

XRF-FP CALIBRATION AND AUTO-RUN

Amptek's "XRF-FP Quick Start" guide explains how to get started and carry out simple analyses. This note provides information on some additional analysis methods and stepping through specific examples. This note describes (1) how to calibrate the XRS-FP with elemental standards and (2) how to operate in a "batch" mode. This note assumes the user is familiar with XRF analysis and with Amptek's products such as the XR100 and PX4. For further information on these products and on the details of XRSF-FP, please refer to their manuals.

Calibration with elemental standards

There are two major steps in taking the raw spectrum and obtaining the concentrations of the elements: processing and analysis. In processing, XRS-FP determines the intensities of the X-ray lines which were selected. It applies several corrections to the spectrum (escape peaks, sum peaks), removes the background, then fits the data to a sum of Gaussians at the energies of the selected elements. The output of this step is the set of intensities. In analysis, the intensities are related to the concentrations of the elements in the sample, taking into account the stopping power of the detector for each energy, absorption in the Be window and in air, absorption and enhancement in the sample. XRS-FP has a set of "fundamental parameters" which relate the intensity of the lines to the concentrations in the sample. These parameters depend strongly on the details of the geometry and material properties of the setup, the detector, etc.

In the "standardless" mode described in the Quick Start guide, XRS-FP uses simple models and the nominal geometric quantities entered by the user to estimate these parameters. Much more accurate results can be obtained if the response is measured for a particular geometry, tube spectrum, and for samples with properties similar to those in the unknown samples which are to be measured. To determine the response, the spectrum analysis routines must be calibrated using standards. This calibration of the fundamental parameters is distinct from the energy calibration which is always required.

The basic steps in elemental calibration are: (1) Measure the spectrum from a standard with known elemental concentrations. It is a good idea to measure these spectra for a longer time than will be used for data acquisition to reduce the uncertainty in the calibration parameters. (2) Process the spectrum using exactly the same steps as will be used for the material under test. (3) In the Specimen Component Table, enter the known elements and concentrations. (4) Instead of analyzing the results, select "Calibrate", "Spectrum". (5) Repeat 1-4 for however many reference samples you need. (6) Finally, and critically, get a sample containing all the elements of interest, select "Process", and then "Analyze". If the calibration runs correctly, then in the Element Table (middle of the screen) clicking the Coefficients button will show a table and the calibration constants will be nonzero.

We have found this elemental calibration procedure to be the source of much confusion, so will illustrate its use through a detailed example. In this example, the goal is to measure the composition of steel alloys. We will use a single calibration standard, a sample of stainless steel 316, to calibrate the parameters. We will then measure the composition of two NIST standard reference materials, stainless 316 and 321, and compare the results to standardless analysis.

1. Set up the system as described in the "Quick Start" guide. Make certain all the XRS-FP parameters are set correctly and perform an energy calibration.
2. In the "Setup Quant" dialog, select "Fundamental Parameters", "One standard" for calibration mode.

Note: This dialog also permits multiple standards but there are two quite different multi-standard approaches. One can use many, single element standards, in which case each element has parameters derived from a single spectrum, or one can use several multi-element standards. In the latter case least-squares fitting can be done with various models. This is available with the latest XRS-FP releases as the MLSP mode and described in the XRS-FP manual.

3. Enter the composition for the standard in the "Component Table". Also enter data into the "Thickness Table". Figure 1 shows these entries for the example. The composition values came from data supplied with the standard. The standard used was a thick, bulk sample. Ensure the Normalize option is checked, and the Total set to 100.0%.

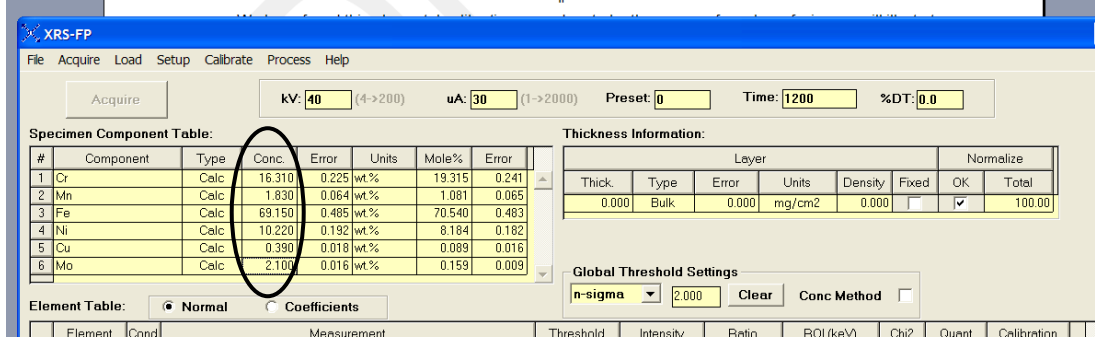


Figure 1. Screen capture showing the data entered for the standard. The concentrations, reported with the sample are entered in the elements shown in the oval.

- Place the standard in the spectrometer and take the calibration spectrum, under conditions identical to those that will be used for later routine sample analysis – except that we recommend taking calibration data for a longer time. Figure 2 shows the calibration spectrum, which was taken for 300 sec.

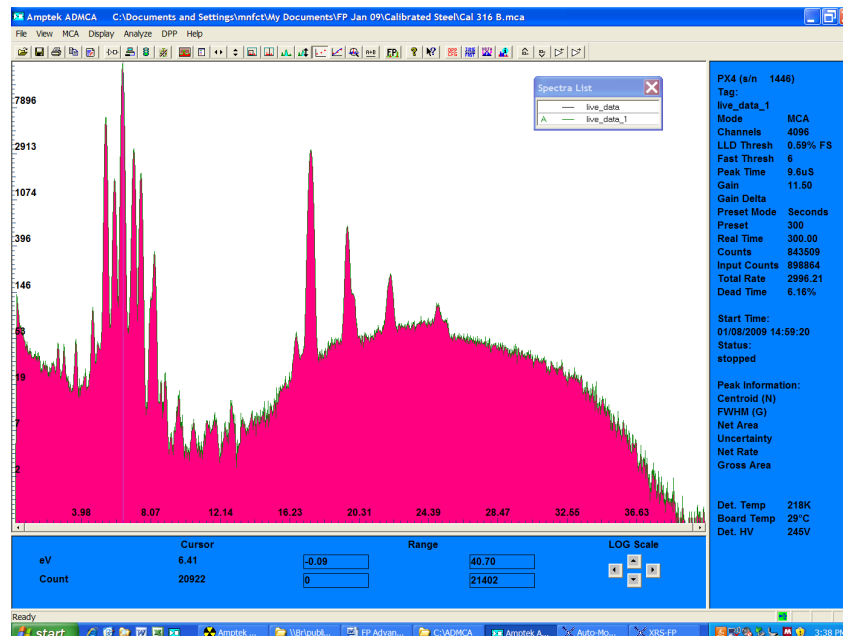


Figure 2. Calibration spectrum acquired from the SS316 standard.

- Check the calibration spectrum. Make sure that all of the expected elements are present and look for contaminants. In Figure 2, the Fe peak is largest, as expected for steel. The Cr and Ni peaks are clearly visible nearby. The Mo peaks can be seen at 17.4 and 19.6 keV. Other peaks correspond to known contaminants (e.g. Ag from a shield in the setup, Ar from air), escape peaks, sum peaks, etc. Save the calibration spectrum in ADMCA as a *.mca file and then reopen it in ADMCA.
- Load the spectrum into XRS-FP. Either step through the appropriate spectrum processing steps using the various Process commands, or use the Process Spectrum All command. The latter performs all processing steps as defined in the Condition Table. The spectrum processing should yield net intensities, for the elements defined in the Element Table.

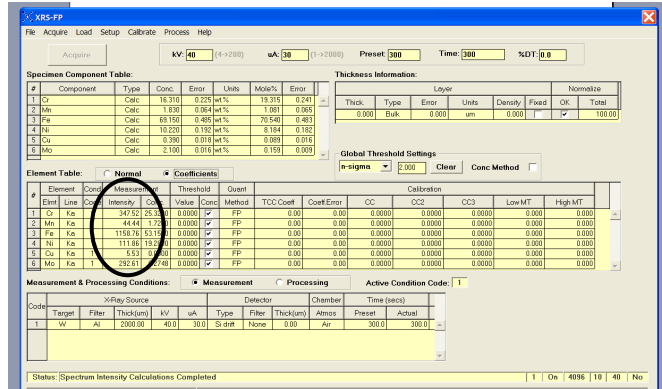
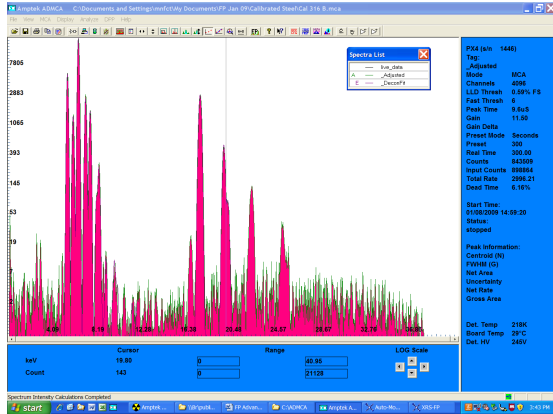
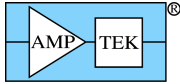
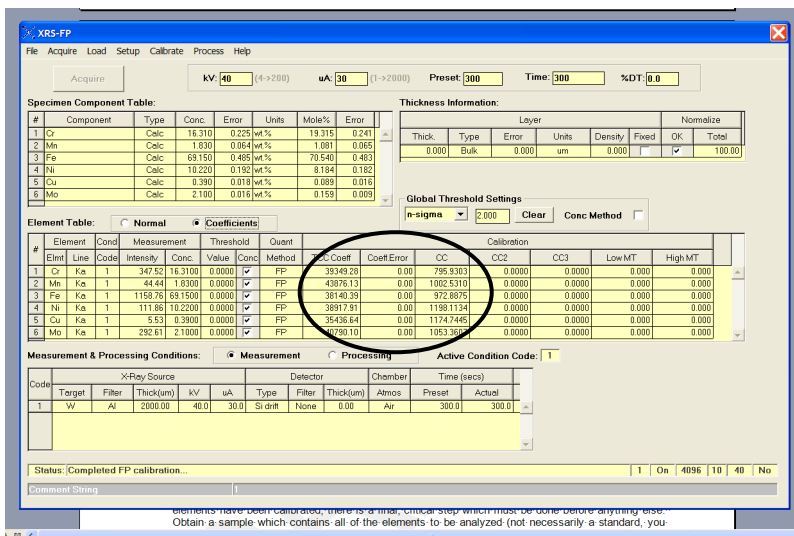


Figure 3. Processed, deconvolved spectrum from the SS316 calibration standard (left) and XRS-FP screen (right). The net intensities (in the oval) have been changed to show the result of the deconvolution. Note that all of the coefficients in the Element Table are zero.

7. Check the processed, deconvolved spectrum, as shown in Figure 3. Verify that the peaks were well fit and that there are no unexpected peaks. Select the “Calibrate FP menu item, which will then calculate the calibration coefficient(s). To verify that these have been computed, select the “coefficients” radio button beside the Element Table.

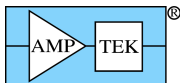


	Ref	Measured
Cr	16.31	16.44 ± 0.18
Mn	1.83	1.81 ± 0.06
Fe	69.15	68.96 ± 0.48
Ni	10.22	10.28 ± 0.19
Cu	0.39	0.42 ± 0.03
Mo	2.10	2.08 ± 0.03

Figure 4. Left: Plot showing the coefficients in the Element Table after calibration (in the ovals). Right: Table comparing the actual values in the sample used to calibrate (Ref) with the results measured from the same sample, as a check.

8. Place an “unknown” sample to be analyzed in the spectrometer. Enter the thickness data. Make sure that the Component Table has all of the elements which have been used. As a calibration check with a single standard, it is useful to start by reanalyzing the sample used for calibration. Acquire a spectrum, load it into FP, process it, and the click analyze. Compare the results with the known values, as a check.

Note: If you are calibrating using multiple single element standards, where each elements has its values derived from one sample, then repeat steps (3) through (7) for each sample. Once all the elements have been calibrated, there is a final, critical step which must be done before anything else. Obtain a sample which contains all of the elements to be analyzed (not necessarily a standard, you don't need to know its composition). Reconfigure the Component (and Element) Table to describe this sample, checking to see that the Condition Table matches the conditions used in the previous standardization steps. These tables do not need the concentrations entered in the Component and



Element Tables, but may need the thickness if it is known. Otherwise set the Thickness Type to Calculated or Bulk, as appropriate. Measure the spectrum, load it into FP, processes it, and then click “Analyze”. The first part of this operation will be to merge all the calibration coefficients from the previous calibration step(s). At the end of this process, values for concentrations will be calculated and stored in the Component and Element Tables. Also, the calibration coefficients for all the elements will now be displayed in the rightmost column of the Element Table. These are needed for future analysis.

9. Save the result as a *.TFR file. In the future, when you start XRS-FP you can load this .TFR file and you will have all of the calibration coefficients. You can save several different .TFR files, e.g. one for brass and one for steel, to run different analyses. When XRS-FP launches, it uses MASTER.TFR for default parameters and it also uses this file for the “Auto-Run” or batch processing. Therefore, save these results in MASTER.TFR if you will always be analyzing similar samples or for Auto-Run.
10. Now analyze the materials to be tested. For purposes of this example, we took ten spectra from each of the NIST SS316 and SS321 standard reference materials. These were analyzed using the calibrated parameters. We also analyzed them using “standardless” FP. Results are shown below. The column labeled “NIST Value” shows the concentration measured by NIST, with their measurement uncertainty. The “standardless” and “calibrated” columns show the results of running XRS-FP in the two modes. The “Std Dev” column shows the actual standard deviation determined from the ten measurements, while the “Uncert” column is XRS-FP’s estimate of the measurement uncertainty. The calibrated results all agree with the NIST values, to within the total uncertainty.

		NIST value	Standard less	Calibrated	Std Dev	Uncert
Steel 316	Cr	18.45 ± 0.05	19.00	18.50	0.10	0.25
	Mn	1.63 ± 0.01	1.82	1.67	0.07	0.07
	Fe	65.19 ± 0.07	64.39	65.00	0.18	0.52
	Ni	12.18 ± 0.05	12.20	12.27	0.16	0.27
	Cu	0.169 ± 0.001	0.137	0.167	0.021	0.026
	Mo	2.38 ± 0.01	2.46	2.39	0.02	0.03
Steel 321	Cr	17.4 ± 0.1	17.78	17.59	0.10	0.23
	Mn	1.80 ± 0.05	2.09	1.80	0.07	0.07
	Fe	69.31 ± 0.15	68.34	68.91	0.14	0.53
	Ni	11.2 ± 0.1	11.53	11.42	0.16	0.27
	Cu	0.121 ± 0.001	0.094	0.119	0.021	0.022
	Mo	0.165 ± 0.005	0.177	0.167	0.005	0.009

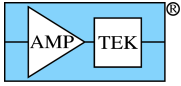
Auto-Run Analysis

The software can run in either an “Expert” mode or an “Auto-Run” mode. Auto-Run is essentially a one-button mode. Once the system is completely setup, calibrated, and ready to go, one can put in the sample, turn on the X-ray tube and click Auto-Run. The system will acquire the spectrum, save it, process it, analyze it, save the .TFR report, and then repeat as many times as specified. Expert mode is useful when the user wants to intervene during the steps: observing the spectrum, verifying the processing steps, tuning parameters, calibrating, etc.

The key to using Auto-Run is to recognize that the software will use specific files to define the hardware and software configuration. It will use PX4.CFG for the PX4’s configuration and will use MASTER.TFR for the FP processing and analysis configuration. If you change the parameters in the PX4, you must save these to PX4.CFG, otherwise Auto-Run will default to the PX4.CFG parameters. Similarly, when you change parameters in FP, you must save them to MASTER.TFR. It looks for these files in the folder containing ADMCA.EXE and XRS-FP.EXE.

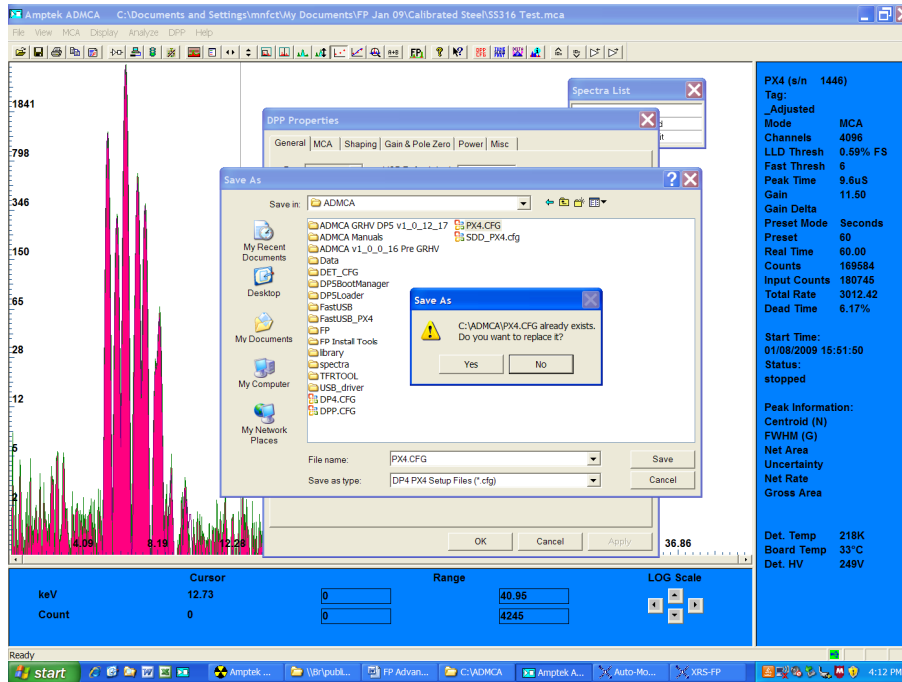
The following step-by-step procedures illustrates how to use Auto-Run. The example came from the ten measurements of the NIST SRM for stainless 316 with results shown above.

1. Open ADMCA and configure the PX4 as desired. Then save this configuration to the PX4.CFG file. To do this, click the “Acquisition Setup” toolbar button, then on the “General” tab, select “Save

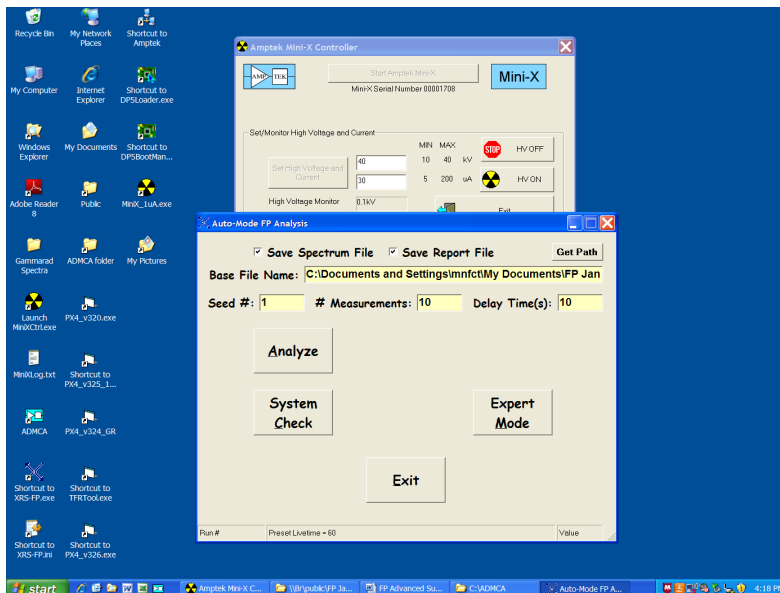


XRF-FP Advanced Suggestions

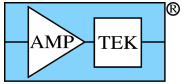
current configuration to file". For filename, select the pre-existing PX4.CFG in the same folder as ADMCA.EXE, then click "Yes" to replace. The screen shot is shown below.



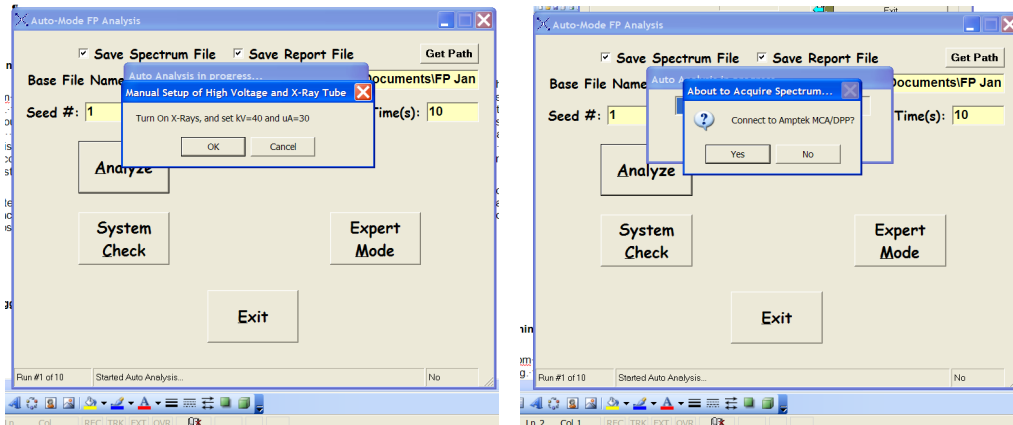
2. Open XRS-FP and set its configuration. This includes doing elemental calibration, if desired. We recommend taking a sample spectrum and running a sample analysis, as a check. Once all is set right, save this as "MASTER.TFR" in the same folder as XRS-FP.exe and click "Yes" to replace the existing file.
3. Close FP. From within ADMCA, click the FP icon. Click anywhere on the yellow screen that appears. The screen shot below shows the screen that appears next.



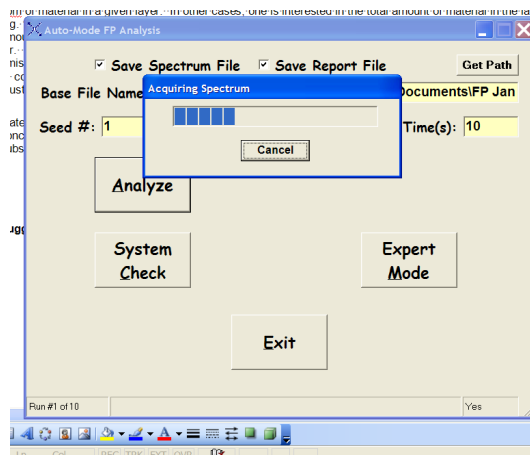
4. Use "Get path" to define the folder and the file name (the software will automatically add the measurement number, 1, 2, etc). Set the number of measurements (# Measurements) and delay between measurements. In this case, we set this to 10 measurements.



- Click "Analyze". The next screen, shown below, prompts the user to turn on the X-ray tube. When it is on, click "OK". The next screen asks to "Connect to the DPP". Click "Yes".



- The software then begins taking data. The screen below shows the system starting the first run of the ten. At the bottom, it will show which spectrum number it is on (e.g. 10 sec of 60). When the acquisition is done, the .MCA file is saved, loaded into FP, processed, analyzed, the .TFR file saved, and another acquisition is started.



- After the ten acquisitions are completed, the system pauses. You can turn off the tube, replace the sample, turn the tube back on, then click "Analyze" and it will take another ten. If the number of measurements is "one", then after each acquisition the system pauses for you to replace the sample.
- The results are written into a .CSV file. A sample is shown below. For each element, there are four columns: Intensity (in cts/sec), the uncertainty in the intensity (called Err(c/s)), the concentration, and then the uncertainty in the concentration (called Error).

XRS-FP Summary Report

Date	Time	Cr-Int(c/s)	Err(c/s)	Cr-Conc	Error	Mn-Int(c/s)	Err(c/s)	Mn-Conc	Error	Fe-Int(c/s)	Err(c/s)	Fe-Conc	Error
1/9/2009	15:37:14	376.29	5.01	17.41	0.23	44.01	1.71	1.80	0.07	1,102.50	8.57	68.90	0.54
1/9/2009	15:38:39	384.89	5.07	17.71	0.23	45.49	1.74	1.85	0.07	1,101.64	8.57	68.90	0.54
1/9/2009	15:40:03	382.68	5.05	17.56	0.23	45.28	1.74	1.84	0.07	1,108.64	8.60	69.00	0.54
1/9/2009	15:41:27	381.67	5.04	17.57	0.23	45.64	1.74	1.86	0.07	1,104.61	8.58	68.94	0.54
1/9/2009	15:42:51	380.82	5.04	17.50	0.23	43.96	1.71	1.78	0.07	1,107.81	8.59	68.81	0.53
1/9/2009	15:44:15	380.82	5.04	17.65	0.23	45.01	1.73	1.84	0.07	1,094.63	8.54	68.86	0.54
1/9/2009	15:45:39	383.09	5.05	17.67	0.23	45.09	1.73	1.84	0.07	1,100.47	8.57	68.98	0.54
1/9/2009	15:47:04	382.21	5.05	17.64	0.23	41.71	1.67	1.70	0.07	1,099.13	8.56	68.73	0.54
1/9/2009	15:48:28	382.73	5.05	17.63	0.23	40.67	1.65	1.65	0.07	1,103.67	8.58	69.00	0.54
1/9/2009	15:49:52	379.82	5.03	17.54	0.23	44.58	1.72	1.82	0.07	1,102.10	8.57	68.98	0.54