



# Analysis of ceiling tiles and raw materials for Strontium and Sulfur via handheld XRF– a case study for ASTM WK28941

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## Background – why Armstrong cares....



- Received multiple requests from certain countries to confirm that our mineral fiber ceiling products do not contain any Strontium sulfide (SrS). Third party test results were required before material could clear customs.
- Officials are concerned because at one time high levels of SrS were considered to be a potential cause of severe sulfidation corrosion associated with some Chinese-made drywall. CPSC reports point to high levels of strontium, “carbonates”, and elemental sulfur as indicators (in combination), but the sources of these are not addressed.
- Some are using handheld XRF detectors to identify Sr in drywall as a method of “screening” for Chinese drywall.
- XRF was the first method suggested by the 3<sup>rd</sup> party test lab
- Most glasses contain strontium compounds, but not as SrS, so we tested a range of finished ceilings and raw materials for Sr and S using a research-grade handheld XRF unit.

# Testing

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- Performed at the Scientific Research and Analysis Laboratory at the Winterthur Museum and Country Estate (DE).
- Handheld KeyMaster TRACer III-V XRF spectrometer
  - Rhenium tube (broad detection capability)
  - Can easily detect elements with atomic number of greater than 19; Strontium has an atomic number of 38.
  - To detect elements with low atomic numbers, including Sulfur at 16, the detection system can be modified.
- Each ceiling board sample was analyzed in three planes: the painted back, painted face and unpainted edge.
  - For the CPSC study, sampling was done through any surface decoration.
- Raw materials were analyzed only once.

# Equipment



XRF unit and ceiling tiles (with vacuum system in place for low atomic # detection)

# Samples tested



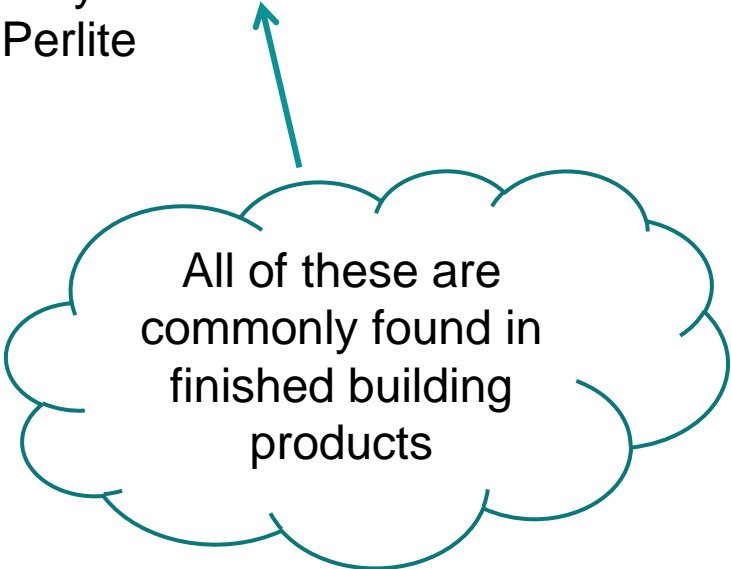
A broad selection of ceiling board types and inorganic raw materials were tested.

## Raw materials:

- Mineral wool
- Fiberglass – insulation
- Fiberglass – E glass fibers
- Limestone
- Clay
- Perlite

## Ceiling Board Types:

- Armstrong China
- Armstrong Europe (2 plants, 3 products)
- Armstrong NA (2 plants, 2 products)
- 2 German competitors
- Competitive rock wool board



All of these are commonly found in finished building products

# Results

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- All the ceiling tiles had detectable amounts of Sr, but had **barely detectible levels of S.**
- The vitreous fibers all had detectible amounts of Sr.
- XRF analysis done using a bench top unit routinely shows Sr in mineral wool, fiberglass and limestone. It is believed that the Sr is present in limestone/flux (as  $\text{SrCO}_3$ ) used in the production of fibers and steel, and is present in the man-made vitreous fibers as a harmless oxide (ppm levels).
- Limestone and clay both had detectible amounts of Sr. According to mineral data bases,  $\text{SrCO}_3$  commonly occurs in limestone and clay deposits.
- The paint analyses suggest that the limestones used in the paints all contain  $\text{SrCO}_3$ , regardless of the geography or manufacturer.
- In no case was Sr the strongest peak. However, in all instances but one it was the 2<sup>nd</sup> or 3<sup>rd</sup> strongest peak.
  - To an uneducated observer, this could indicate “high” levels of Sr, and would consistent with drywall, where Ca would be the largest peak

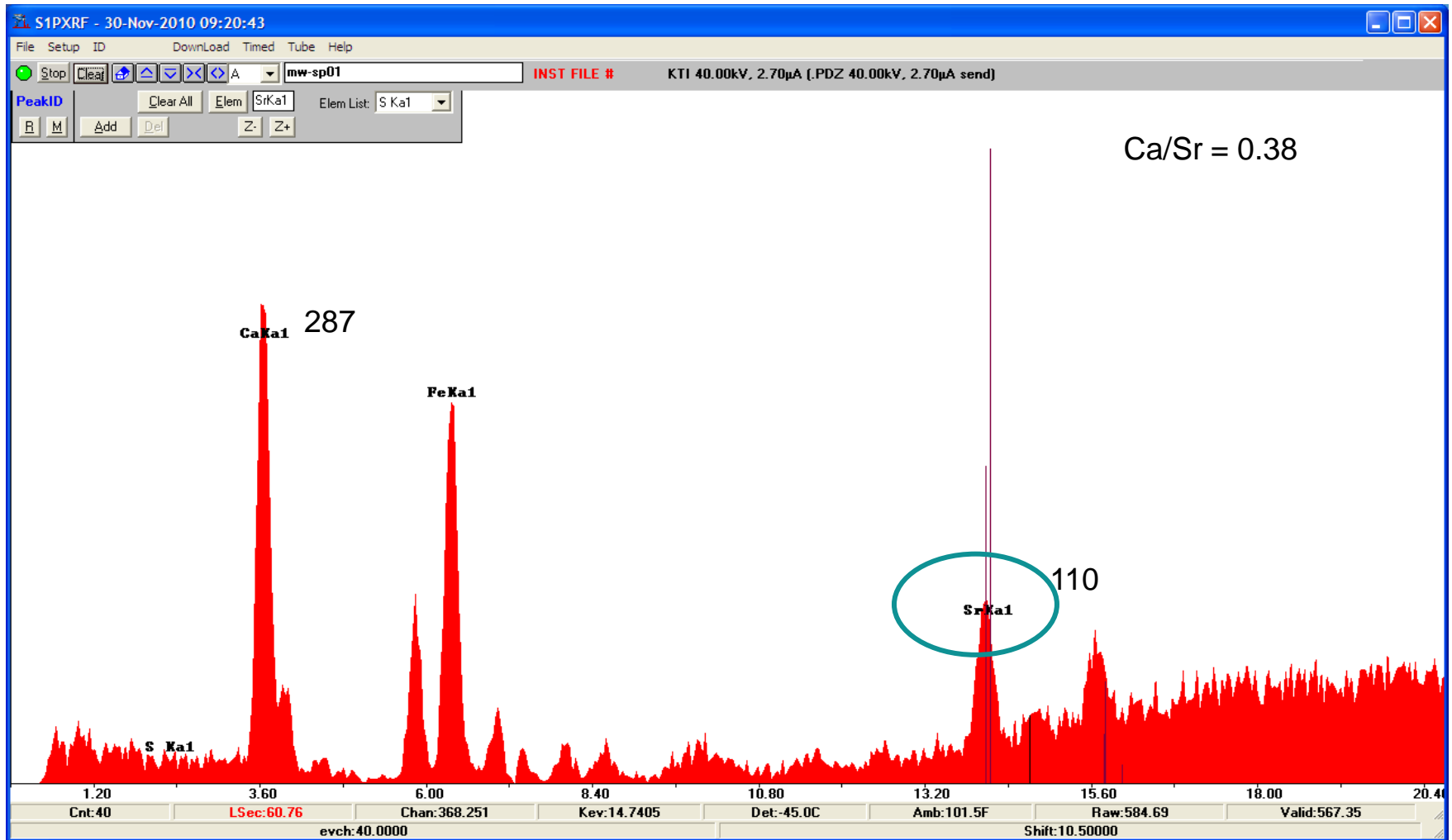
# Representative Spectra & Data

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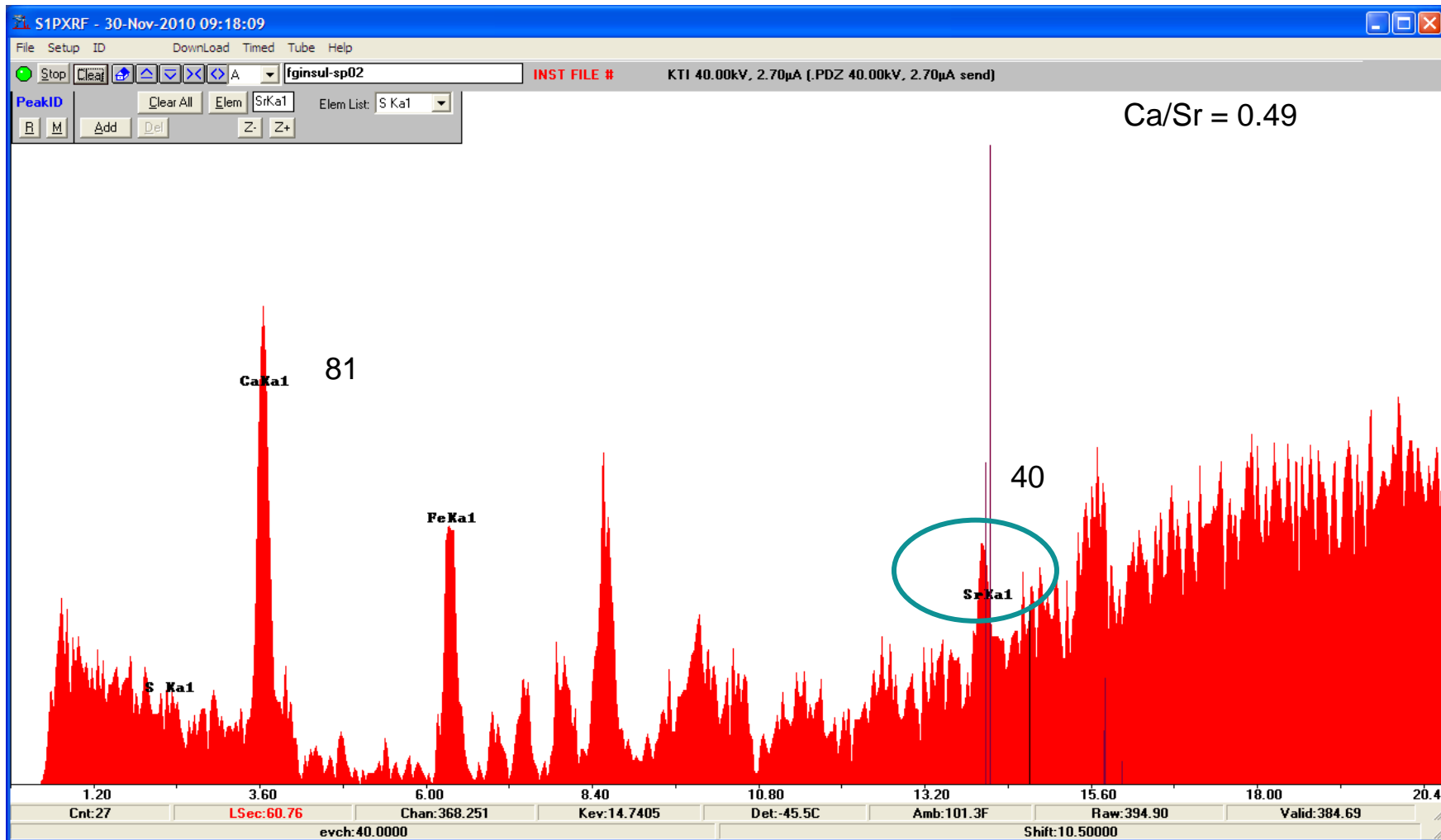


- Each spectra plots counts v. energy level at which the fluorescence occurs.
- The analysis is qualitative.
- Peak height is loosely correlated to quantity. For example, the tallest peak is generally associated with the component with the largest weight percent.
- Strontium and sulfur peaks are both noted. Peaks for calcium and iron are also noted.
- The strongest peak and the Sr peak height are both noted, along with the ratio (strictly for relative comparison)

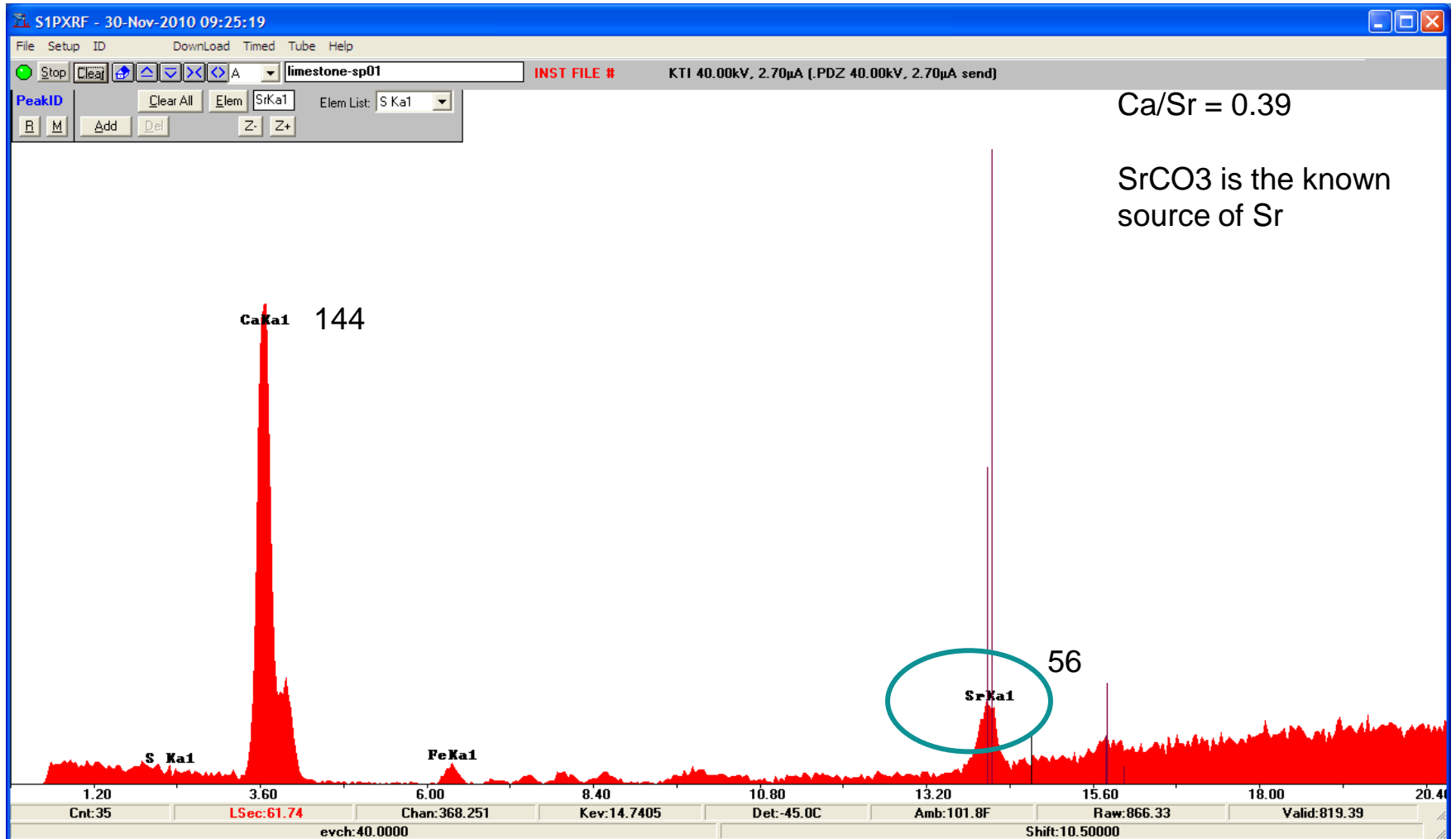
# Mineral wool (slag)



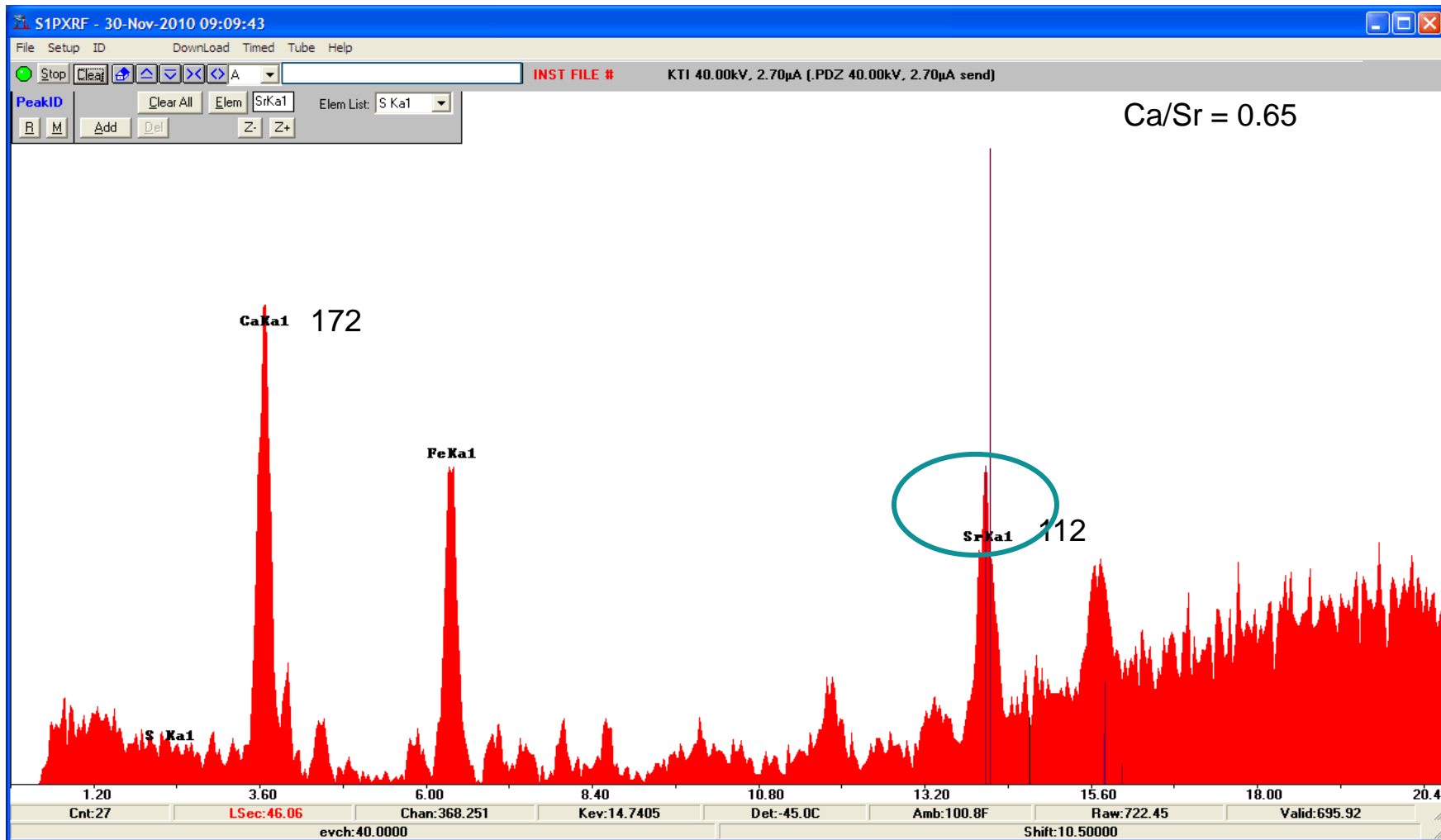
# Fiberglass insulation



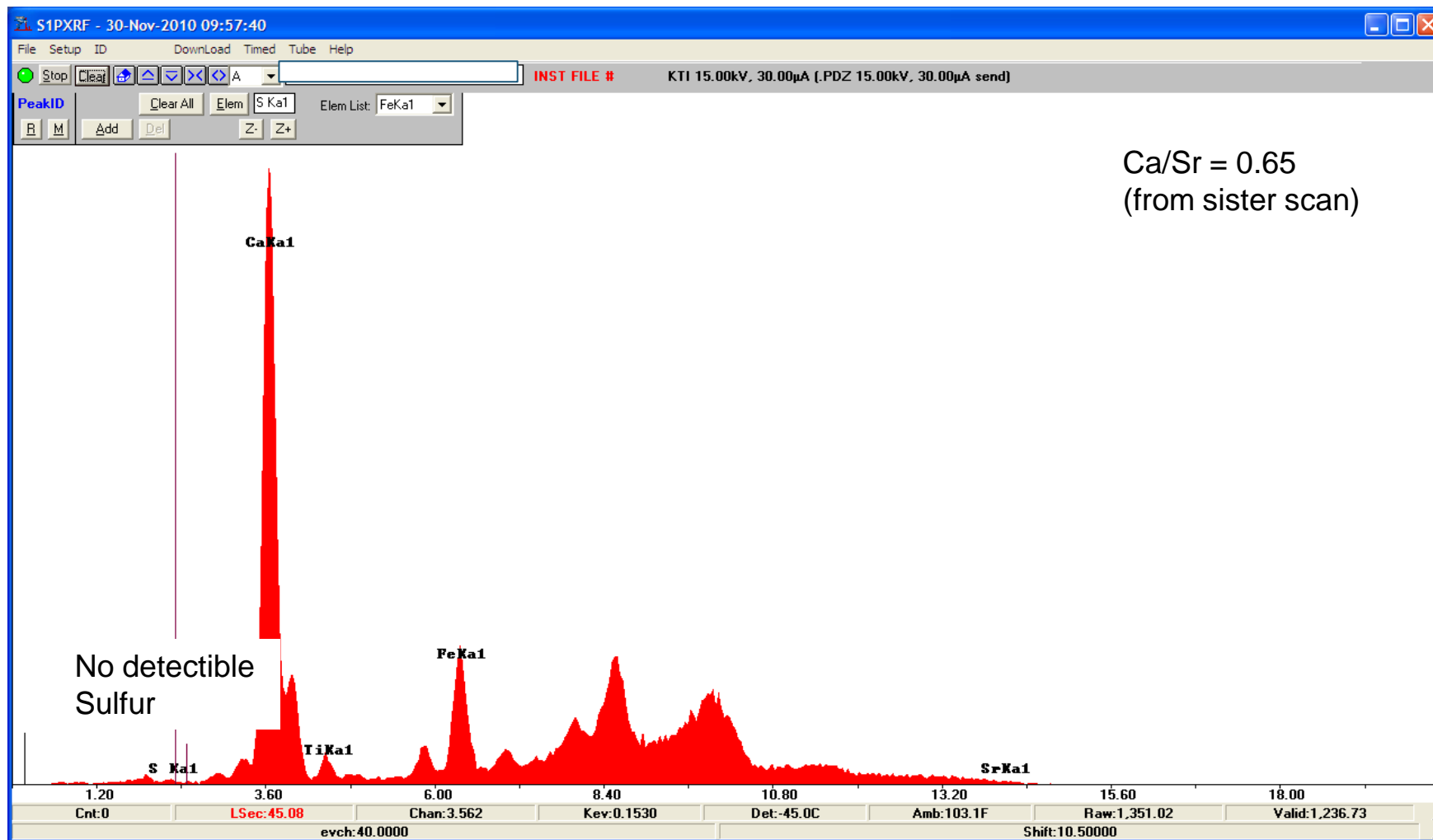
# Limestone



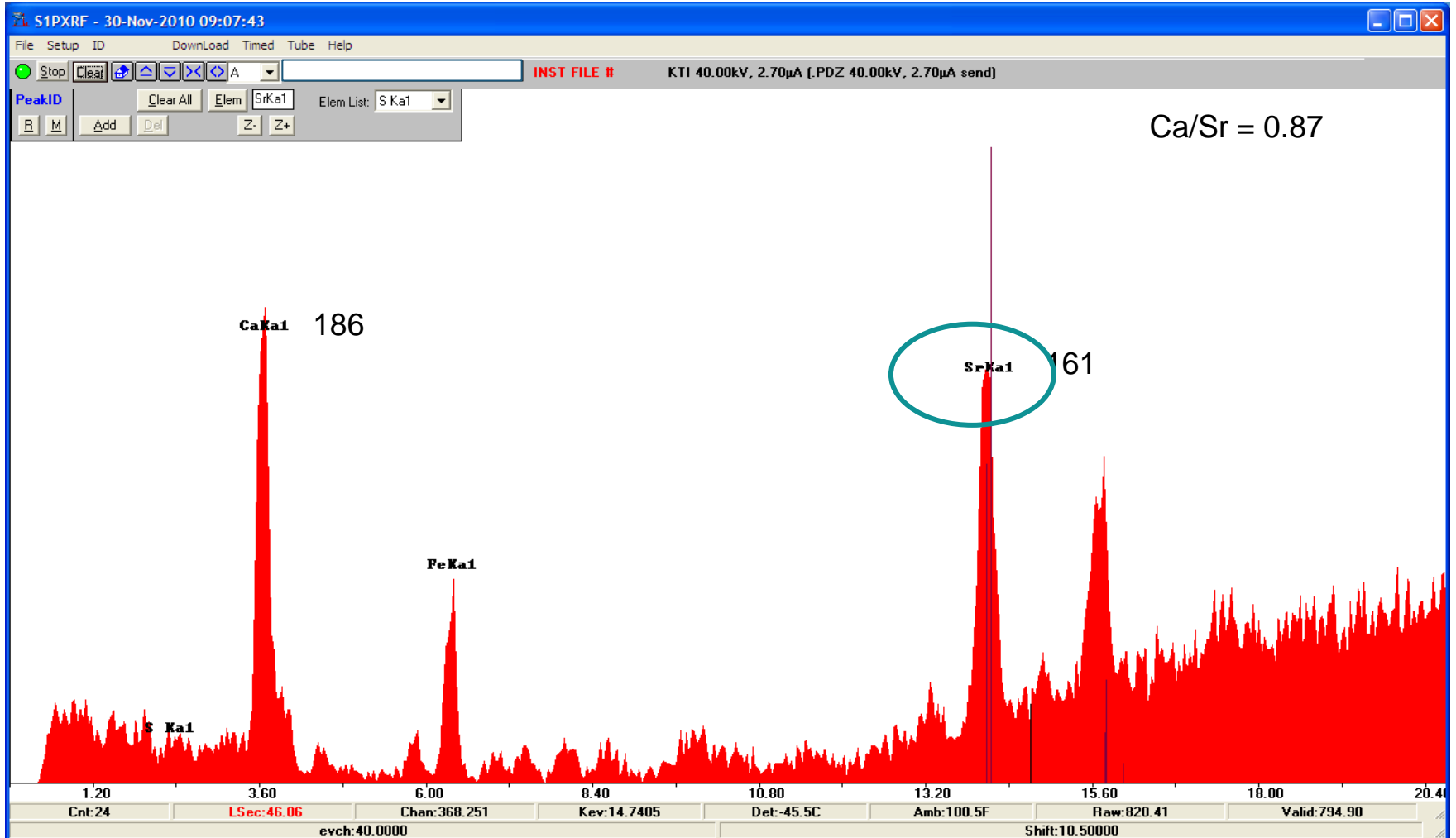
# Armstrong NA #1, edge (standard detection)



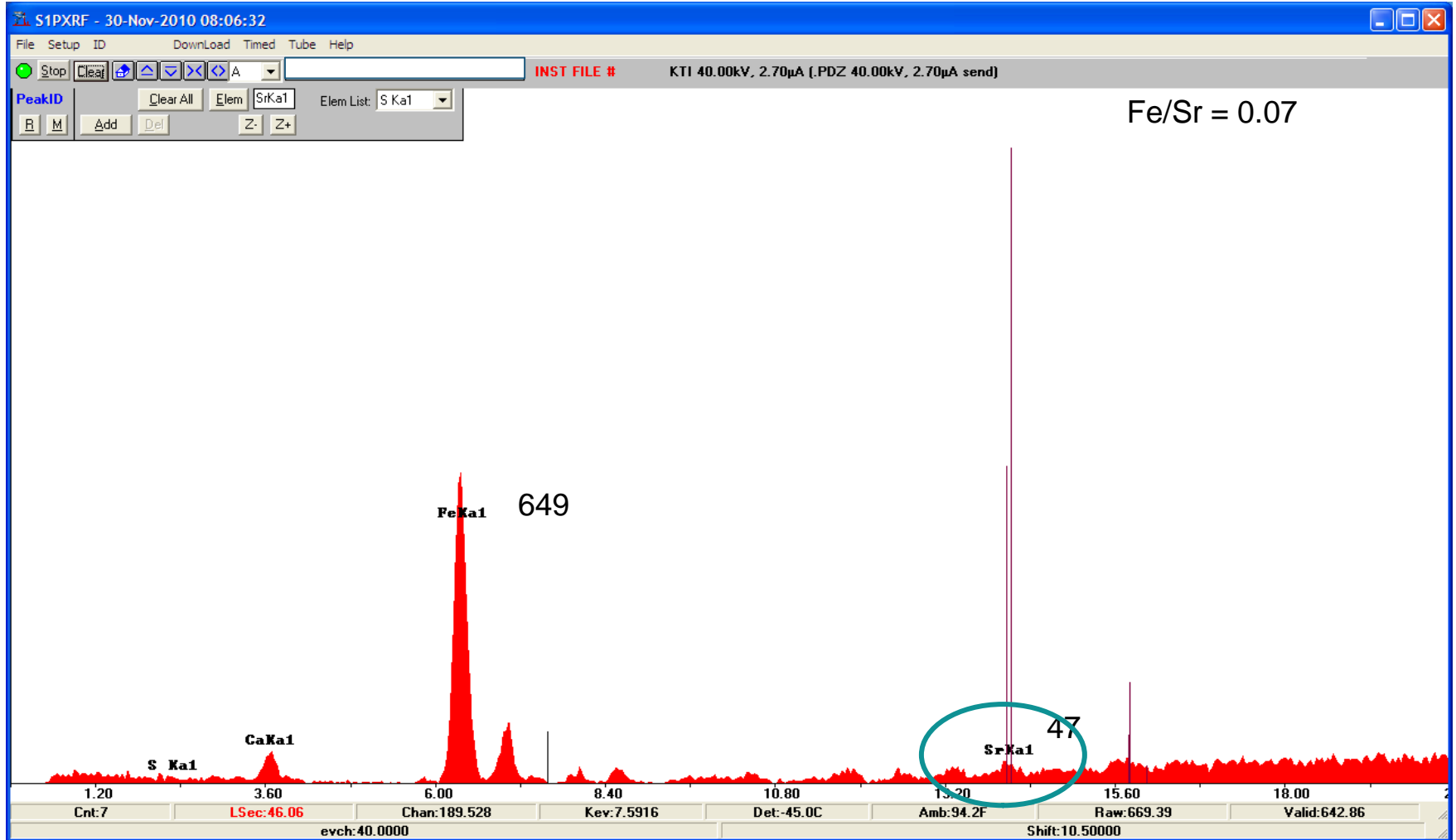
# Armstrong NA #1, edge, low atomic # detection



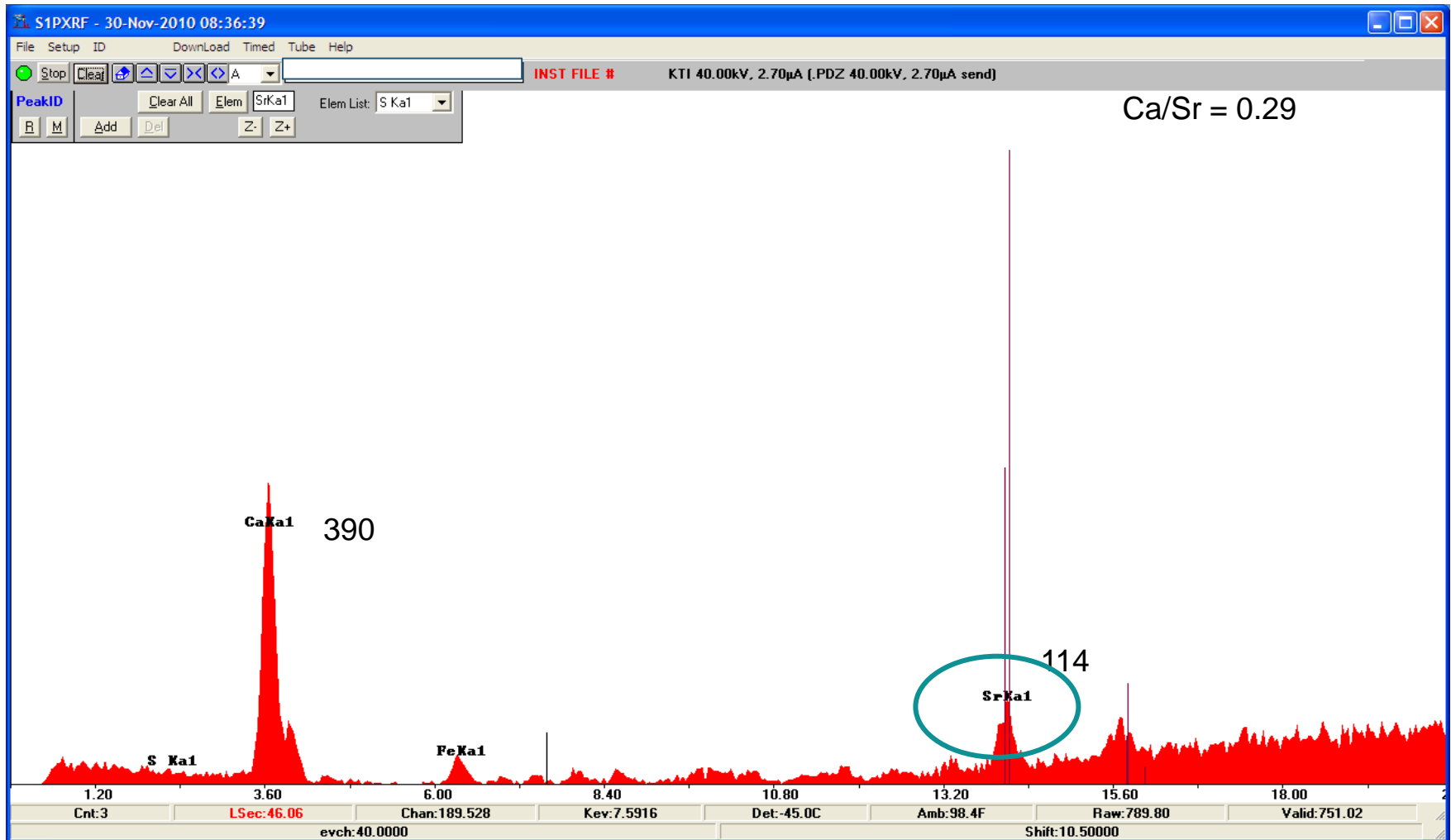
# Armstrong China, unpainted edge



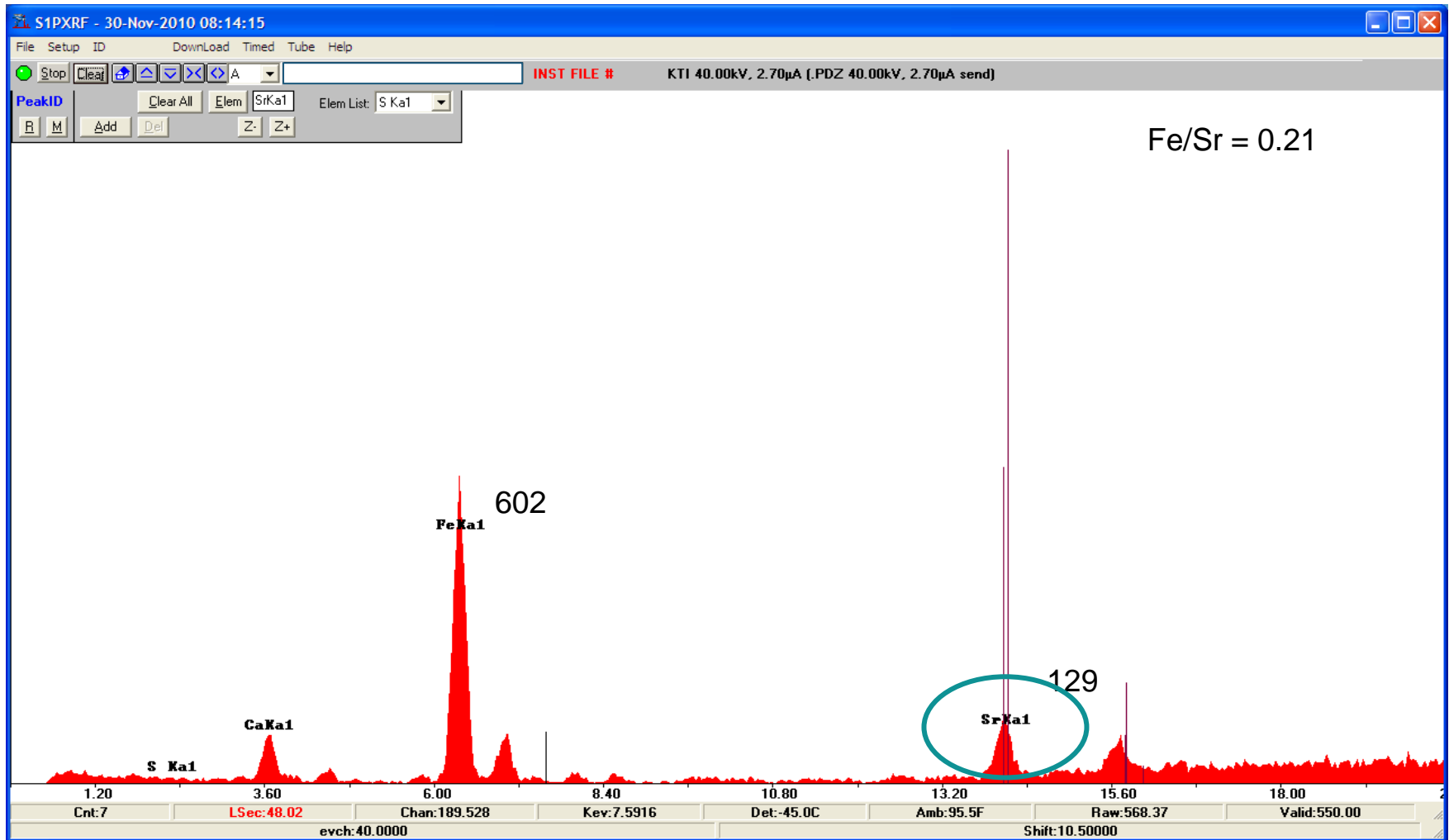
# Armstrong Europe #1, painted back



# German competitor, painted face



# Rock wool, unpainted



# Bench top XRF Summary data



- The following data have been collected at Franklin and Marshall's Geology department on Armstrong's behalf using a bench-top XRF detector.
- 16 different wool manufacturers from 3 continents are represented

Wool type	Range of SrO levels, ppm
Slag wool	400 - 2300
Rock wool	400 - 800
Fiberglass	Approx. 100

This is in the "range of concern" (most recent guidance is > 1200 ppm)

# Conclusions

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- A variety of raw materials and finished mineral fiber products all had detectable levels of Strontium.
- There were no significant amounts of Sulfur in any the materials.
- The original source of strontium is a naturally occurring  $\text{SrCO}_3$  contaminant in limestone; in the vitreous products, this is has been converted to  $\text{SrO}$ .
  - Limestone is a common, inexpensive, white filler used in a large number of building materials and coatings found in houses and commercial finishes.
  - We are unaware of  $\text{SrCO}_3$  or  $\text{CaCO}_3$  being linked to corrosion issues in any other product category.
- If an examiner is unskilled and is only looking for Sr, as would be the case with anyone used to examining gypsum wallboard ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), they might incorrectly conclude that these products contain SrS.

## What the Case Study means for ASTM C11

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- The CPSC has ruled SrS out as the definitive cause of the corrosion. However, they believe that Sr is an indicator, along with “carbonates.” (50-60% of the time.)
- If there is an ASTM standard for Sr in drywall, it will be specified for use with other building materials. This is commonly done. It could also be adopted by other international standards bodies, or by regulators.
- Sr can be observed in a variety of common building products, including insulation, acoustical materials, white paints, cements and floor products.
- Unless one tests for S simultaneously, it would be very easy to assume that the source of Sr in these materials is SrS. And if both Sr and S are found, you can't be sure that the source is SrS, or that the Sulfur is free sulfur. Calcium sulfates are also common fillers.
- Proof of no SrS is already being required in some countries, and some 3<sup>rd</sup> party test labs are apparently prepared to use XRF as a test method for confirming. If the tester only looks for Sr, the potential for false positives is very real.
- The same potential for false positives exists in the field.

# Can XRF be used to help ID Problematic Chinese DW?



- Inspectors and others desire a protocol to help them assess the issue, especially in lieu of the CPSC guidance saying that Sr is a “marker.”
  - However, Sr is NOT listed as corroborating evidence
  - “The Task Force **does not believe strontium has a causative role**, and in light of the possibility for false-positives, **we no longer consider elevated strontium levels to be valid corroborating evidence for problem drywall**. However, in many cases, screening for strontium **can be an effective tool in identifying** what boards may warrant additional testing for elemental sulfur.”  
*[CPSC guidance document, 3/18/11]*
  - However, the latest study showed that Sr was in 5/9 homes with issues (all assumed to be made with domestic drywall).
  - This suggests that one must test for free, elemental sulfur in some way.
- All of the published evaluations suggest that the issue is sulfidation corrosion of copper.
- A better approach would be to test for copper sulfide using the handheld XRF detectors.

# Can XRF be used to help ID Problematic Chinese DW?



- Is there a way to use copper/silver coupons in the home, and then test after the 2 week exposure with the handheld XRF unit?
  - This avoids potential high costs of 3<sup>rd</sup> lab testing of coupons
  - The use of a common coupon material standardizes the method
    - Easier way to write a standardized test method because the variability of the home's construction and decoration are eliminated as factors
    - One uniform substrate involved (planar, infinitely thick to the beam, etc.)
    - Uniform surface texture and composition – no contamination issue
    - Minimizes damage to the home
    - Measures the corrosion product
    - Confirmed the copper sulfidation reactions
  - Avoids the possibility of misuse on other materials
  - Issue: if S can't be detected, CuO could be mistaken for CuS

## Are there other simple methods to explore?



- One option is to use the coupons and then do a simple chemical test in the field.
  - CuS is soluble in dilute hydrochloric acid.
    - $\text{CuS} + \text{HCl} \rightarrow$  hydrogen sulfide gas (rotten eggs)
    - Plus the CuS will be cleaned off the coupon.
    - The CuO will dissolve, but no rotten egg smell will result.
- There are probably others.