.3 of Additional Checks/Procedures.

7.9 Recording Sample Changes

1) Each instrument has its own physical log book as well as an electronic log in Microsoft Access. The physical log book is labeled with the instrument

name and is located on the shelf above the respective computer, while the Access log is located on the computer desktop.

2) Open the physical log book to the first available row. Write the date, time, first and last samples loaded, and the letters of the trays loaded. Sign the entry. Make sure to follow the same format as previous entries.
3) Open the Access log by clicking on the icon entitled "Enter_LogBooks .accdb." Click on "Add New Record." The date and time will automatically fill in. The default Code Action is LD, for "Loading." Fill in the first and last filter information and the "Initials" box. Then click, "Save This New Record." Close the log.

8.0 Additional Checks/Procedures

8.1 Accessing Pre-Made Batch Files from the Sharepoint Website

1) Open an internet browser.
2) Type in http://cl-ds if on a CNL server. Otherwise, type in the full address: http://cl-ds.ou.ad3.ucdavis.edu.
3) If on a CNL server, login will happen automatically. If not on a CNL server, Sharepoint requires Kerberos usernames and passwords to sign in. Make sure to add ad3\ before the username.
4) On the left side of the Sharepoint home page, click on "Panalytical Tray Files."
5) On the top of the page, there will be a line that says "Home->Panalytical Tray Files->Six Tray Files." Click on "Six Tray Files" and a drop-down menu will appear. Click on "All Documents." A list of files will appear, one for each tray.
6) Go to the "XRF Device" column and select the appropriate instrument. Then, click the "Downloaded" column and select "No," to list the tray files that have not yet been downloaded. The files should organize themselves so that tray file ID #001 (or lowest number) is at the top of the list. This is the first file that needs to be downloaded.
7) Move the mouse over the file name and right click. Then select "Save Target As." Save the file directly to the "Trayfiles" folder on the desktop. If necessary, files can be saved one at a time onto a USB flash drive and then moved to the "Trayfile" folder of the appropriate instrument.
8) After the file has been downloaded, right click the file name and click on the arrow that appears.

9) Click on “Edit Properties.”
10) Click the “Downloaded” box and click “Save.”

8.2 Adding the New Samples to the Queue without a Pre-Made Batch File

1) To add filters to the queue, double-click on the first position that will be loaded in the sample changing software. This will open the “Add Measurement” screen.
2) The “location” should already be the correct position.
3) For “Application,” select the current version of the application being run on the particular Epsilon. As of February 2013, Froya and Odin run on “CNL-IMPROVE-V1.2A” and Thor runs on “CNL-IMPROVE-V1.2B.”
4) Place the cursor in the “Sample Identification” box.
5) Scan (if barcode is available) or type the ID of the filter.
6) Press F9 to save the entry and the program will automatically move on to the next position.

8.3 Changing the Order of the Queue (Usually for “S” Tray)

1) In the “Measure Batch” tab, click on “Measure Queue.”
2) Highlight the samples of the “S” tray (or whatever samples need to be moved).
3) Use the “Move Up” or “Move Down” buttons on the right as many times as needed to change the order.

8.4 Aborting Sample Analysis

1) To abort a sample while in mid-analysis, go to the “Measure Batch” tab, then “Overview.”
2) Click the “Abort” button towards the bottom right.
3) The instrument will first come to air; then, the sample will be removed and put back to its original tray position. No new analysis will begin until the “Measure” button is clicked or the ☢ button is used to re-queue.

8.5 Special Circumstances When Using “Stop” to Suspend Analysis

1) When activated, the “Stop” button will let the current sample finish analyzing, then stop all actions without emptying the queue. The only issue with this button is that it does not change the current sample to green when completed, even though the data is in the “Results” file.

2) To be sure that the filter was successfully analyzed, click on “File,” then “Open.”
3) On the left of the window that pops up, click on “Results.”
4) Then, click on the current version of the application being run on the particular Epsilon. Click “Open.”
5) Check the boxes for “Routine,” “Measured,” “Standard,” and “Blank.” Then type the name of the sample, standard, or blank. Click “Apply.”
6) If the filter was analyzed, it will appear on the list. Otherwise, use the ☢ symbol to queue it for analysis.

8.6 Changing Status of Files on Sharepoint to “Analyzed”

1) Open an internet browser.
2) Type in the address of the Sharepoint site (http://cl-ds.ou.ad3.ucdavis.edu)
3) If not on a CNL server, the program will ask for login information. It accepts Kerberos usernames and passwords.
4) On the left side, click on “Panalytical Tray Files.”
5) At the top, there will be a line named “Six Tray Files.” Click on it and a drop-down menu will appear. Click on “All Documents.”
6) One file per tray will appear. Locate the files that have been analyzed. Sort by instrument if necessary.
7) Roll the mouse over the file name and a box will appear to the left. Check the box.
8) Click on “Edit Properties.”
9) Check the “Analyzed” box and click “Save.”

8.7 Creating Tray Files

Detailed instructions on how to create tray files are located in TI 301B Tray file creation.

8.8 Weekly Check of Blank Identities

1) On a weekly basis, the blank filter is checked to make sure it is properly designated before new samples are loaded during the sample change. To do this, look up the blank used for the last sample analyzed by first clicking on “File,” then “Open.” On the left of the window that pops up, click on “Results.”

2) Click on “CNL-IMPROVE-V#” with “V#” being the version number currently being run on the Epsilon. Click “Open.”
3) In the window that pops up, type a “*” in the Sample ID box. Make sure “Routine” and “Measured” are checked. Then, click “Apply.”
4) The list generated should be in descending order so that the top filter is the last filter that was analyzed. Click on the top sample to highlight it and the analysis data will appear.
5) Check that the Blank ID is correct for the Epsilon in use. Refer to the laboratory manager or spectroscopist for the current Blank IDs for each Epsilon. If the blank is not correct, make a note of it and inform the lab manager and spectroscopist immediately. If the blank is correct, close the “Results” window and continue.

8.9 Changing Inserts in Filter Mount Cups

The plastic inserts in the filter mount cups are changed on average every 2 days or upon completion of the A-F tray cycle. Inserts are removed from the filter mount cups and placed in a bin, which is located in a cabinet drawer in the XRF Room. These used inserts will later be cleaned with ethanol and Kimwipes™. Clean inserts can be found in a labeled bin in the same drawer. Exchange used inserts for clean inserts, place the new inserts in the filter mount cups, and continue with the sample change.

TI 301D: XRF Data Processing

Table of Contents

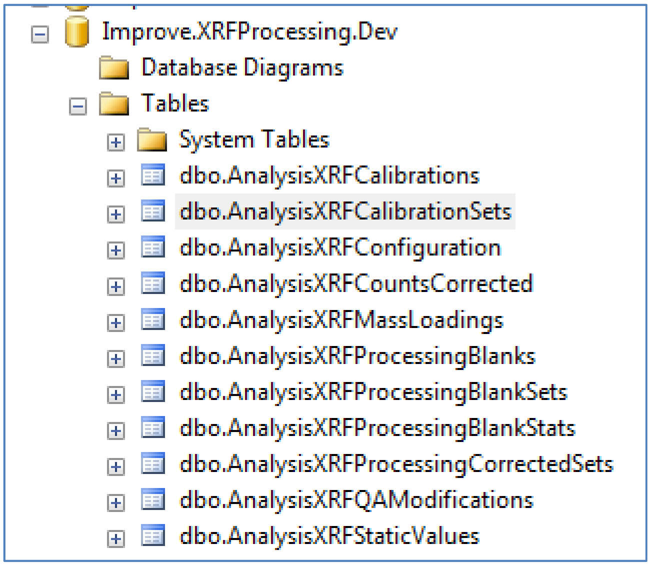
1. PURPOSE AND APPLICABILITY

The purpose of this document is to explain the stored procedures/tables/workflows involved in the blank correction and conversion of PANalytical analysis data into mass loadings, as well as their respective error and detection limits. This document is intended for users of the stored procedures and those involved in the IMPROVE data processing in total. The general audience is required to have a fundamental knowledge of SQL. The audience who wants to use the stored procedures must understand how to query data and execute stored procedures with parameters.

2. DATABASE INFORMATION

The stored procedures will be located in the CL-SQL (169.237.146.117), specifically in the database Improve.XRFProcessing. Users must have Execute/Insert/Select permissions on the Improve.XRFProcessing database, and Select in the Improve database.

3. TABLES

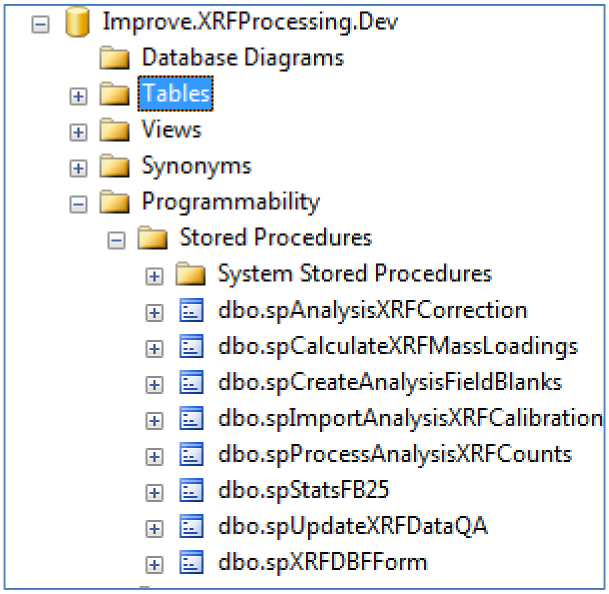


Improve.XRFProcessing.Dev
Database Diagrams
Tables
System Tables
dbo.AnalysisXRFCalibrations
dbo.AnalysisXRFCalibrationSets
dbo.AnalysisXRFConfiguration
dbo.AnalysisXRFCountsCorrected
dbo.AnalysisXRFMassLoadings
dbo.AnalysisXRFProcessingBlanks
dbo.AnalysisXRFProcessingBlankSets
dbo.AnalysisXRFProcessingBlankStats
dbo.AnalysisXRFProcessingCorrectedSets
dbo.AnalysisXRFQAModifications
dbo.AnalysisXRFStaticValues

Name	Description
dbo.AnalysisXRFCalibrations	Stores the calibration E values for each PANalytical XRF Machine. Many to one AnalysisXRFCalibrationSets on [CalibrationSetId].
dbo.AnalysisXRFCalibrationSets	Set information for the calibrations. Which machine and dates the calibrations are pertinant. One to many AnalysisXRFCalibrations
dbo.AnalysisXRFConfiguration	Contains the different configurations for the XRF Machines and their effective dates.
dbo.AnalysisXRFCountsCorrected	Stores the analysis counts after blank subtraction using 25 field blanks and their median.
dbo.AnalysisXRFMassLoadings	Stores the mass loadings for each result after processing the corrected counts using the Calibrations.
dbo.AnalysisXRFProcessingBlanks	Stores the actual blanks used for blank correction. Many to one AnalysisXRFProcessingBlankSets on [BlankSetId].
dbo.AnalysisXRFProcessingBlankSets	Stores the set information for field blanks: the configuration, determination date, processed date. One to many AnalysisXRFBlanks and AnalysisXRFBlankStats on [BlankSetId]

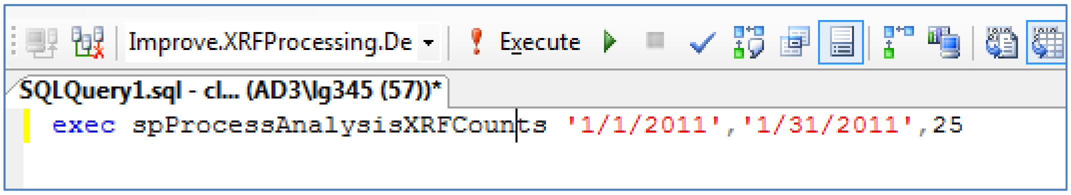
dbo.AnalysisXRFProcessingBlankStats	Contains the statistical calculations (median/95th) for each element in each field blank set. Many to one AnalysisXRFProcessingBlankSets on [BlankSetId]
dbo.AnalysisXRFProcessingCorrectedSets	Contains the information about each set of counts processed: the minimum/maximum date and processed date. One to many AnalysisXRFCountsCorrected on [ProcessedSetId].
dbo.AnalysisXRFQAModifications	The QA Modification that have been made to the XRF data on validity, sampleident, xrfdate, and source. Used in tandem with spUpdateXRFDataQA to keep the migrated data up to date if it is ever reimported.
dbo.AnalysisXRFStaticValues	The values chose by Warren to be used in the ERR and MDL calculations for each machine when they are converted into their mass loadings.

4. THE STORED PROCEDURES


Improve.XRFProcessing.Dev
Database Diagrams
Tables
Views
Synonyms
Programmability
Stored Procedures
System Stored Procedures
dbo.spAnalysisXRFCorrection
dbo.spCalculateXRFMassLoadings
dbo.spCreateAnalysisFieldBlanks
dbo.spImportAnalysisXRFCalibration
dbo.spProcessAnalysisXRFCounts
dbo.spStatsFB25
dbo.spUpdateXRFDataQA
dbo.spXRFDBFForm

1) dbo.spProcessAnalysisXRFCounts:

This stored procedure is the start for the entire XRF Data Process. It accepts three parameters: startdate(datetime), enddate (datetime), and number of field blanks (int). Dates are used so sets can be processed outside of the normal month datespan. The number of field blanks will be 25, but the parameter is there to allow future expansion.

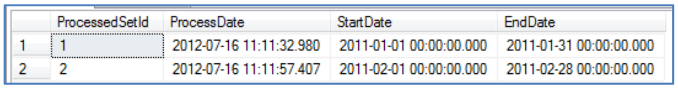


```
exec spProcessAnalysisXRFCounts '1/1/2011','1/31/2011',25
```

Sections of spProcessAnalysisXRfCounts

Generate the Correction Set:

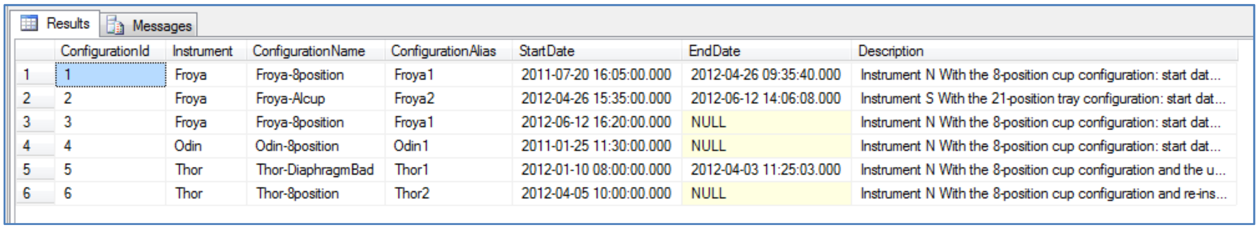
Inserts the stored procedure parameters into AnalysisXRFProcessingCorrectedSets for historical purposes and binding the corrected values for this run of the stored procedures into a single set which will be manipulated later.



	ProcessedSetId	ProcessDate	StartDate	EndDate
1	1	2012-07-16 11:11:32.980	2011-01-01 00:00:00.000	2011-01-31 00:00:00.000
2	2	2012-07-16 11:11:57.407	2011-02-01 00:00:00.000	2011-02-28 00:00:00.000

Configuration Cursor:

The cursor is used to find all of the distinct active configurations that were used during the sampling dates specified through the parameters. It uses each configuration in a loop to execute the rest of the stored procedures.



	ConfigurationId	Instrument	ConfigurationName	ConfigurationAlias	StartDate	EndDate	Description
1	1	Froya	Froya-8position	Froya1	2011-07-20 16:05:00.000	2012-04-26 09:35:40.000	Instrument N With the 8-position cup configuration: start dat...
2	2	Froya	Froya-Alcup	Froya2	2012-04-26 15:35:00.000	2012-06-12 14:06:08.000	Instrument S With the 21-position tray configuration: start dat...
3	3	Froya	Froya-8position	Froya1	2012-06-12 16:20:00.000	NULL	Instrument N With the 8-position cup configuration: start dat...
4	4	Odin	Odin-8position	Odin1	2011-01-25 11:30:00.000	NULL	Instrument N With the 8-position cup configuration: start dat...
5	5	Thor	Thor-DiaphragmBad	Thor1	2012-01-10 08:00:00.000	2012-04-03 11:25:03.000	Instrument N With the 8-position cup configuration and the u...
6	6	Thor	Thor-8position	Thor2	2012-04-05 10:00:00.000	NULL	Instrument N With the 8-position cup configuration and re-ins...

Cursor Loop:

The cursor loop section opens the cursor and each distinct configuration is passed as parameters into other stored procedures.

Loop Member – Choosing Fieldblanks:

Executes the stored procedure spCreateAnalysisFieldBlanks passing in the startdate, enddate, configuration, and number of fieldblanks as parameters. This generates the 25 field blanks per configuration and their statistics

Loop Member – Correction:

Executes the stored procedure spAnalysisXRFCorrection passing in the startdate, enddate, and configuration as parameters. This performs the blank subtraction using the statistics generated in "Loop Member – Choosing Fieldblanks".

Calculate Mass Loadings:

This data is the converted to mass loadings values by applying the PANalytical machine calibration values to the corrected energies calculated in section "Loop Member –Correction".

2) dbo.spCreateAnalysisFieldBlanks

This stored procedure finds the 25 field blanks and their statistics for the configuration specified in the parameters of this stored procedure. This procedure also needs a startdate and enddate as parameters to select the correct field blanks.

Sections of spCreateAnalysisFieldBlanks

Determination Date:

This section finds the date that determines which field blanks to use. The date is determined by the greatest analysis date of the sampling dates specified by the parameters for the configuration.

Create Blank Set:

This section generates the blank set value by inserting into dbo.analysisXRFProcessingBlankSets. It inserts the run date, determination date, and XRF Machine Configuration.

Choose Blanks:

This section selects the 25 field blanks that will be members of the set. It selects 25 field blanks that were analyzed from the determination date backwards. If it cannot fill 25, it will continue filling going forwards from the determination date until it reaches 25.

Generate Field Blank Statistics:

This section generates the median and 95th percentile for each element of the 24 we currently use. It runs the stored procedure 24 times (one for each element). This was not hardcoded into a single stored procedure to allow the expansion later on.

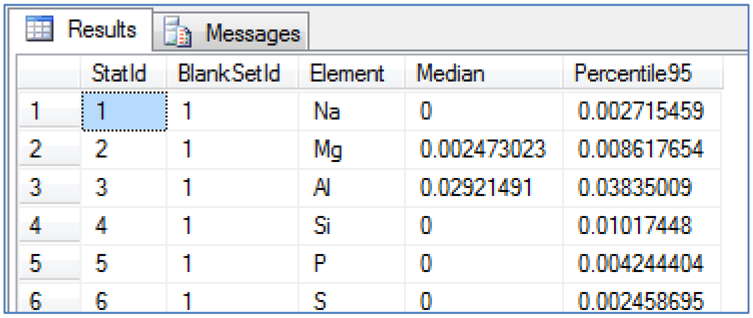
3) dbo.spStatsFB25

This stored procedure generates the statistics (median/95th) for a given set of field blanks. It accepts the parameters element and the blank set ID.

Sections of spStatsFB25

Generate Field Blank Statistics:

This section inserts the statistics for a given field blank set and given element as defined by the parameters. It does this by ordering the values for the given element from least to greatest and selecting the 13th (median) and 24th (95th percentile).



	StatId	BlankSetId	Element	Median	Percentile95
1	1	1	Na	0	0.002715459
2	2	1	Mg	0.002473023	0.008617654
3	3	1	Al	0.02921491	0.03835009
4	4	1	Si	0	0.01017448
5	5	1	P	0	0.004244404
6	6	1	S	0	0.002458695

4) dbo.spAnalysisXRFCorrection

This stored procedure corrects the XRF values for the datespan (it accepts as a parameter) using the field blank statistics generated in the former stored procedure. It also accepts the configuration.

Sections of spAnalysisXRFCorrection

Set Identity Columns:

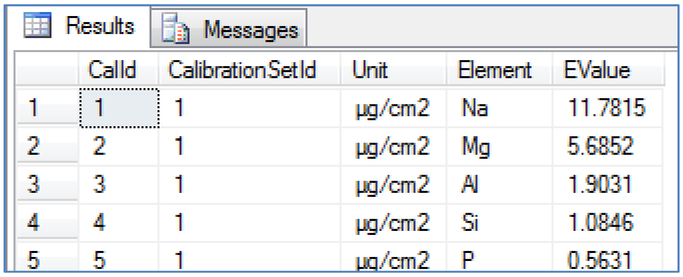
This section selects the currently incremented identity values that were established in the previous stored procedures: Blank set identity and corrected set. These are inserted with the corrected values to establish relationships.

Blank Correction:

This section performs the actual blank correction of the date span; based on validity of the sample, the configuration, and the field blank statistics. It inserts these values into dbo.AnalysisXRFCountsCorrected.

5) dbo.spCalculateXRFMassLoadings

This stored procedure converts the corrected count values into their mass loading values by using the calibrations from each machine. It accepts only the Processed Set Id. This stored procedure is called last and outside of the main loop of spProcessAnalysisXRFCounts.



	CalId	CalibrationSetId	Unit	Element	EValue
1	1	1	µg/cm2	Na	11.7815
2	2	1	µg/cm2	Mg	5.6852
3	3	1	µg/cm2	Al	1.9031
4	4	1	µg/cm2	Si	1.0846
5	5	1	µg/cm2	P	0.5631

Sections of spCalculateXRFMassLoadings

Insert Corrected Mass Loadings:

This section takes the corrected counts, applies the calibration factor, and inserts them into dbo.AnalysisXRFMassLoadings. Likewise, it inserts the error and detection limit values. The detection limits are static and in dbo.AnalysisXRFStaticValues. The errors are calculated using an equation applied to the corrected intensities, proportional uncertainties, and detection limits.

6) dbo.spXRFDBFForm

This stored procedure accepts a processed set Id. The procedure converts the XRF Data into a form readable for the SWAP visual foxpro application. This procedure is called separately from spProcessAnalysisXRFCounts.

Sections of spXRFDBFForm

Column Matching to DBF:

This section selects from the next section subquery. This section selects dummy values into unused columns, and selects the elements, errors, and detection limits with the appropriate names and prefixes.

Max Values for the Pivot Query:

This section holds the elemental select subquery which selects the maximum values for all columns for each split record. Because it selects from a triple pivoted subquery, three records are generated for each one record being pivoted. This query forces them back into one record by selecting the non-null values for each column per triplet record.

The Pivoted Query:

This section contains the initial query from dbo.AnalysisXRFMassLoadings. It casts the sampling dates, and has the three pivots (and titles the pivoted columns). It pivots the data on the concentration, errors and detection limits for each record.

7) dbo.spUpdateXRFDataQA

This stored procedure is separate and is used to update dbo.AnalysisXRFCountsMigrate by joining with AnalysisXRFQAModifications. It also stores comments and the date performed.

Remarks:

Tips:

- **[**Columns**]**, **dbo.**TableName, **vw**ViewName, **sp**StoredProcedureName, **fx**FunctionName are the naming conventions both in this document and in the code.
- cps/mA is referred to as counts or energies. ng/cm^2 is usually referred to as mass loadings or two dimensional density. These units are interchangeable by using the elemental calibrations of each PANalytical XRF machine.
- CamelCasing is keeping multiple words together but making the first letter of each word capital. This is useful for when only one word is allowed or if it makes it easier to deal with (column names).
- SAMDAT is always explicitly called [SAMDAT]. [XRFDate] and [DateTime] correspond to the analysis date/time.
- All properties of a filter (site,samdat,status) are derived from the [SAMPLEIDENT]. This is the only way that properties of filter can be persisted through XRF analysis.

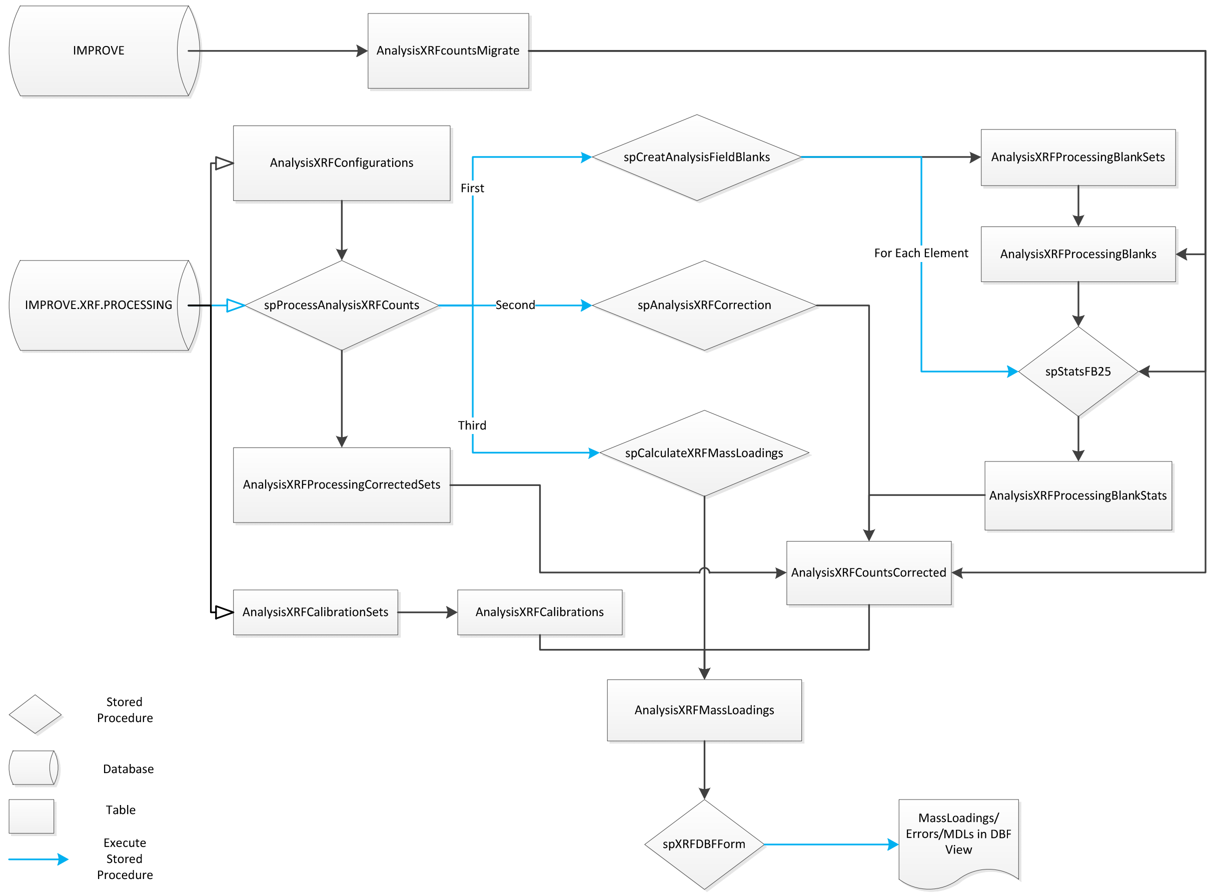
ChangeLog:

Version	**Completion Date**	**Changes**
0.900	6/25/2012	Initial Creation
0.905	6/27/2012	Fixed error with Thor checking for Odin data to determine BlankSet existence. Added the Processed set to identify processed data.
0.907	6/28/2012	Converted some Functions into correlated subqueries for performance. This translates to higher performance when there is more data. However, there is less performance when there is no data.

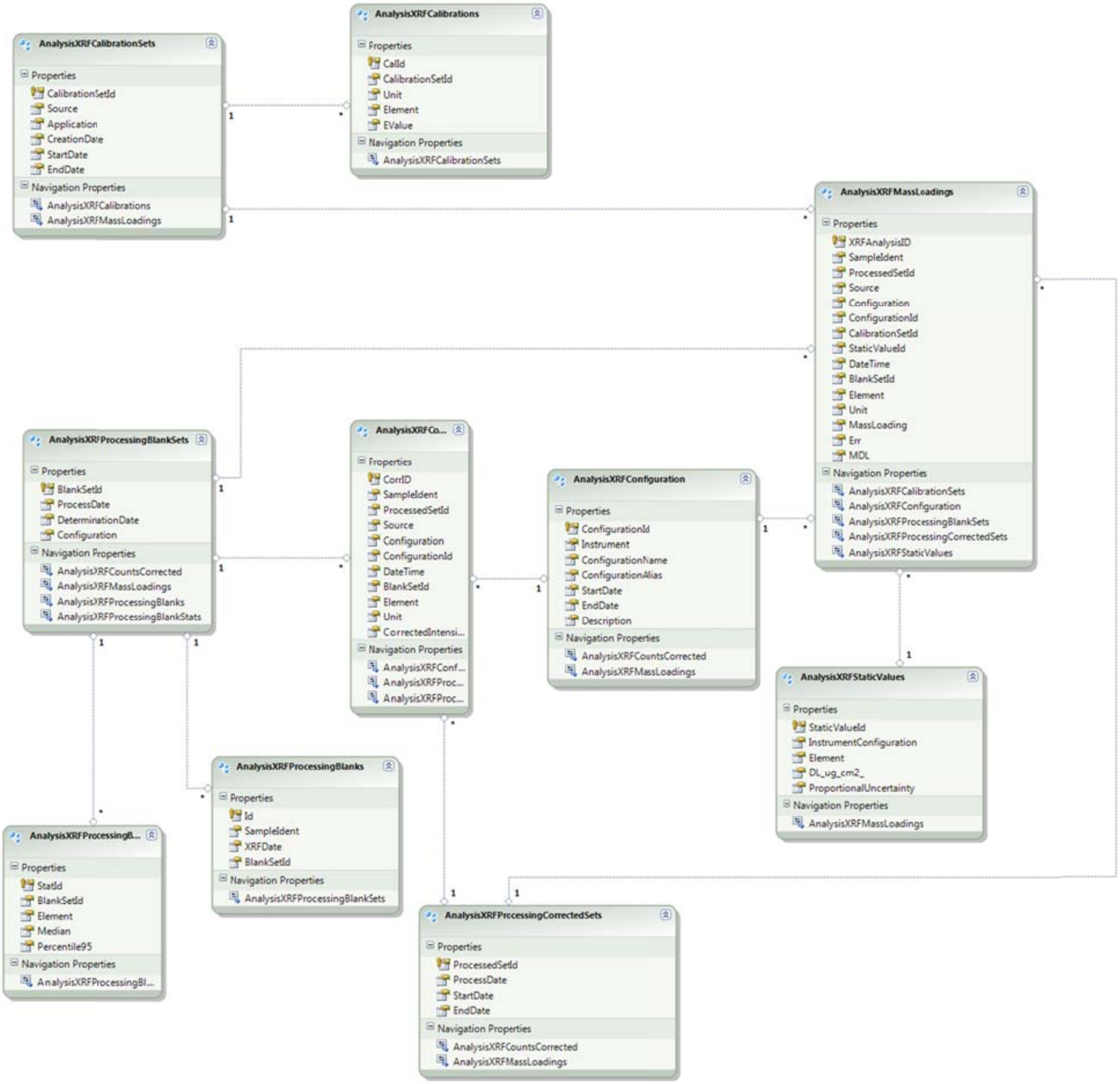
0.909	7/2/2012	Optimized queries (Median/95th, max/min analysis date for configuration determination). Made the calibration import SP import the calibrations correctly assigning them to sets. Even if a calibration import contains data from multiple or one machine, it will assign sets correctly.
0.914	7/3/2012	Queries further optimized using multiple joins for the configuration aliases (incomplete). Created spCalculateXRFMassLoadings as a primitive form of the mass loading conversion.
0.925	7/5/2012	Changed the statistical queries to avoid joining to views. The performance increases are very good. The sp for creating the dbf view will now incorporate the static statistical values warren calcluated. Seeding for the static statistics The dbf view sp is not complete still.
0.965	7/6/2012	Massive overhaul of query structure. Especially for the blank correction. The table join was not effective given the possibility that the same set of data could be processed again. Instead the sproc was changed to accept a configuration paramter and run per configuration as part of the cursor in the calling procedure. Added indexing and some table statistics. The processing takes 2-4 seconds now. The competing factors are table size and SQL server query optimization. DBF view proc is tentatively complete. Columns must be verified. Values must also be verified. Function is complete. At first glance of the march data it seems to be pretty close to the Panalytical corrected values.
0.980	7/12/2012	Added the mass loading conversion as a hard coded table. This has increased processing time to 10-13 seconds. Testing has thus so far confirmed correct values at all levels of processing.

Appendices

Appendix 1: Stored Procedure Process Flow Diagram.


IMPROVE
AnalysisXRFcountsMigrate
AnalysisXRFConfigurations
spCreatAnalysisFieldBlanks
AnalysisXRFProcessingBlankSets
First
For Each Element
AnalysisXRFProcessingBlanks
IMPROVE.XRF.PROCESSING
spProcessAnalysisXRFCounts
Second
spAnalysisXRFCorrection
spStatsFB25
Third
spCalculateXRFMassLoadings
AnalysisXRFProcessingCorrectedSets
AnalysisXRFProcessingBlankStats
AnalysisXRFCountsCorrected
AnalysisXRFCalibrationSets
AnalysisXRFCalibrations
AnalysisXRFMassLoadings
spXRFDBFForm
MassLoadings/ Errors/MDLs in DBF View
Stored Procedure
Database
Table
Execute Stored Procedure

Appendix 2: Table Design and Relationships.



Appendix 3: Database Technical Description.

Improve.XRFProcessing.Dev Database

CL-DEV-SQL > Improve.XRFProcessing.Dev

Project Information

Author	Leland Gee
Created	25 June 2012 11:16

Tables

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables

Name
dbo.AnalysisXRFCalibrations
dbo.AnalysisXRFCalibrationSets
dbo.AnalysisXRFConfiguration
dbo.AnalysisXRFCountsCorrected
dbo.AnalysisXRFMassLoadings
dbo.AnalysisXRFProcessingBlanks
dbo.AnalysisXRFProcessingBlankSets
dbo.AnalysisXRFProcessingBlankStats
dbo.AnalysisXRFProcessingCorrectedSets
dbo.AnalysisXRFQAModifications
dbo.AnalysisXRFStaticValues

[dbo].[AnalysisXRFCalibrations]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFCalibrations

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	CalId	bigint	8	✗	1 – 1
🔑	CalibrationSetId	bigint	8	✗	
	Unit	nchar(10)	20	✗	
	Element	nvarchar(4)	8	✗	
	EValue	float	8	✗	

Indexes

	Name	Columns	Unique
🔑	PK_CalId	CalId	✓

Foreign Keys

Name	Columns
FK_AnalysisXRFCalibrations_AnalysisXRFCalibrationSets	CalibrationSetId->[dbo].[AnalysisXRFCalibrationSets].[CalibrationSetId]

Uses

[dbo].[AnalysisXRFCalibrationSets]

dbo

[dbo].[AnalysisXRFCalibrationSets]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFCalibrationSets

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	CalibrationSetId	bigint	8	✗	1 – 1
	Source	nvarchar(255)	510	✗	
	Application	nvarchar(255)	510	✗	
	CreationDate	datetime	8	✗	
	StartDate	datetime	8	✗	
	EndDate	datetime	8	✓	

Indexes

	Name	Columns	Unique
🔑	PK_CalibrationSetId	CalibrationSetId	✓

Uses

dbo

Used By

[dbo].[AnalysisXRFCalibrations]

[dbo].[AnalysisXRFMassLoadings]

[dbo].[AnalysisXRFConfiguration]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFConfiguration

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	ConfigurationId	int	4	✘	1 – 1
	Instrument	nvarchar(100)	200	✘	
	ConfigurationName	nvarchar(100)	200	✘	
	ConfigurationAlias	nvarchar(100)	200	✘	
	StartDate	datetime	8	✘	
	EndDate	datetime	8	✓	
	Description	nvarchar(max)	max	✓	

Indexes

	Name	Columns	Unique
🔑	PK_ConfigurationId	ConfigurationId	✓

Uses

dbo

Used By

[dbo].[AnalysisXRFCountsCorrected]

[dbo].[AnalysisXRFMassLoadings]

[dbo].[spCalculateXRFMassLoadings]

[dbo].[spImportAnalysisXRFCalibration]

[dbo].[AnalysisXRFCountsCorrected]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFCountsCorrected

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	CorrID	bigint	8	✗	1 – 1
	SampleIdent	nvarchar(128)	256	✗	
🔑	ProcessedSetId	bigint	8	✗	
	Source	nvarchar(100)	200	✗	
	Configuration	nvarchar(100)	200	✗	
🔑	ConfigurationId	int	4	✗	
	DateTime	datetime	8	✗	
🔑	BlankSetId	bigint	8	✗	
	Element	nvarchar(4)	8	✗	
	Unit	nvarchar(10)	20	✗	
	CorrectedIntensity	real	4	✗	

Indexes

	Name	Columns	Unique
🔑	PK_CorrID	CorrID	✓
	_dta_index_AnalysisXRFCountsCorrected_10_85575343__K3_K4_K6_K8_2_110	SampleIdent, CorrectedIntensity, ProcessedSetId, Source, DateTime, Element	

Statistics

Name	Columns
_dta_stat_85575343_3	ProcessedSetId

Foreign Keys

Name	Columns
FK_AnalysisXRFCountsCorrected_AnalysisXRFProcessingBlankSets	BlankSetId->[dbo].[AnalysisXRFProcessingBlankSets].[BlankSetId]
FK_AnalysisXRFCountsCorrected_AnalysisXRFProcessingConfiguration	ConfigurationId->[dbo].[AnalysisXRFConfiguration].[ConfigurationId]
FK_AnalysisXRFCountsCorrected_AnalysisXRFProcessingCorrectedSets	ProcessedSetId->[dbo].[AnalysisXRFProcessingCorrectedSets].[ProcessedSetId]

Uses

[dbo].[AnalysisXRFConfiguration]

[dbo].[AnalysisXRFProcessingBlankSets]

[dbo].[AnalysisXRFProcessingCorrectedSets]

dbo

[dbo].[AnalysisXRFMassLoadings]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFMassLoadings

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	XRFAnalysisID	bigint	8	✘	1 – 1
🖧	SampleIdent	nvarchar(128)	256	✘	
🗝 🖧	ProcessedSetId	bigint	8	✘	
🖧	Source	nvarchar(100)	200	✘	
	Configuration	nvarchar(100)	200	✘	
🗝	ConfigurationId	int	4	✘	
🗝	CalibrationSetId	bigint	8	✘	
🗝	StaticValueId	int	4	✘	
🖧	DateTime	datetime	8	✘	
🗝	BlankSetId	bigint	8	✘	
🖧	Element	nvarchar(4)	8	✘	
	Unit	nvarchar(10)	20	✘	
🖧	MassLoading	real	4	✘	
	Err	real	4	✘	
	MDL	real	4	✘	

Indexes 🖧

	Name	Columns	Unique
🔑	PK_XRFAnalysisId	XRFAnalysisID	✓
	_dta_index_AnalysisXRFMassLoadings_10_85575343__K3_K4_K6_K8_2_101	SampleIdent, MassLoading, ProcessedSetId, Source, DateTime,	

		Element	

Foreign Keys

Name	Columns
FK_AnalysisXRFMassLoadings_AnalysisXRFProcessingBlankSets	BlankSetId->[dbo].[AnalysisXRFProcessingBlankSets].[BlankSetId]
FK_AnalysisXRFMassLoadings_AnalysisXRFCalibrationSets	CalibrationSetId->[dbo].[AnalysisXRFCalibrationSets].[CalibrationSetId]
FK_AnalysisXRFMassLoadings_AnalysisXRFConfiguration	ConfigurationId->[dbo].[AnalysisXRFConfiguration].[ConfigurationId]
FK_AnalysisXRFMassLoadings_AnalysisXRFProcessingCorrectedSets	ProcessedSetId->[dbo].[AnalysisXRFProcessingCorrectedSets].[ProcessedSetId]
FK_AnalysisXRFMassLoadings_AnalysisXRFStaticValues	StaticValueId->[dbo].[AnalysisXRFStaticValues].[StaticValueId]

Uses

[dbo].[AnalysisXRFCalibrationSets]

[dbo].[AnalysisXRFConfiguration]

[dbo].[AnalysisXRFProcessingBlankSets]

[dbo].[AnalysisXRFProcessingCorrectedSets]

[dbo].[AnalysisXRFStaticValues]

dbo

Used By

[dbo].[spAnalysisXRFCorrection]

[dbo].[AnalysisXRFProcessingBlanks]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFProcessingBlanks

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
	Id	bigint	8	✗	1 - 1
	SampleIdent	nvarchar(128)	256	✗	
	XRFDate	datetime	8	✗	
	BlankSetId	bigint	8	✗	

Indexes

	Name	Columns	Unique
	PK_Id	Id	✓
	_dta_index_AnalysisXRFProcessingBlanks_10_117575457__K4_K2_K3	Id, BlankSetId, SampleIdent, XRFDate	
	_dta_index_AnalysisXRFProcessingBlanks_10_117575457__K4_K2_K6	BlankSetId, SampleIdent, XRFDate	

Foreign Keys

Name	Columns
FK_AnalysisXRFProcessingBlanks_AnalysisXRFProcessingBlank-Sets	BlankSetId->[dbo].[AnalysisXRFProcessingBlankSets].[BlankSet-Id]

Uses

[dbo].[AnalysisXRFProcessingBlankSets]

dbo

Used By

[dbo].[spCalculateXRFMassLoadings]

[dbo].[spStatsFB25]

[dbo].[AnalysisXRFProcessingBlankSets]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFProcessingBlankSets

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	BlankSetId	bigint	8	✗	1 - 1
	ProcessDate	datetime	8	✗	
	DeterminationDate	datetime	8	✗	
	Configuration	nvarchar(100)	200	✗	

Indexes

	Name	Columns	Unique
🔑	PK_BlankSetId	BlankSetId	✓

Uses

dbo

Used By

[dbo].[AnalysisXRFCountsCorrected]

[dbo].[AnalysisXRFMassLoadings]

[dbo].[AnalysisXRFProcessingBlanks]

[dbo].[AnalysisXRFProcessingBlankStats]

[dbo].[spCalculateXRFMassLoadings]

[dbo].[AnalysisXRFProcessingBlankStats]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFProcessingBlankStats

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	StatId	bigint	8	✗	1 - 1
🔑	BlankSetId	bigint	8	✗	
	Element	nchar(4)	8	✗	
	Median	real	4	✗	
	Percentile95	real	4	✓	

Indexes

	Name	Columns	Unique
🔑	PK_StatId	StatId	✓

Foreign Keys

Name	Columns
FK_AnalysisXRFBlankStats_AnalysisXRFProcessingBlankSets	BlankSetId->[dbo].[AnalysisXRFProcessingBlankSets].[BlankSetId]

Uses

[dbo].[AnalysisXRFProcessingBlankSets]

dbo

Used By

[dbo].[spStatsFB25]

[dbo].[AnalysisXRFProcessingCorrectedSets]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFProcessingCorrectedSets

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	ProcessedSetId	bigint	8	✗	1 - 1
	ProcessDate	datetime	8	✗	
	StartDate	datetime	8	✗	
	EndDate	datetime	8	✗	

Indexes

	Name	Columns	Unique
🔑	PK_ProcessedSetId	ProcessedSetId	✓

Uses

dbo

Used By

[dbo].[AnalysisXRFCountsCorrected]

[dbo].[AnalysisXRFMassLoadings]

[dbo].[spImportAnalysisXRFCalibration]

[dbo].[AnalysisXRFQAModifications]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFQAModifications

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	ModificationId	bigint	8	✗	1 - 1
	SampleIdentOld	nvarchar(100)	200	✗	
	XRFDateOld	datetime	8	✗	
	SourceOld	nvarchar(100)	200	✗	
	ValidityOld	int	4	✗	
	SampleIdentNew	nvarchar(100)	200	✗	
	XRFDateNew	datetime	8	✗	
	SourceNew	nvarchar(100)	200	✗	
	ValidityNew	int	4	✗	
	ChangeDate	datetime	8	✗	
	Comment	nvarchar(4000)	8000	✓	

Indexes

	Name	Columns	Unique
🔑	PK_ModificationId	ModificationId	✓

Uses

dbo

Used By

[dbo].[spUpdateXRFDataQA]

[dbo].[AnalysisXRFStaticValues]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Tables > dbo.AnalysisXRFStaticValues

Columns

	Name	Data Type	Max Length (Bytes)	Allow Nulls	Identity
🔑	StaticValueId	int	4	✗	1 - 1
	InstrumentConfiguration	nvarchar(255)	510	✗	
	Element	nvarchar(255)	510	✗	
	DL(ug/cm2)	float	8	✗	
	ProportionalUncertainty	float	8	✗	

Indexes

	Name	Columns	Unique
🔑	PK_ValueId	StaticValueId	✓

Uses

dbo

Used By

[dbo].[AnalysisXRFMassLoadings]

Stored Procedures

CL-DEV-SQL > Improve.XRFProcessing.Dev > Stored Procedures

Name
dbo.spAnalysisXRFCorrection
dbo.spCalculateXRFMassLoadings
dbo.spCreateAnalysisFieldBlanks
dbo.spImportAnalysisXRFCalibration
dbo.spProcessAnalysisXRFCounts
dbo.spStatsFB25
dbo.spUpdateXRFDataQA
dbo.spXRFDBFForm

[dbo].[spAnalysisXRFCorrection]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Stored Procedures > dbo.spAnalysisXRFCorrection

Parameters

Name	**Data Type**	**Max Length (Bytes)**
@startdate	datetime	8
@enddate	datetime	8
@configuration	nvarchar(100)	200

Uses

[dbo].[AnalysisXRFMassLoadings]

dbo

Used By

[dbo].[spImportAnalysisXRFCalibration]

[dbo].[spCalculateXRFMassLoadings]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Stored Procedures > dbo.spCalculateXRFMassLoadings

Properties

Property	Value
ANSI Nulls On	✓
Quoted Identifier On	✓

Parameters

Name	Data Type	Max Length (Bytes)
@ProcessedSetId	bigint	8

Uses

[dbo].[AnalysisXRFConfiguration]

[dbo].[AnalysisXRFProcessingBlanks]

[dbo].[AnalysisXRFProcessingBlankSets]

[dbo].[spStatsFB25]

dbo

[Improve].[dbo].[AnalysisXRFCountsMigrate]

Used By

[dbo].[spImportAnalysisXRFCalibration]

[dbo].[spCreateAnalysisFieldBlanks]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Stored Procedures > dbo.spCreateAnalysisFieldBlanks

Parameters

Name	**Data Type**	**Max Length (Bytes)**
@startdate	datetime	8
@enddate	datetime	8
@Configuration	nvarchar(100)	200
@NumberOfFieldBlanks	int	4

Uses

dbo

Used By

[dbo].[spImportAnalysisXRFCalibration]

[dbo].[spImportAnalysisXRFCalibration]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Stored Procedures > dbo.spImportAnalysisXRFCalibration

Parameters

Name	**Data Type**	**Max Length (Bytes)**
@SourceTable	varchar(100)	100
@EffectiveStart	varchar(10)	10

Uses

[dbo].[AnalysisXRFConfiguration]

[dbo].[AnalysisXRFProcessingCorrectedSets]

[dbo].[spAnalysisXRFCorrection]

[dbo].[spCalculateXRFMassLoadings]

[dbo].[spCreateAnalysisFieldBlanks]

dbo

[Improve].[dbo].[AnalysisXRFCountsMigrate]

[dbo].[spProcessAnalysisXRFCounts]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Stored Procedures > dbo.spProcessAnalysisXRFCounts

Parameters

Name	Data Type	Max Length (Bytes)
@StartDate	datetime	8
@EndDate	datetime	8
@NumberOfFieldBlanks	int	4

Uses

Dbo

[dbo].[spStatsFB25]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Stored Procedures > dbo.spStatsFB25

Parameters

Name	Data Type	Max Length (Bytes)
@Element	nvarchar(4)	8
@BlankSetId	bigint	8

Uses

[dbo].[AnalysisXRFProcessingBlanks]

[dbo].[AnalysisXRFProcessingBlankStats]

dbo

[Improve].[dbo].[AnalysisXRFCountsMigrate]

Used By

[dbo].[spCalculateXRFMassLoadings]

[dbo].[spUpdateXRFDataQA]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Stored Procedures > dbo.spUpdateXRFDataQA

Uses

[dbo].[AnalysisXRFQAModifications]

dbo

[Improve].[dbo].[AnalysisXRFCountsMigrate]

[dbo].[spXRFDBFForm]

CL-DEV-SQL > Improve.XRFProcessing.Dev > Stored Procedures > dbo.spXRFDBFForm

Properties

Property	**Value**
ANSI Nulls On	✓
Quoted Identifier On	✓

Parameters

Name	Data Type	Max Length (Bytes)
@ProcessedSetId	bigint	8

Uses

Dbo

Appendix 4: Source Code.

Note: Readability is decreased in .doc format. For better readability see the solution code itself in visual studio.

CREATE PROCEDURE [dbo].[spProcessAnalysisXRFCounts]

```
-- =============================================
-- Author: Leland Gee (LBGEE@ucdavis.edu)
-- Create date: 7/12/2012
-- Description: Begins the Processing of XRF Data.
-- =============================================
        @StartDate datetime,
        @EndDate datetime,
        @NumberOfFieldBlanks integer
AS
set nocount on
declare
--
@configuration nvarchar(100),
@processedsetId bigint,
@today datetime = getdate()
begin
BEGIN TRAN T1
-- =============================================
-- Section:     Generate the Correction Set
-- Description: Inserts the SP parameters
--      into AnalysisXRFProcessingCorrectedSets for historical purposes
--      and binding the corrected values for this run of the SP into a single set
-- =============================================

insert into AnalysisXRFProcessingCorrectedSets(ProcessDate,StartDate,EndDate) values
(@today,@startdate,@enddate)

-- =============================================
-- Section:     Configuration Cursor
-- Description: The cursor is used to find all of
--      the distinct active configurations that were occuring
--      during the sampling dates specified in the parameters
--      and is also used to loop through other SPs.
-- =============================================
declare configuration_cursor CURSOR for
select distinct(f.ConfigurationAlias)
from improve.dbo.AnalysisXRFCountsMigrate c join dbo.AnalysisXRFConfiguration f
on c.[Source] = f.[Instrument] and c.[DateTime] between f.StartDate and isnull(f.EndDate,@today)
where c.Validity = 1  and   LEN(c.SampleIdent) = 15
and RIGHT(c.SampleIdent,2) in ('NM','QD','FB')
and Cast(SUBSTRING(c.[SampleIdent],10,2)+ CHAR(47)+
                                 SUBSTRING(c.[SampleIdent],12,2)+ CHAR(47)+
                                 SUBSTRING(c.[SampleIdent],6,4)as DateTime)
 between @startdate and @enddate

open configuration_cursor
-- =============================================
-- Section:     Cursor Loop
-- Description: The Cursor is opened and each distinct
--      configuration is processed through other SPs to generate the fieldblanks/statistics then
correction.
-- =============================================
Fetch Next from configuration_cursor
into @configuration
while @@FETCH_STATUS = 0
Begin
```

```
-- =============================================
-- Section:      Loop Member - Choosing FieldBlanks
-- Description: Create Analysis Field Blank will
--      generate the 25 fieldblank and statistics necessary for Blank Subtraction.
-- =============================================
        exec spCreateAnalysisFieldBlanks @StartDate, @EndDate, @configuration,@NumberOfFieldBlanks
-- =============================================
-- Section:      Loop Member - Correction
-- Description: Performs actual blank correction for the set of data.
--      Using the statistics generated in the previous section.
-- =============================================
        exec spAnalysisXRFCorrection @StartDate, @EndDate, @configuration
        Fetch Next from configuration_cursor into @configuration
End
Close configuration_cursor
DEALLOCATE configuration_cursor
--Duplicity of data requested.
-- =============================================
-- Section:      Calculate Mass Loadings
-- Description: This is an intentional duplicity of the counts data as mass loadings.
--      In the future if everything goes as planned we should not have to store actual counts
--      values that were generated, but merely the parameters/statistics that were part of their
generation.
-- =============================================
select @processedSetId = ident_Current ('AnalysisXRFProcessingCorrectedSets')
exec spCalculateXRFMassLoadings @processedSetId
if @@ERROR <>0
        begin
        Rollback TRAN T1
        End
Else
        begin
        Commit TRAN T1
        end

end
```

CREATE PROCEDURE [dbo].[spCreateAnalysisFieldBlanks]

```
-- =============================================
-- Author: Leland Gee (LBGEE@ucdavis.edu)
-- Create date: 7/12/2012
-- Description: Finds the field blanks to use for processing. Creates Statistics.
-- =============================================
(@startdate datetime,
@enddate datetime,@Configuration NVARCHAR(100), @NumberOfFieldBlanks int)
as
begin
declare
@BlankSetId bigint,
@DetDate datetime,
@today datetime =getdate()

-- =============================================
-- Section: Determination Date
-- Description: Find the date that determines which field blanks to use.
--      In this case that date will be the latest analysis date of
--      the datespan of sampling dates specified in the parameters.
-- =============================================
select  @DetDate = MAX(t.[DateTime])
                                                 FROM improve.dbo.AnalysisXRFCountsMigrate t join
AnalysisXRFConfiguration y on t.[Source] =y.Instrument and t.[DateTime] between y.StartDate and
ISNULL(y.EndDate,@today)
                                                 where Validity=1 and LEN(t.SampleIdent) = 15
                                                         and RIGHT(t.SampleIdent,2)in ('FB','NM','QD')
                                                         and Cast(SUBSTRING(t.[SampleIdent],10,2)+
CHAR(47)+
                                                                 SUBSTRING(t.[SampleIdent],12,2)+
CHAR(47)+
                                                                 SUBSTRING(t.[SampleIdent],6,4)as
DateTime) <= @enddate
                                                                         and y.ConfigurationAlias =
@Configuration
-- =============================================
-- Section: Create Blank Set
-- Description: This section generates the blank set
--      which includes the SP run date, determination date,
--      and XRF Machine Configuration
-- =============================================
Insert into AnalysisXRFProcessingBlankSets (ProcessDate, DeterminationDate, Configuration)
                                                                         values  (getdate(),@DetDate,
@Configuration )

-- =============================================
-- Aside: @BlankSetId is set to whatever the identity column in AnalysisXRFProcessingBlankSets
--      was incremented to on the insert in Section: Create Blank Set. This will allow the next insertion
to associate the blanks correctly with their set.
--      This is a safety to match the fieldblank to their set
--      and circumvent issues involved with MAX(identKey). More reliability and faster.
-- =============================================
SET @BlankSetId = IDENT_CURRENT('AnalysisXRFProcessingBlankSets')
  IF @NumberOfFieldBlanks = 25
  Begin
-- =============================================
-- Section: Choose Blanks
-- Description: This section selects the 25 field blanks
--      that will be the members of the set.  It selects 25 field
--      blanks that were analyzed from the determination date backwards.
--      If it cannot fill 25, it will add going from the determination date
--      forward until 25 field blanks are found.
-- =============================================
        Insert into AnalysisXRFProcessingBlanks (SampleIdent,XRFDate,BlankSetId)
```

```
Select  top 25 SampleIdent,[DateTime]as XRFDate,@BlankSetId as BlankSetId
                FROM
                (select * from (
                        select top 25 n.SampleIdent, n.[DateTime]
                                FROM
                                improve.dbo.AnalysisXRFCountsMigrate n
                                        join AnalysisXRFConfiguration z
                                        on n.Source=z.Instrument and n.[DateTime] between z.StartDate and
isnull(z.EndDate,@today)
                                                        where Validity=1 and n.[DateTime] <= @DetDate and
                                                        z.ConfigurationAlias= @Configuration and
RIGHT(n.SampleIdent,2)='FB'and LEN(sampleident) =15 group by n.SampleIdent, n.[DateTime] order by DateTime
desc)a
                        union all
                        select * from (select top 25 n.SampleIdent, n.[DateTime]
                                FROM
                                improve.dbo.AnalysisXRFCountsMigrate n
                                        join AnalysisXRFConfiguration z
                                        on n.Source=z.Instrument and n.[DateTime] between z.StartDate and
isnull(z.EndDate,@today)
                                                where Validity=1 and n.[DateTime] > @DetDate and
                                                z.ConfigurationAlias= @Configuration and
RIGHT(n.SampleIdent,2)='FB' and LEN(sampleident) =15 group by n.SampleIdent, n.[DateTime] order by
DateTime asc)b)c
-- =============================================
-- Section: Generate Field Blank Statistics
-- Description: This section generates the median and
--      95th percentile for each element of the 24 we currently use.
--      This has not been hardcoded into one stored procedure to allow expansion
--      for more elements if necessary. The SPs take the @BlankSetId and generate the Median/95th
--      using the fieldblanks associated with the set.
-- =============================================

  exec spStatsFB25 'Na', @BlankSetId
  exec spStatsFB25 'Mg', @BlankSetId
  exec spStatsFB25 'Al', @BlankSetId
  exec spStatsFB25 'Si', @BlankSetId
  exec spStatsFB25 'P', @BlankSetId
  exec spStatsFB25 'S', @BlankSetId
  exec spStatsFB25 'Cl', @BlankSetId
  exec spStatsFB25 'K', @BlankSetId

  exec spStatsFB25 'Ca', @BlankSetId
  exec spStatsFB25 'Ti', @BlankSetId
  exec spStatsFB25 'V', @BlankSetId
  exec spStatsFB25 'Cr', @BlankSetId
  exec spStatsFB25 'Mn', @BlankSetId
  exec spStatsFB25 'Fe', @BlankSetId
  exec spStatsFB25 'Ni', @BlankSetId
  exec spStatsFB25 'Cu', @BlankSetId

  exec spStatsFB25 'Zn', @BlankSetId
  exec spStatsFB25 N'As', @BlankSetId
  exec spStatsFB25 'Se', @BlankSetId
  exec spStatsFB25 'Br', @BlankSetId
  exec spStatsFB25 'Rb', @BlankSetId
  exec spStatsFB25 'Sr', @BlankSetId
  exec spStatsFB25 'Zr', @BlankSetId
  exec spStatsFB25 'Pb', @BlankSetId

  END

End
go
```

CREATE PROCEDURE [dbo].[spStatsFB25]

```
-- =============================================
-- Author: Leland Gee (LBGEE@ucdavis.edu)
-- Create date: 7/12/2012
-- Description: Generates the Median and 95th Percentile for 25
--       Field blanks that are associated with a blanksetId
-- =============================================
(@Element nvarchar(4),
@BlankSetId bigint)

as
begin
-- =============================================
-- Section: Generate FieldBlank Statistics
-- Description: This section inserts the statistics
--       for a given Field Blank Set and a given Element as
--       defined by the parameters. It does this by ordering
--       the values for the given element from least to greatest
--       and selecting the 13th (median) and 24th(95th)
-- =============================================
Insert into AnalysisXRFProcessingBlankStats (BlankSetId, Element, Median, Percentile95)
Select @BlankSetId as BlankSetId, @Element as Element,   Median, Percentile95
from
        (select Median as Median, blanksetId
        from
                (select ROW_NUMBER() over (order by v.[RawIntensity] asc) R,BlankSetId , v.RawIntensity as
Median
                from
                        improve.dbo.AnalysisXRFCountsMigrate v
                                join dbo.AnalysisXRfProcessingBlanks c
                                on v.sampleident = c.sampleident and v.[DateTime] = c.XRFDate
                where v.Validity=1 and c.BlankSetId = @BlankSetId and v.element= @Element   )t where R =
13)p

 join
        (select Percentile95,blanksetid
        from
                (select ROW_NUMBER() over (order by v.[RawIntensity] asc) R,BlankSetId, v.RawIntensity as
Percentile95
                from
                        improve.dbo.AnalysisXRFCountsMigrate v
                                join dbo.AnalysisXRfProcessingBlanks c
                                on v.sampleident = c.sampleident and v.[DateTime] = c.XRFDate
                where v.Validity=1 and   c.BlankSetId = @BlankSetId  and v.element = @Element)i
where R = 24)y
on p.BlankSetId=y.BlankSetId

End
GO
```

CREATE PROCEDURE [dbo].[spAnalysisXRFCorrection]

```
-- ============================================
-- Author: Leland Gee (LBGEE@ucdavis.edu)
-- Create date: 7/12/2012
-- Description: Corrects the XRF values using the
--      previously generated statistics.
-- ============================================
(@startdate datetime,
@enddate datetime,
@configuration nvarchar(100))
as
begin
declare @AnalysisXRFCorrectionSet as bigint,
@today as datetime = getdate(),
@AnalysisBlankSet as bigint
-- ============================================
-- Section: Set Identity Columns
-- Description: The Currently incremented value of the blankset
--      and corrected set is assigned to their respective
--      variables so they can be associated with the corrected values.
-- ============================================
select @AnalysisBlankSet  = IDENT_CURRENT('AnalysisXRFProcessingBlankSets')
select @AnalysisXRFCorrectionSet = IDENT_Current('AnalysisXRFProcessingCorrectedSets')


-- ============================================
-- Section: Blank Correction
-- Description: Performs the configuration specific blank
--      correction by applying the statistic previously
--      generated.
-- ============================================
Insert into AnalysisXRFCountsCorrected
(SampleIdent,ProcessedSetId,[Source],[Configuration],[ConfigurationId],[DateTime],BlankSetId,Element,Unit,
CorrectedIntensity)
select  c.SampleIdent, @AnalysisXRFCorrectionSet as ProcessedSetId, c.[Source],
                        x.ConfigurationAlias as [Configuration], x.ConfigurationId,
                        c.[DateTime],
                        @AnalysisBlankSet as BlankSetId,
                        c.Element, c.Unit,
                        (c.RawIntensity - u.Median) as CorrIntensity
        from
                improve.dbo.AnalysisXRFCountsMigrate c
                        join AnalysisXRFConfiguration x
                        on c.[DateTime] between x.StartDate and isnull(x.EndDate,@today) and c.[Source] =
x.Instrument
                        join AnalysisXRFProcessingBlankStats u
                        on u.BlankSetId = @analysisblankset and c.Element = u.Element
        where c.Validity=1 and x.ConfigurationAlias =@configuration and c.Element
        in ('Na','Mg','Al','Si','P','S','Cl','K','Ca','Ti','V','Cr','Mn','Fe','Ni','Cu','Zn'
      ,'As','Se','Br','Rb','Sr','Zr','Pb')
                and   LEN(c.SampleIdent) = 15
                and RIGHT(c.SampleIdent,2) in ('NM','QD')
                and Cast(SUBSTRING(c.[SampleIdent],10,2)+ CHAR(47)+
                                SUBSTRING(c.[SampleIdent],12,2)+ CHAR(47)+
                                SUBSTRING(c.[SampleIdent],6,4)as DateTime)
                        between @startdate and @enddate
END

GO
```

CREATE PROCEDURE **[dbo].[spCalculateXRFMassLoadings]**

```
-- =============================================
-- Author: Leland Gee (LBGEE@ucdavis.edu)
-- Create date: 7/12/2012
-- Description: Converts the corrected count values into
--      their mass loading values by using the calibrations
--      from each machine.
-- =============================================
        @ProcessedSetId bigint
AS
declare @today as datetime
set @today = GETDATE()

-- =============================================
-- Section: Insert Corrected Mass Loadings
-- Description: This section takes the corrected counts.
--      applies the calibration factor, and inserts them into
--      AnalysisXRFMassLoadings. It also calculates the uncertainties and inserts the MDLs
-- =============================================

insert into AnalysisXRFMassLoadings (Sampleident, ProcessedSetId, Source, Configuration, CalibrationSetId,
[DateTime],
BlanksetId, Element, Unit, MassLoading, Err, MDL)

        SELECT c.SampleIdent, @ProcessedSetId as ProcessedSetId,
c.Source,c.Configuration,q.CalibrationSetId,c.[DateTime],
                c.BlankSetId,c.Element ,'ng/cm2' as Unit,
                (c.CorrectedIntensity *p.EValue*1000) as MassLoading,
                        SQRT(square(0.608*y.[DL(ug/cm2)]*1000)+square(y.ProportionalUncertainty*(case
when c.CorrectedIntensity< 0 then 0 else c.CorrectedIntensity end)*1000*p.EValue)) as 'err',
                                y.[DL(ug/cm2)]*1000 as 'mdl'
        from AnalysisXRFCountsCorrected c
                join AnalysisXRFCalibrationSets q
                        on c.Source = q.Source and c.[DateTime] between q.StartDate and
isnull(q.EndDate,@today)
                join AnalysisXRFCalibrations p
                        on p.CalibrationSetId = q.CalibrationSetId and c.Element = p.Element
                join AnalysisXRFConfiguration t
                        on c.Source = t.Instrument and c.[DateTime] between t.StartDate and
ISNULL(t.EndDate,@today)
                join AnalysisXRFStaticValues y
                        on t.ConfigurationAlias = y.InstrumentConfiguration and c.Element = y.Element
        where c.ProcessedSetId = @ProcessedSetId
```

```
CREATE PROCEDURE [dbo].[spXRFDBFForm]
        @ProcessedSetId bigint
AS
declare @today as datetime
set @today = GETDATE()
select [Site], Samdat,
 0000 Strtim,
 'NM' as Pesstat,
 CHAR(32)as Pixstat,
 [StatusCode] as Xrmstat,
 [StatusCode] as Xrcstat,
 0.00 H,
 0.00 H_err,
 0.00 H_mdl,
 S,
 S_err,
 S_mdl,
 Cl,
 Cl_err,
 Cl_mdl,
 K,
 K_err,
 K_mdl,
 Ca,
 Ca_err,
 Ca_mdl,
 Char(32) Ba,
 Char(32) Ba_err,
 Char(32) Ba_mdl,
 Ti,
 Ti_err,
 Ti_mdl,
 V,
 V_err,
 V_mdl,
 Cr,
 Cr_err,
 Cr_mdl,
 Mn,
 Mn_err,
 Mn_mdl,
 Fe,
 Fe_err,
 Fe_mdl,
 Char(32) Co,
 Char(32) Co_err,
 Char(32) Co_mdl,
 Ni,
 Ni_err,
 Ni_mdl,
 Cu,
 Cu_err,
 Cu_mdl,
 Zn,
 Zn_err,
 Zn_mdl,
 Char(32) Ga,
 Char(32) Ga_err,
 Char(32) Ga_mdl,
 Char(32) Au,
 Char(32) Au_err,
 Char(32) Au_mdl,
 Char(32) Hg,
 Char(32) Hg_err,
 Char(32) Hg_mdl,
 [As],
 As_err,
 As_mdl,
 Pb,
 Pb_err,
 Pb_mdl,
 Se,
 Se_err,
 Se_mdl,
 Br,
 Br_err,
 Br_mdl,
 Rb,
 Rb_err,
 Rb_mdl,
 Sr,
 Sr_err,
 Sr_mdl,
 Char(32) Y,
 Char(32) Y_err,
 Char(32) Y_mdl,
 Zr,
 Zr_err,
 Zr_mdl,
 Char(32) Cd,
 Char(32) Cd_err,
 Char(32) Cd_mdl,
 Char(32) Ag,
 Char(32) Ag_err,
 Char(32) Ag_mdl,
 na Yna,
 na_err Yna_err,
 na_mdl Yna_mdl,
 mg Ymg,
 mg_err Ymg_err,
 mg_mdl Ymg_mdl,
 al Yal,
 al_err Yal_err,
 al_mdl Yal_mdl,
 si Ysi,
 si_err Ysi_err,
 si_mdl Ysi_mdl,
 p Yp,
 p_err Yp_err,
 p_mdl Yp_mdl,
 s Ys,
 s_err Ys_err,
 s_mdl Ys_mdl,
 cl Ycl,
 cl_err Ycl_err,
 cl_mdl Ycl_mdl,
 k Yk,
 k_err Yk_err,
 k_mdl Yk_mdl,
 ca Yca,
 ca_err Yca_err,
 ca_mdl Yca_mdl,
 Char(32) Yba,
 Char(32) Yba_err,
 Char(32) Yba_mdl,
 ti Yti,
 ti_err Yti_err,
 ti_mdl Yti_mdl,
v Yv,
v_err Yv_err,
v_mdl Yv_mdl,
cr Ycr,
cr_err Ycr_error,
cr_mdl Ycr_mdl,
mn Ymn,
mn_err Ymn_err,
mn_mdl Ymn_mdl,
fe Yfe,
fe_err Yfe_err,
fe_mdl Yfe_mdl,
Char(32) Yco,
Char(32) Yco_err,
Char(32) Yco_mdl,
ni Yni,
ni_err Yni_err,
ni_mdl Yni_mdl,
0.00 Pesalt,
Char(32) Pixelt,
0.99 Xrmlt,
0.99 Xrclt,
configuration Cuxrfid



from(
select Site,StatusCode,Samdat,Unit,Configuration,max(Na) as Na,max(Na_err) as Na_err,     max(Na_mdl) as
Na_mdl,
max(Mg) as Mg,  max(Mg_err) as Mg_err,   max(Mg_mdl) as Mg_mdl,
max(Al) as Al,  max(Al_err) as Al_err,   max(Al_mdl) as Al_mdl,
max(Si) as Si,  max(Si_err) as Si_err,   max(Si_mdl) as Si_mdl,
max(P) as P,    max(P_err) as P_err,     max(P_mdl) as P_mdl,
max(S) as S,    max(S_err) as S_err,     max(S_mdl) as S_mdl,
max(Cl) as Cl,  max(Cl_err) as Cl_err,   max(Cl_mdl) as Cl_mdl,
max(K) as K,    max(K_err) as K_err,     max(K_mdl) as K_mdl,
max(Ca) as Ca,  max(Ca_err) as Ca_err,   max(Ca_mdl) as Ca_mdl,
max(Ti) as Ti,  max(Ti_err) as Ti_err,   max(Ti_mdl) as Ti_mdl,
max(V) as V,    max(V_err) as V_err,     max(V_mdl) as V_mdl,
max(Cr) as Cr,  max(Cr_err) as Cr_err,   max(Cr_mdl) as Cr_mdl,
max(Mn) as Mn,  max(Mn_err) as Mn_err,   max(Mn_mdl) as Mn_mdl,
max(Fe) as Fe,  max(Fe_err) as Fe_err,   max(Fe_mdl) as Fe_mdl,
max(Ni) as Ni,  max(Ni_err) as Ni_err,   max(Ni_mdl) as Ni_mdl,
max(Cu) as Cu,  max(Cu_err) as Cu_err,   max(Cu_mdl) as Cu_mdl,
max(Zn) as Zn,  max(Zn_err) as Zn_err,   max(Zn_mdl) as Zn_mdl,
max([As]) as [As],       max([As_err]) as [As_err],       max([As_mdl]) as [As_mdl],
max(Se) as Se,  max(Se_err) as Se_err,   max(Se_mdl) as Se_mdl,
max(Br) as Br,  max(Br_err) as Br_err,   max(Br_mdl) as Br_mdl,
max(Rb) as Rb,  max(Rb_err) as Rb_err,   max(Rb_mdl) as Rb_mdl,
max(Sr) as Sr,  max(Sr_err) as Sr_err,   max(Sr_mdl) as Sr_mdl,
max(Zr) as Zr,  max(Zr_err) as Zr_err,   max(Zr_mdl) as Zr_mdl,
max(Pb) as Pb,  max(Pb_err) as Pb_err,   max(Pb_mdl) as Pb_mdl
from

        (SELECT LEFT(c.[SampleIdent],5) AS 'Site',
                         RIGHT(c.[SampleIdent],2) AS 'StatusCode',
                                 Cast(SUBSTRING(c.[SampleIdent],10,2)+ CHAR(47)+
                                 SUBSTRING(c.[SampleIdent],12,2)+ CHAR(47)+
                                 SUBSTRING(c.[SampleIdent],6,4)as DateTime) AS 'Samdat',  c.Unit,
c.element,
         c.MassLoading,
 c.Err,
        c.Element+'_err' as Element_err,
        c.Element+'_mdl' as Element_mdl,
         mdl, c.Configuration from AnalysisXRFMassLoadings c

        where c.ProcessedSetId = @ProcessedSetId) as query
        pivot (max(MassLoading)
        for Element in (Na,Mg,Al,Si,P,
        S,Cl,K,Ca,Ti,V,Cr,Mn,Fe,Ni,Cu,Zn,
        [As],Se,Br,Rb,Sr,Zr,Pb)) as pivot1

        pivot (max(err)
        for Element_err in (Na_err,     Mg_err, Al_err, Si_err, P_err,
        S_err,  Cl_err, K_err,  Ca_err, Ti_err, V_err,  Cr_err, Mn_err,
        Fe_err, Ni_err, Cu_err, Zn_err,
        [As_err],Se_err,Br_err,  Rb_err, Sr_err, Zr_err, Pb_err
)) as pivot2

        pivot (max(mdl)
        for Element_mdl in (Na_mdl,     Mg_mdl, Al_mdl, Si_mdl, P_mdl,
        S_mdl,  Cl_mdl, K_mdl,  Ca_mdl, Ti_mdl, V_mdl,  Cr_mdl,
        Mn_mdl, Fe_mdl, Ni_mdl, Cu_mdl, Zn_mdl,
        [As_mdl],Se_mdl,Br_mdl,  Rb_mdl, Sr_mdl, Zr_mdl, Pb_mdl)) pivot3 group by
Site,StatusCode,Samdat,Unit,Configuration)outside
```

TI 301E: QA/QC of XRF Analysis

Table of Contents

1. PURPOSE AND APPLICABILITY

The subject of this standard operating procedure (SOP) is the quality assurance/control (QA/QC) steps applied in the elemental mass loadings measurements of $PM_{2.5}$ loaded filters collected in IMPROVE sites using EDXRF systems, namely Panalytical Epsilon5. The scope is to ensure good laboratory practice of measurements of elements on $PM_{2.5}$ loaded filters including calibration, verification of calibration, regular quality control checks of calibration/EDXRF systems and air quality in the laboratory for three Epsilon 5 EDXRF spectrometers (E5s).

2. EQUIPMENT AND SUPPLIES

Micromatter thin film standards
NIST SRM 2783
AWIM standards
Teflon Filters (Pall Inc, 3 µm pore size, 25 mm diameter)
Nuclepore Filters Provided from Micromatter inc.
Microbalances (Mettler Toledo, XP6 with 1µg readability)

3. DEFINITIONS

Lab Blanks: Teflon and Nuclepore filters placed in the S trays of each Epsilon 5 (E5) for long term monitoring. Teflon blanks are drawn from those passing acceptance tests of filter lots for routine IMPROVE-network sampling.
Field Blanks: Teflon Blanks included in some filter cartridges to monitor possible contamination due to shipping, handling, and passive exposure. Field blanks are mounted in the sampler but have no air drawn through them.
Reanalysis Samples: A fixed collection of 16 actively sampled IMPROVE filters and one NIST SRM 2783 sample that are reanalyzed monthly to monitor the stability and consistency of the three E5 instrument systems.
Reference Values: All the values of 16 Reanalysis Samples obtained just after the calibration in Jan2013.
Z-score: The ratio of absolute difference between each result from monthly reanalysis and reference value to accompanying uncertainty. Z-score should remain <1.
Raw Intensity: The intensity (counts per second/mA, cps/mA) generated by the E5's software without any blank subtraction.
Corrected Intensity: The intensity (cps/mA) generated by the E5's software with assigned blank subtraction.
Mass Loading: The areal density (mass/cm^2) of an element on a sample filter or standard.
Calibration Factor: The instrumental sensitivity for an element ([cps/mA] / [µg/cm^2]) determined from the linear regression between reference mass loadings and instrumental corrected intensities.
Relative Expanded Uncertainty (Urel): The ratio of uncertainty estimated by the summation of contributions of each factor effective on the measurement to the result of measurement (%). Urel is estimated by the summation of contribution from the lack of fit of the linear regression between reference mass loadings and instrumental corrected intensities, repeatability and uncertainty of calibration standards.

Bias: The ratio of difference between measured and assigned (reference) value to assigned value (%).

Acceptance Limit for Teflon filters: The mean+3 SD (standards deviation) of net intensities of Teflon filters analyzed during the filter acceptance test

4. PROCEDURE

The operations included in this SOP are illustrated in the following flowchart:

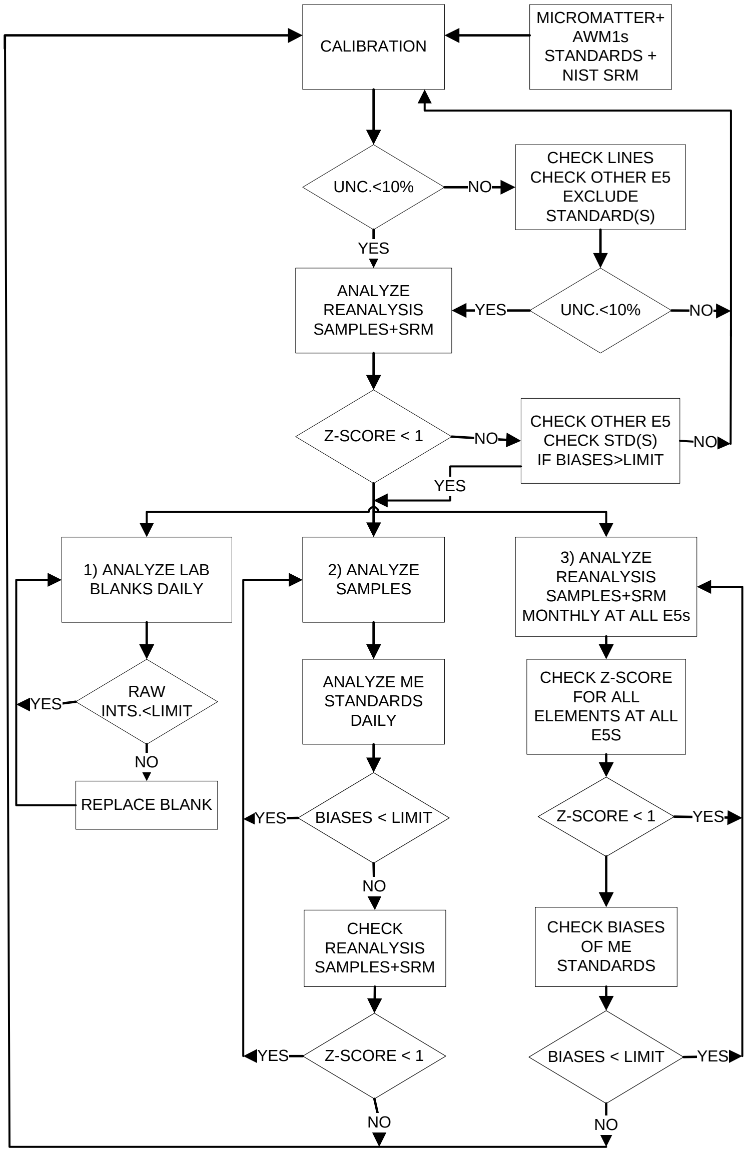

CALIBRATION
MICROMATTER+ AWM1s STANDARDS + NIST SRM
UNC.<10%
NO
CHECK LINES CHECK OTHER E5 EXCLUDE STANDARD(S)
YES
ANALYZE REANALYSIS SAMPLES+SRM
YES
UNC.<10%
NO
Z-SCORE < 1
NO
CHECK OTHER E5 CHECK STD(S) IF BIASES>LIMIT
NO
YES
1) ANALYZE LAB BLANKS DAILY
2) ANALYZE SAMPLES
3) ANALYZE REANALYSIS SAMPLES+SRM MONTHLY AT ALL E5s
RAW INTS.<LIMIT
YES
NO
REPLACE BLANK
ANALYZE ME STANDARDS DAILY
BIASES < LIMIT
YES
NO
CHECK REANALYSIS SAMPLES+SRM
Z-SCORE < 1
YES
NO
CHECK Z-SCORE FOR ALL ELEMENTS AT ALL E5S
Z-SCORE < 1
YES
CHECK BIASES OF ME STANDARDS
BIASES < LIMIT
YES
NO

Figure 1. the steps of quality assurance and quality checks in the XRF measurement

4.1 Calibration and Quality Assurance/Quality Check

1) Perform the calibrations of each E5s following instructions.

2) Estimate the relative expanded uncertainty (Urel) of each element’s calibration line. Use the designated excel sheet to calculate the uncertainty.

3) If Urel equals or is less than 10% for stoichiometric standards of IMPROVE reported elements, go to step 6.

4) If Urel for stoichiometric standards of IMPROVE reported elements is higher than 10%, check calibration lines to detect the reason of higher Urel. If any of standards deviate from the calibration line, inspect visually the corresponding standards for any defect. If defected, exclude from calibration and recalculate Urel. If recalculated Urel meets 10% criterion, go to step 6, otherwise, go to step 5.

5) Check the calibration lines of corresponding elements at other E5s. If similar deviations are observed on the other E5s, the orientation of the standard needs to be examined. If the orientation is correct, one can suspect the quality of corresponding standards and exclude them from calibration. In this case, recalculate Urel. If recalculated Urel meets 10% criterion, go to 6, otherwise, check the line again to determine deviated standards. If the problem cannot be solved with excluding standard(s), redo calibration with the current standards. If recalibration does not show changes from previous one, notify Laboratory Manager for further instructions (i.e. stop analysis, order new standards, etc.)

6) Verify the finalized calibration lines analyzing reanalysis samples (16 preselected IMPROVE samples) and NIST SRM. Check for Z-score lower than 1.

7) If Z-score lower than 1, continue analyzing S-tray containing Teflon blank, Nuclepore blank and Micromatter ME sample. Check the compliance with the acceptance limits. If everything is within the limit, start analyzing IMPROVE samples.

8) If Z-score is higher than 1, investigate the reason employing more tests and checking other E5s. If problem cannot be fixed, recalibrate the instrument.

9) If problem continues after recalibration, purchase new standards and recalibrate instruments. If recalibration does not solve the problematic one, notify Laboratory Manager for further instructions (i.e. stop analysis, etc.)

4.2 Quality Check for Routine Analysis

1) After initial checks following calibration, start analyzing IMPROVE samples, if all the initial checks are OK.

2) Every day, analyze S tray containing lab blanks and ME sample. Analyze once a week Al&Si ME standards on three E5s.

3) Analyze Reanalysis Samples and SRM monthly.

4) Every Friday, check the biases of daily/weekly analyzed ME standards. Use the designated excel file to plot the last week’s variation. If variations of elements in the MEs are within warning and acceptance limits (±3 and ±5% of assigned reference values) or are exceeded only once a week (random), continue analyzing IMPROVE samples. If the acceptance limits are exceeded at least 2 times for at least 2 elements, check for the same pattern in the Reanalysis Samples and SRM.

5) Every last Friday of the month, check the results of Reanalysis samples and SRM for being Z-score lower than 1 for each instrument versus itself and versus the mean of other 2 E5. Put

the results of each monthly analysis at the designated excel sheet. This excel sheet will show the mean z-score of each E5. Check the mean Z-score for 24 IMPROVE elements. Normally, the mean Z-score of all elements except P remain lower than 1. Furthermore, another excel sheet will calculate slope and intercept of each monthly results versus assigned reference values of each instrument and versus other 2 E5 as well as the between instrument uncertainty and uncertainty of each instrument versus it's' reference values. Normally, for elements with well higher than detection limits (i.e., As, Si, S, K, Ca, Ti, Fe and Zn), the slopes are close to 1 and relative uncertainty remains at around 10%. If checking Z-score is OK, continue analyzing IMPROVE samples. Otherwise, check monitoring ME standards (step 6).

8) If crosschecking of Reanalysis Samples/SRM and monitoring ME standards ends up with biases higher than acceptance limit, continue analyzing one more week, including analyses of Reanalysis Samples and SRM, even they are not in the routine analysis schedule. If the biases continue, recalibrate biased E5 only. Otherwise, continue analyzing IMPROVE samples following schedule.

9) The following will be in effect for samples analyzed during the period between valid and invalid checks (biased period). Notify Laboratory Manager for further instructions.

10) Every month, check the quality of delivered data checking ratio of sum of elements to mass of PM, correlated elements, ratios of crustal elements, outlier in the field blanks etc. To do that, use the designated excel workbook and follow the instructions. Notify the Laboratory Manager for any anomaly in the XRF data before delivery for final validation.