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**IDENTIFICATION OF PROBLEMATIC DRYWALL:  
SOURCE MARKERS AND DETECTION METHODS**

Prepared For:

**Lori Saltzman, M.S.  
Director, Division of Health Sciences  
U. S. Consumer Product Safety Commission  
4330 East West Highway  
Bethesda, MD 20814**

Prepared By:

**Environmental Health & Engineering, Inc.  
117 Fourth Avenue  
Needham, MA 02494-2725**

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#### LIST OF ABBREVIATIONS AND ACRONYMS

A/30d	angstroms per 30 days
Ag <sub>2</sub> S	silver sulfide
AgCl	silver chloride
AHU	air handling unit
CPSC	U. S. Consumer Product Safety Commission
CS <sub>2</sub>	carbon disulfide
CuO	copper oxide
Cu <sub>2</sub> S	copper sulfide
DFTPP	decafluorotriphenylphosphine
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
EH&E	Environmental Health & Engineering, Inc.
EPA	U.S. Environmental Protection Agency
ERT	Environmental Response Team
FTIR	Fourier transform infrared spectroscopy
GC/MS	gas chromatography/mass spectrometry
GC/ECD	gas chromatography electron capture detector
H <sub>2</sub> O <sub>2</sub>	hydrogen peroxide
H <sub>2</sub> S	hydrogen sulfide
HCl	hydrochloric acid
HNO <sub>3</sub>	nitric acid
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ISA	Instrumentation, Systems, and Automation Society
LBNL	Lawrence Berkeley National Laboratory
LOD	limit of detection
LPM	liters per minute
mg/kg	milligram per kilogram
mL	milliliter
PTFE	polytetrafluoroethylene
REAC	Response Engineering and Analytical Contract
RH	relative humidity
S <sub>8</sub>	orthorhombic sulfur
SO <sub>2</sub>	sulfur dioxide
SOP	standard operating procedure
SRM	standard reference materials
XRF	x-ray fluorescence
°F	degrees Fahrenheit
μL	microliter
μm	micrometer

## 1.0 EXECUTIVE SUMMARY

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### 1.1 BACKGROUND

The U.S. Consumer Product Safety Commission (CPSC) has been investigating homeowner reports of corrosion and adverse health effects in homes constructed with problematic wallboard that has also been termed 'Chinese drywall'. To date, CPSC has received approximately 3,300 homeowner reports from 37 states. The vast majority of complaints are from people with homes around the Gulf Coast and coastal Virginia.

CPSC initiated a multi-track investigation to examine health and safety concerns potentially associated with this building product. As part of this investigation, Environmental Health & Engineering, Inc. (EH&E) conducted a 51-home study in the summer of 2009 to characterize the relationship between source markers, gas concentrations, building dynamics, and corrosion. A complete report outlining the methods, results and findings of that study are available on-line at the CPSC website.

The results of the 51-home study demonstrated that carbonate and strontium measured by the combination of Fourier transform infrared spectroscopy (FTIR) and x-ray fluorescence (XRF), respectively, were reliable indicators of Chinese drywall in these study homes. These study homes qualified for inclusion in the study by meeting specific pre-established criteria that included homeowner reports of corrosion, odor, possible health issues, and whether or not homes were constructed or used drywall for renovations during the period of interest (2006 – 2007). The utility of the carbonate/strontium marker determined using FTIR/XRF when applied to homes without these pre-selection criteria is unknown. Additionally, during the time that the in-home study was conducted, additional source characterization work by government agencies and private laboratories identified orthorhombic sulfur ( $S_8$ ) as a potential marker of not only Chinese drywall, but problematic drywall, defined hereafter as drywall associated with elevated rates of copper and silver corrosion, emissions of certain reduced sulfur gases, and possessing a distinctive malodor.

Homeowners, government agencies and other parties have a need to reliably determine which homes have problematic drywall. While several markers have been proposed, the

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robustness of the individual markers used to identify problematic drywall has not been evaluated extensively. EH&E was contracted by CPSC to conduct a detailed characterization of source markers of problematic drywall.

### 1.2 OBJECTIVES

The objective of the source characterization study was to evaluate proposed markers of problematic drywall, defined as drywall associated with elevated rates of copper and silver corrosion. In this study, we investigated two proposed markers—strontium and  $S_8$ . The robustness of each source marker was evaluated by first comparing different instruments/methods for quantifying each, examining parameters such as within-board variability and determining method precision. The source markers were then compared to both chamber-based and field-based measurements of gases and corrosion.

### 1.3 METHODS

Drywall samples of varying sizes from thirty-five unique boards were supplied to EH&E by CPSC for analysis. Drywall samples provided to EH&E by CPSC were collected by CPSC staff from manufacturers, drywall suppliers, and storage warehouses. North American drywall samples were manufactured in 2009 while Chinese drywall samples were manufactured from 2005 through 2009. These drywall boards, identified in this report as 'catalog samples' and labeled by EH&E as CPSC1-CPSC35, are of known origin and represent a diverse cross-section of domestic and foreign drywall.

Many of the drywall samples sent to EH&E were sub-samples obtained from larger sheets (source-samples) of drywall board that have been retained by the CPSC. Several government organizations also received sub-samples from the same larger source-sample drywall boards. This allowed for comparison of chemical measurement data in some instances.

In addition to the catalog samples, EH&E also had access to archived samples of drywall obtained from each room of all homes examined in the 51-home study. During that field study, a coring tool 1 centimeter in diameter was used in areas behind electrical outlets/faceplates to obtain a sample of drywall up to approximately 0.5 grams

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in mass. Additionally, one larger sample (1'x1') was also obtained from each home. A selection of these samples was analyzed for source markers to enable a comparison with in-home gas and corrosion measurements that were previously obtained.

Drywall samples were analyzed for strontium and  $S_8$  source markers using several different techniques. Strontium concentrations were determined using multiple portable XRF analyzers as well as inductively-coupled plasma atomic emission spectrometry.  $S_8$  concentrations were determined in all samples by gas chromatography electron capture detector (GC/ECD). A comparison of analytic methods for  $S_8$  was also undertaken. In a subset of samples,  $S_8$  was determined using three different methods: GC/ECD, gas chromatography mass spectrometry (GC/MS) using a toluene-based extraction, and U.S. Environmental Protection Agency's (EPA's) Response Engineering and Analytical Contract Standard Operating Procedure (REAC SOP1805) (EPA 2009a, EPA 2009b).

Drywall samples were also tested for their potential to cause corrosion. Drywall samples from the catalog samples provided by CPSC were placed in a sealed chamber for eight days at a constant temperature and humidity (90 degrees Fahrenheit [°F]; 50% relative humidity [RH]). A corrosion classification coupon containing pre-cleaned strips of both silver and copper was added to the chamber with the drywall sample to record rates of corrosion.

### 1.4 RESULTS AND CONCLUSIONS

The following observations were made during the course of this investigation:

- Strontium is a useful, but non-specific marker of problematic drywall when used in isolation

*Elevated strontium concentrations were observed in all problematic drywall, but also in some non-problematic drywall. Strontium concentrations were correlated with orthorhombic sulfur concentrations in problematic drywall. Therefore, in the 51-home study where homes were pre-screened based on specific criteria contained in a CPSC questionnaire (EH&E, 2010) strontium was found to be predictive of problematic drywall. Strontium content in drywall measured by XRF is non-destructive, field portable and nearly instantaneous, and, therefore,*



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*remains a useful marker of problematic drywall when used as part of a multi-level screening approach.*

- Analysis of strontium in drywall samples can be reliably performed using XRF  
*Strontium measurements using XRF were accurate when compared to strontium as determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (inductively coupled plasma-atomic emission spectroscopy). Models from three different manufacturers yielded highly similar response factors and strongly correlated results (1:1 slope). Instrument method calibration specific to strontium is necessary to ensure accuracy of the measurements.*
- Orthorhombic sulfur ( $S_8$ ) is a sensitive and specific marker of problematic drywall  
*Orthorhombic sulfur concentrations in drywall were associated with chamber-based measurements of hydrogen sulfide and corrosion. Consistent findings were observed when this relationship was evaluated using archived samples of drywall and measurements of hydrogen sulfide and corrosion in the 51-home study.*
- Orthorhombic sulfur ( $S_8$ ) was not detected in any drywall samples from the non-complaint homes in the 51-home study  
*Three drywall samples from each of the 10 non-complaint homes in the 51-home study were analyzed for orthorhombic sulfur. Orthorhombic sulfur was not detected in any of these samples. In contrast, orthorhombic sulfur concentrations in the complaint homes ranged from <5 milligrams per kilogram (mg/kg) to 830 mg/kg (median = 54 mg/kg), and were significantly higher than the levels in the non-complaint homes.*
- Orthorhombic sulfur ( $S_8$ ) determined using two toluene-based extraction methods showed strong agreement  
*Orthorhombic sulfur concentrations determined using the GC/MS (toluene extraction) and GC/ECD methods showed excellent agreement. Results using EPA's REAC SOP 1805 did not show consistent agreement when compared with the other two methods, in a limited number of samples. GC/ECD appears to be*

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*an attractive option for future analysis of drywall samples due to its potentially lower cost for laboratories with this capability.*

- Orthorhombic sulfur ( $S_8$ ) and strontium both exhibited low intra-board variability  
*Repeat measurements of orthorhombic sulfur and strontium on different locations of the same drywall board showed strong consistency.*

## 2.0 INTRODUCTION

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### 2.1 BACKGROUND

The CPSC has been investigating homeowner reports of corrosion and adverse health effects associated with 'Chinese drywall'. To date, CPSC has received approximately 3,300 homeowner reports from 37 states. The vast majority of complaints are from people with homes around the Gulf Coast and coastal Virginia.

CPSC initiated a multi-track investigation to examine health and safety concerns potentially associated with this building product. As part of this investigation, EH&E conducted a 51-home study in the summer of 2009 to characterize the relationship between source markers, gas concentrations, building dynamics, and corrosion. A complete report outlining the methods, results and findings of that study are available on-line at the CPSC website. The key findings of the 51-home study are:

- Study homes with imported drywall had elevated rates of objectively quantified corrosion

*CPSC complaint homes were found to have elevated rates of corrosion as measured objectively by metal coupon and visual inspection, compared to non-complaint homes. This finding remained when house status was determined using an objective source marker of imported drywall (carbonate and strontium measured using FTIR and XRF, respectively).*

- The presence of drywall with the carbonate/strontium objective source marker was associated with increased levels of hydrogen sulfide in indoor air

*Homes with the source marker of imported drywall had significantly greater hydrogen sulfide concentrations compared to non-complaint homes.*

- Hydrogen sulfide concentrations in air were associated with higher dew points for complaint homes

*A positive association was observed between elevated dew points and hydrogen sulfide concentrations for homes with the source marker of imported drywall.*

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*Hydrogen sulfide was present where the dew point reached typical room temperatures and condensation of water vapor would be expected.*

- Hydrogen sulfide and formaldehyde concentrations in indoor air were associated with elevated corrosion rates

*Hydrogen sulfide was associated with corrosion rates in these study homes. For silver, a potential interactive effect was seen with formaldehyde; the effect of formaldehyde on corrosion rates was dependent upon the presence of hydrogen sulfide. Formaldehyde may be a marker of some other factor associated with corrosion (e.g., formic acid).*

- Objective source markers of imported drywall in CPSC complaint homes can be quantified using portable FTIR and XRF analyzers

*FTIR and XRF analyzers provide additional metrics for characterizing drywall in homes that can be used in conjunction with objectively measured corrosion rates and malodor.*

- Air exchange rates in the study homes were all on the low-end of typical air exchange rates in homes

*Both complaint and non-complaint homes were newly constructed homes with air exchange rates consistent with the low end of the distribution for North American housing stock (i.e., tightly constructed homes). These low air exchange rates may play an important role in the effect of gases and indoor environmental conditions on corrosion and possible exposures to indoor contaminants.*

The results of the 51-home study demonstrated that carbonate and strontium measured by the combination of FTIR and XRF, respectively, were reliable indicators of Chinese drywall in these study homes. These study homes qualified for inclusion in the study by meeting specific pre-established criteria that included homeowner reports of corrosion, odor, possible health issues and whether or not the home was constructed during the period of interest (2006 – 2007). The utility of the FTIR/XRF marker when applied to homes without these pre-selection criteria is unknown. Additionally, during the time that the in-home study was conducted, additional source characterization work by government agencies and private laboratories identified  $S_8$  as a potential marker of not

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only Chinese drywall, but problematic drywall, defined hereafter as drywall associated with elevated rates of copper and silver corrosion, emissions of certain reduced sulfur gases, and possessing a distinctive malodor.

### 2.2 OVERVIEW AND OBJECTIVES

Homeowners, government agencies and other parties have a need to reliably determine which homes have problematic drywall. While several markers have been proposed, the robustness of the individual markers used to identify problematic drywall has not been evaluated extensively. EH&E was contracted by CPSC to conduct a detailed characterization of source markers of problematic drywall.

This report was prepared by EH&E on behalf of CPSC and describes an investigation of source markers of problematic drywall. The investigation included:

1. Determination of the precision and accuracy of strontium concentration measurements in drywall made with field portable instruments.
2. Determination of orthorhombic sulfur content in drywall samples from the CPSC inventory ('catalog drywall samples') and drywall samples archived from the 51-home study.
3. Characterization of corrosion potential of catalog drywall samples.
4. Identification of source markers of problematic drywall by comparison of source marker concentrations to both chamber-based and in-home measurements of gases and corrosion.

### 2.3 METHODS SUMMARY

Drywall samples of varying sizes from thirty-five unique boards were supplied to EH&E by CPSC for analysis. These drywall boards, identified in this report as 'catalog samples' and labeled by EH&E as CPSC1 – CPSC35, are of known origin and represent a diverse cross-section of domestic and foreign drywall. Drywall samples were analyzed for source markers using several different techniques, as well as for the potential to cause corrosion in chamber tests. A list of the drywall samples and types of analyses

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performed on each are outlined in Table 2.1. Detailed descriptions of the analyses performed can be found in the following sections.

<b>Table 2.1</b> List of Drywall Samples and Corresponding Analyses Completed for Orthorhombic Sulfur, Strontium and Corrosion									
Catalog ID	CPSC ID	S <sub>8</sub> Laboratory Method Comparison			S <sub>8</sub> Intra-Board Variability	Strontium		Strontium Intra-Board Variability	Chamber Corrosion Test
		REAC	GC/MS	GC/ECD	GC/ECD	XRF	ICP	XRF	
CPSC1	09-302-1429-02	X	X	X		X	X		X
CPSC2	09-840-9139-05			X		X	X		X
CPSC3	09-302-1379-09	X	X	X	X	X		X	X
CPSC4	09-840-9858-01	X	X	X		X	X		X
CPSC5	09-810-7932-05	X	X	X		X			X
CPSC6	09-810-7639-06			X		X			X
CPSC7	09-840-9961-03			X		X			X
CPSC8	09-840-9962-08			X		X		X	X
CPSC9	09-810-8213-02			X		X	X		X
CPSC10	09-810-7069-06	X	X	X	X	X	X		X
CPSC11	09-810-8235-03			X		X			X
CPSC12	09-810-8036-05			X		X			X
CPSC13	09-810-8037-01			X		X			X
CPSC14	09-810-8236-07			X	X	X	X	X	X
CPSC15	09-840-9672-07			X	X	X	X		X
CPSC16	09-302-2636-03			X		X			X
CPSC17	09-840-9707-05	X	X	X		X	X		X
CPSC18	09-840-9673-08			X		X			X
CPSC19	09-302-1487-02	X	X	X		X	X	X	X
CPSC20	09-302-2634-01a			X		X		X	X
CPSC21	09-302-1492-02			X		X		X	X
CPSC22	09-302-1493-02a	X	X	X		X			X
CPSC23	09-302-2631-02b	X	X	X		X	X	X	X
CPSC24	09-810-7077-02	X	X	X		X	X	X	X
CPSC25	09-810-7078-05			X	X	X	X	X	X
CPSC26	09-302-2632-01	X	X	X		X	X		X
CPSC27	09-302-2633-02			X		X	X		X
CPSC28	09-302-2635-02			X		X			X
CPSC29	09-840-9667-01			X		X		X	X
CPSC30	09-302-2637-02a			X		X		X	X
CPSC31	09-302-1484-02a			X		X	X		X
CPSC32	09-840-9175-05			X	X	X	X	X	X
CPSC33	09-840-9174-01			X		X	X		X
CPSC34	09-810-7339-10	X	X	X	X	X		X	X
CPSC35	09-810-8357-01	X	X	X	X	X			X
Archived samples from the 51-home study	3 samples per home (n=153)			X		X			
CPSC	U.S. Consumer Product Safety Commission				S <sub>8</sub>	orthorhombic sulfur			
REAC	Response Engineering and Analytical Contract				GC/MS	gas chromatography mass spectrometry			
GC/ECD	gas chromatography/electron capture detection				XRF	x-ray fluorescence			
ICP	inductively coupled plasma-emission spectroscopy								

Many of the drywall samples sent to EH&E were sub-samples obtained from larger sheets (source-samples) of drywall board that have been retained by the CPSC. Several

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government organizations also received sub-samples from the same larger source-sample drywall boards. This allowed for comparison of chemical measurement data in some instances.

In addition to the catalog samples, EH&E also had access to archived samples of drywall obtained from each room of all homes in the 51-home study. During that field study, a coring tool 1 centimeter in diameter was used in areas behind electrical outlets/faceplates to obtain a sample of drywall up to approximately 0.5 grams in mass. Additionally, one larger sample (1'x1') was also obtained from each home. A selection of these samples was analyzed for source markers to enable a comparison with in-home gas and corrosion measurements that were previously obtained.

### 2.3.1 Statistical Analysis

Statistical analysis included compiling descriptive statistics, scatter plots and box plots. Box plots depict the mean, median, 10<sup>th</sup>, 25<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles, as well as individual points beyond the 10<sup>th</sup> and 90<sup>th</sup> percentiles. Bivariate statistical relationships were assessed using Spearman correlation and linear regression. Multiple linear regression models were used for analysis of variance and multivariate regression. When normality assumptions were not satisfied for the outcome variable, the variable was natural log-transformed. Covariate selection for multivariate models was determined based on modeling results reported in the 51-home study (EH&E 2010) to ensure comparability between reports. Values below the laboratory reporting limit were substituted using one-half of the reporting limit in statistical analyses. Statistical significance for all analyses was defined at the  $\alpha=0.05$  level. All statistical analyses of the study data were performed using SAS statistical software, version 9.1 (Cary, North Carolina).

### 2.3.2 Quality Assurance/Quality Control

All sampling was conducted at the EH&E laboratory. XRF analyzers were calibrated for strontium by the manufacturers prior to use in this study. In addition, internal instrument background checks were run on each Innov-X instrument in accordance with

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manufacturer instructions. Two standard reference materials (SRM) were used for the strontium testing:

- SRM 2709—San Joaquin Soil (Baseline Trace Element Concentration)  
This SRM is intended primarily for use in the analysis of soils, sediments, or other materials of similar matrix.
- SRM 2702—Inorganics in Marine Sediment (Baltimore Harbor, Baltimore, Maryland)  
This SRM is intended for use in evaluating analytical methods for the determination of selected elements in marine or fresh water sediment and similar matrices.

Sample logs were used to record the drywall identification number and sample type during testing. Data files were downloaded daily and saved on EH&E's central file server. Estimates of accuracy and precision were an objective of this project and are discussed in detail in the results sections for strontium and  $S_8$ .



## **3.0 SOURCE MARKER ANALYSIS—STRONTIUM**

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### **3.1 INTRODUCTION**

Evaluating strontium as a reliable marker of problematic drywall included two specific aims. The first was to determine the precision and accuracy of strontium concentration measurements made using portable XRF analyzers. The second was to evaluate the sensitivity and specificity of strontium as a marker of problematic drywall. This section of the report, Section 3, describes the testing done to address the first aim related to evaluating strontium measurements. The second aim, which evaluates two source markers, strontium and sulfur, and their relationships to gases and corrosion is discussed in Section 6.

Strontium, as measured using portable XRF analyzers, has been proposed as a useful marker for identifying Chinese Drywall (EPA 2009c, EH&E 2010). In EH&E's 51-home field study, homes that contained wallboard with a carbonate and strontium marker (carbonate measured by FTIR and strontium measured by XRF) were found to have significantly higher hydrogen sulfide concentrations and corrosion than homes that did not have this marker present. The decision to use a two-component marker was based on sampling conducted on a limited number of drywall samples of known origin. That sampling indicated that using either carbonate or strontium alone could lead to false positives. The combined carbonate/strontium marker using FTIR/XRF was found to be sufficient to detect differences in these sets of homes and important for establishing an empirical relationship between source materials in homes and effects. The extent to which carbonate and strontium are both needed is more fully explored in this analysis based on additional drywall samples supplied by CPSC.

The FTIR/XRF method previously developed by CPSC and EH&E to identify suspect drywall was performed using A2 Technologies brand portable FTIR analyzer and Innov-X brand portable XRF analyzers (EH&E 2010). CPSC desired to know if portable XRF instruments from different manufacturers could be used reliably. Additionally, the overall accuracy and precision of the strontium measurements as determined by XRF analyzers needed to be more fully characterized before final recommendation of a sampling protocol can be made.

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Therefore, the objectives of this task were:

### *Objective 1*

Compare the agreement of strontium measurements within and among different brands of portable XRF analyzers.

### *Objective 2*

Evaluate the accuracy of strontium concentrations measured using XRF against total strontium content in wallboard using inductively-coupled plasma atomic emission spectrometry for comparison.

### *Objective 3*

Determine the intra-board variability of strontium concentrations and evaluate two sampling techniques.

### *Objective 4*

Review the two-component carbonate and strontium marker ('FTIR/XRF marker') for identification of problematic wallboard.

## **3.2 METHODS**

### **3.2.1 X-Ray Fluorescence Analysis**

Portable XRF analyzers were used to measure the concentration of strontium in the catalog samples. XRF analyzers have been used for many years for non-destructive testing of products and materials, most notably for detecting lead in paint. Briefly, XRF analyzers use low-energy x-rays to produce high-energy photons to excite electrons in a sample. Upon excitation, outer shell electrons are replaced by inner orbital electrons. This generates a fluorescent signature that is unique to each element. A detector on the instrument analyzes the fluorescence patterns and quantifies the concentration of each element present in the sample.

Four different XRF analyzers, representing three different brands, were evaluated in this study (Table 3.1).

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<b>Brand</b>	<b>Address</b>	<b>Model</b>	<b>Analysis Mode</b>
Bruker	Kennewick, WA	TRACER turboSD	Mining Elements
Innov-X	Woburn, MA	Alpha Series	Soil
Thermo Fisher	Billerica, MA	NitonXL3T500	Mining
Thermo Fisher	Billerica, MA	NitonXL3T900SHE	Mining

### 3.2.2 Sample Testing

#### 3.2.2.1 Method Precision

Intra-instrument measurement precision was determined for three different brands (four total models) of portable analyzer by conducting repeat sampling at a specific location on each of the eight boards. For each model/brand, 10 consecutive measurements were obtained at the specified location on the first board. The process was then repeated for the remaining seven different drywall boards and two SRMs (10 total drywall boards).

Inter-instrument precision was determined by comparing co-located strontium measurements made using each XRF analyzer on 35 unique drywall samples. One location on each drywall sample was identified and marked. To eliminate any interference and attenuation from surface materials, the paper was removed and each analyzer/method was used to record measurements on the same location of each drywall sample. Measurements were taken directly on the core of intact drywall material (i.e., paper removed) and lasted 30 seconds each.

#### 3.2.2.2 Method Accuracy

To assess accuracy of strontium measurements made using portable XRF analyzers, drywall samples were obtained from 17 boards for analysis of total strontium concentration by ICP-AES. Approximately five grams of core material was removed from each drywall board (i.e., paper removed), crushed and placed in a sampling container. The sample was then analyzed by handheld XRF analyzer before being shipped to an analytic laboratory for determination of strontium content by ICP-AES.

The ICP-AES analysis was performed by Columbia Analytical Sciences (Simi, California). Drywall samples were digested according to EPA Method SW846 3050B,

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“Acid Digestion of Sediments, Sludges, and Soils.” One-gram equivalent of the sample was digested with repeated additions of nitric acid (HNO<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Hydrochloric acid (HCl) was added to the initial digestate and the sample was refluxed prior to dilution to a final volume of 100 milliliters (mL). The digestate was then analyzed following EPA Method SW846 6010B for strontium using ICP-AES. The instrument measured characteristic emission spectra by optical spectrometry. The intensity of emission lines was monitored. Final strontium concentrations were calculated using information regarding the digestion process and results from the ICP analysis.

### 3.2.2.3 *Intra-Board Variability*

Thirteen drywall boards were selected for testing in multiple locations to assess intra-board variability (Table 3.2). Each drywall board was evenly divided by three columns and four rows for a total of 12 sampling locations per board. Strontium concentrations were determined at each of the 12 locations by portable XRF analyzers.

<b>Catalog ID</b>	<b>Original Sample Size</b>	<b>Number of Samples</b>
CPSC3	11" x 12"	12
CPSC8	9" x 12"	12
CPSC14	9" x 6"	12
CPSC19	8" x 16"	12
CPSC20	12" x 11"	12
CPSC21	8" x 16"	12
CPSC23	7" x 14"	12
CPSC24	11" x 15"	12
CPSC25	10" x 16"	12
CPSC29	1' x 1'	12
CPSC30	1' x 1'	12
CPSC32	1' x 1'	12
CPSC34	1' x 1'	12

### 3.2.2.4 *Fourier Transform Infrared (FTIR) Analysis*

All samples tested for strontium by XRF were also tested for carbonate using FTIR. The analytic method has been previously described (EH&E 2010). Briefly, FTIR measurements were obtained using the A2 Technologies Exoscan instrument, a full scanning Fourier transform mid-infrared spectrometer. The diffuse reflectance infrared

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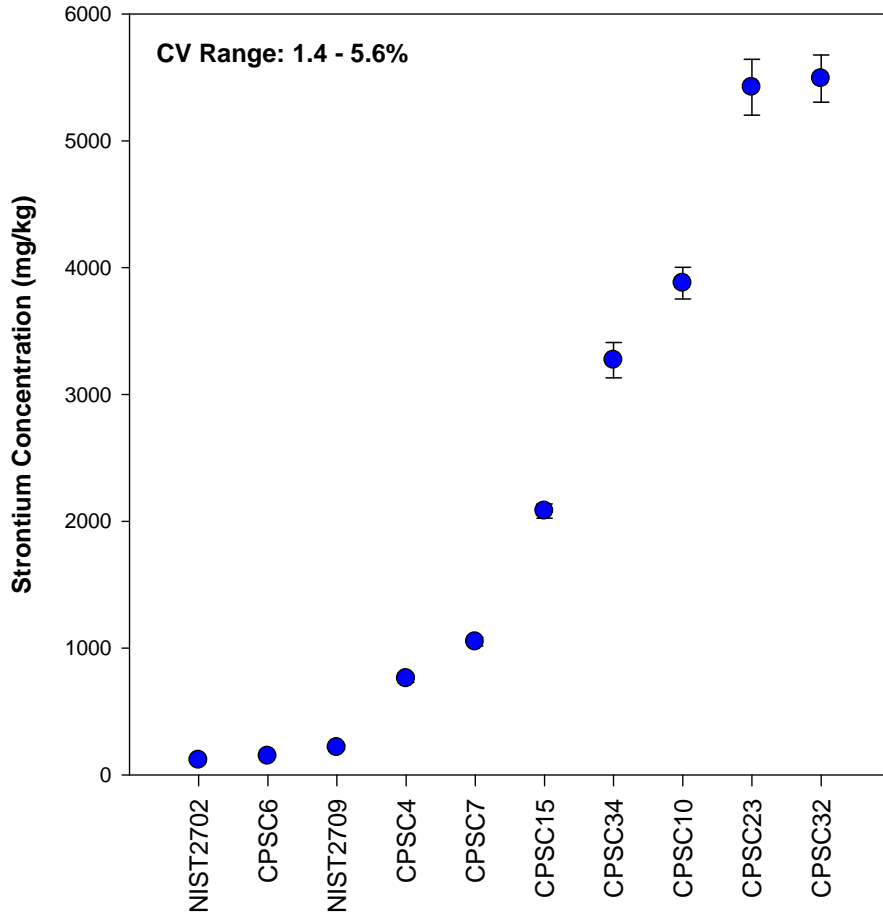
Fourier transform spectroscopy (DRIFTS) technique was used in this study to obtain measurements of relative carbonate content in each sample.

### 3.3 RESULTS

#### 3.3.1 Objective 1—Precision of Strontium Measurements Across XRF Instruments

##### 3.3.1.1 *Intra-Instrument Precision*

Results from the repeat strontium measurement testing of one location on eight drywall boards and two SRMs by XRF (Innov-X brand) are presented in Figure 3.1 and show high precision. Data points represent the average of 10 measurements and the error bars represent two standard deviations. Similar results were observed for the Thermo/Niton and Bruker brand XRF analyzers (not shown). The coefficient of variation among the 10 repeated measurements across all 40 combinations of instruments (4) and boards or SRMs (10) ranged from 0.4 – 14% (median=2%). These results demonstrate strong within-instrument precision for strontium measurements made by XRF analyzers calibrated for strontium.



**Figure 3.1** Mean Strontium Concentrations Obtained from Repeat Measurements by XRF (Innov-X brand analyzer) (Error bars represent 2\*standard deviation)

3.3.1.2 *Inter-Instrument Precision*

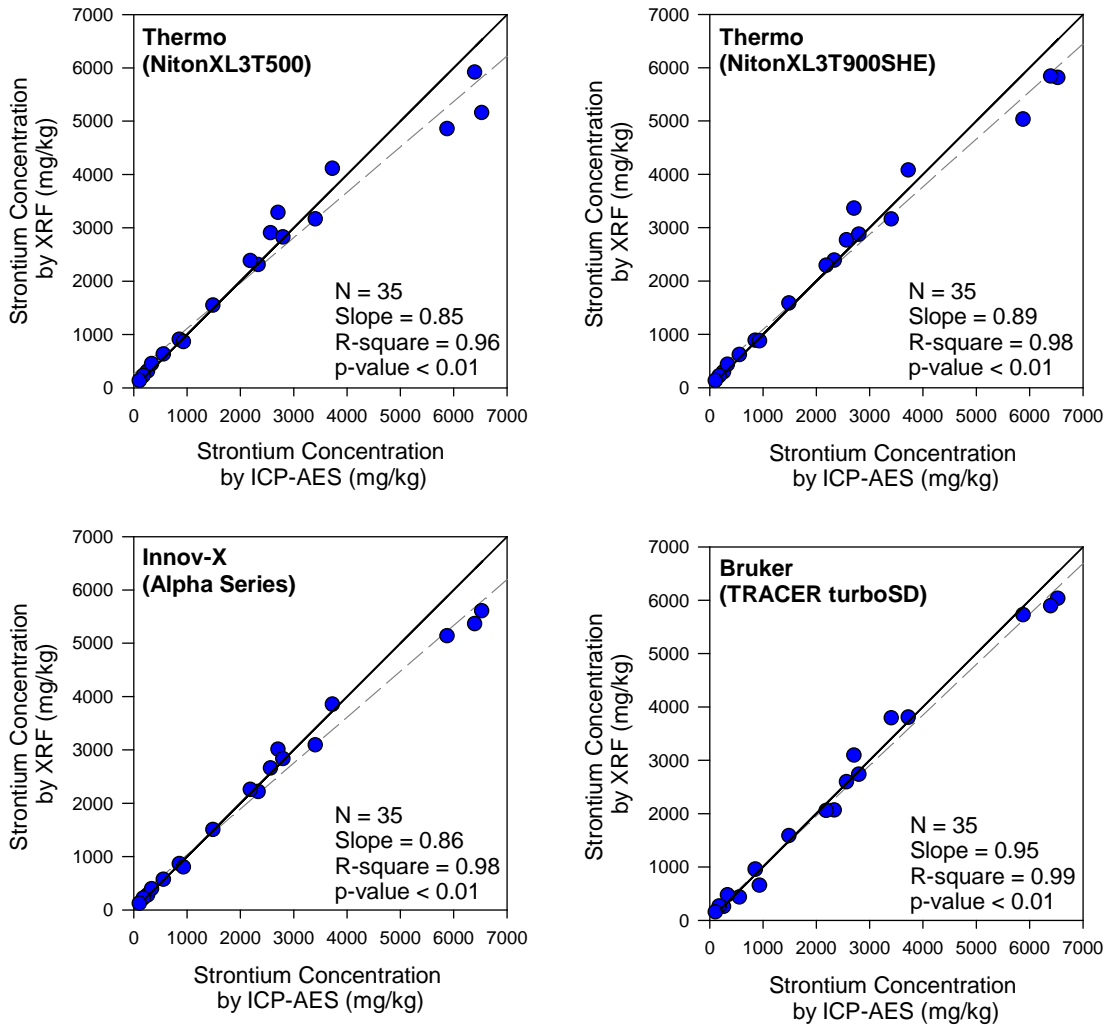
The strontium measurements on the core of intact drywall samples obtained using the four XRF analyzer models/brands were all highly correlated (0.99,  $p < 0.0001$ ) (Table 3.3). This strong agreement indicates that all of the XRF analyzer models tested perform similarly with respect to identifying and quantifying the relative amounts of strontium in drywall. The overall accuracy of each analyzer is discussed in the following section.

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<b>Table 3.3</b> Correlation Matrix of Strontium Concentrations Measured by Four Different XRF Analyzers				
	<b>Thermo</b> (Niton XL3T500)	<b>Thermo</b> (Niton XL3T900SHE)	<b>Innov-X</b> (Alpha Series)	<b>Bruker</b> (TRACER turboSD)
<b>Thermo</b> (NitonXL3T500)	1			
<b>Thermo</b> (NitonXL3T900SHE)	0.998 <.0001	1		
<b>Innov-X</b> (Alpha Series)	0.997 <.0001	0.998 <.0001	1	
<b>Bruker</b> (TRACER turboSD)	0.987 <.0001	0.988 <.0001	0.990 <.0001	1

**3.3.2 Objective 2—Accuracy of Strontium Measurements Across XRF Instruments**

The accuracy of strontium measurements obtained by XRF was assessed by comparison to corresponding strontium results measured by ICP-AES. Scatter plots comparing the measurements made by XRF and ICP-AES are depicted in Figure 3.2. The XRF and ICP-AES measurement results show excellent agreement for strontium (slope = 0.85 – 0.95,  $p < 0.01$ ).

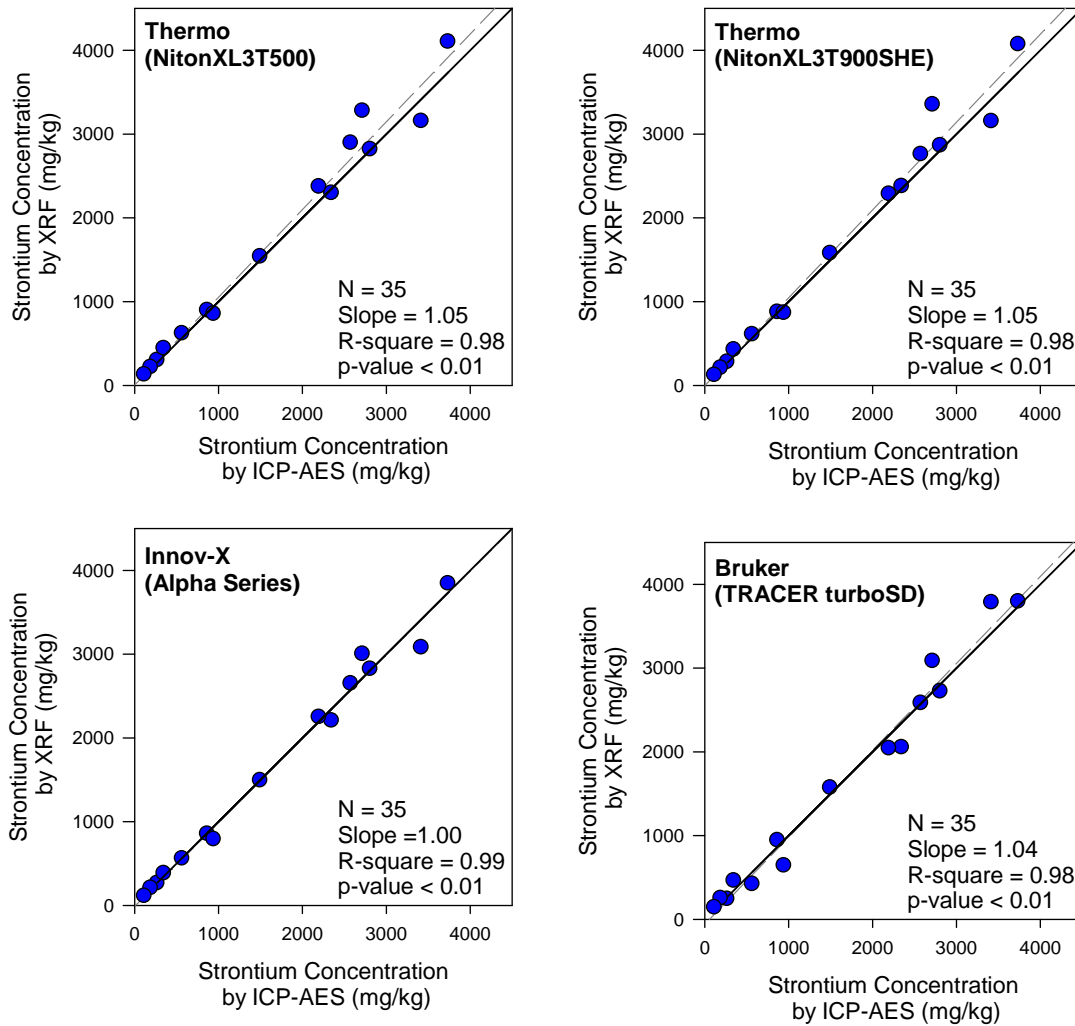


**Figure 3.2** Correlation of Strontium Concentration Measured by ICP and Handheld XRF, Strontium Concentration Ranged Between 0 – 7000 mg/kg (The solid line represents the 1:1 slope.)

The data depicted in Figure 3.2 show that the slopes are influenced by measurements of three boards in the 6,000 mg/kg range. It is important to consider the meaningful range of analysis when analyzing comparative data. For strontium, levels in the range of 1,200 mg/kg have been proposed as the cut point for a marker of problematic drywall. Therefore, the accuracy of measurements that vastly exceed the range of interest (e.g., 5,000 mg/kg) may be less important because these values are clearly above reported thresholds of interest. We re-analyzed the data restricting the data to a range more relevant to these thresholds. When the data are re-examined restricting the data to



values <5000 mg/kg, the accuracy of measurements made by XRF is even greater (slope = 0.98 – 1.04,  $p < 0.01$ ) (Figure 3.3).



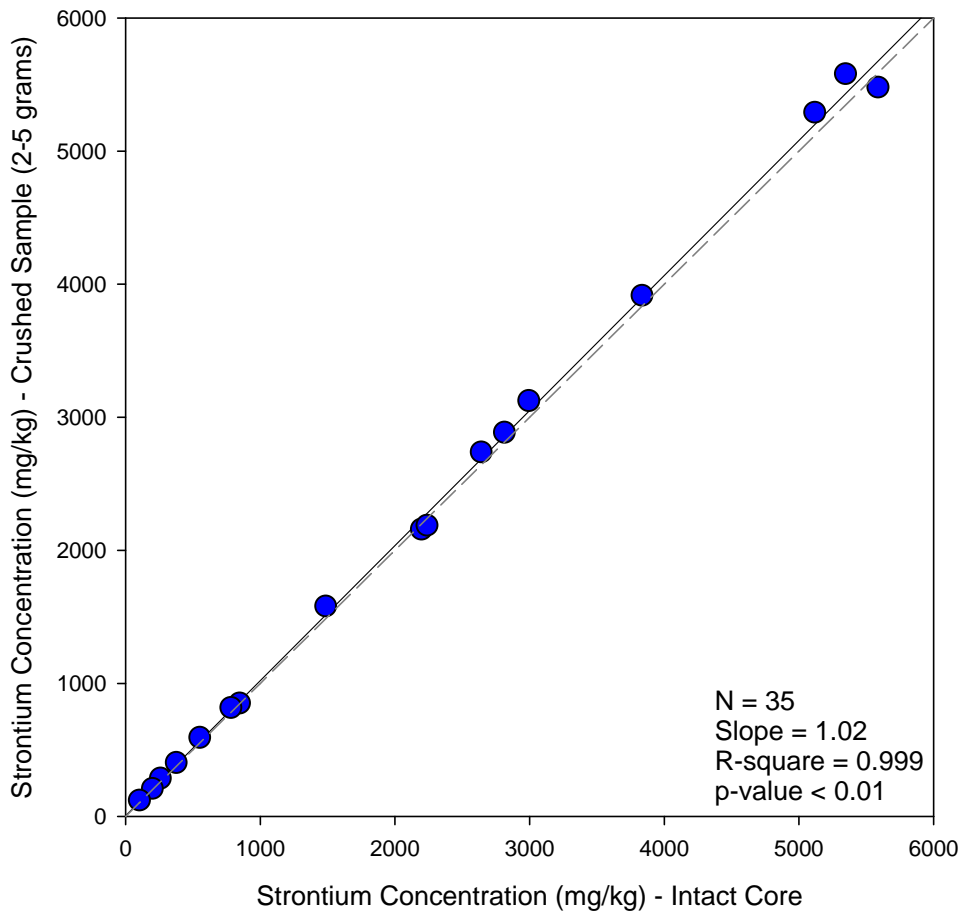
**Figure 3.3** Correlation of Strontium Concentration Measured by ICP and Handheld XRF, Excluding the 3 Samples with Strontium Concentration Greater than 5,000 mg/kg (The solid line represents the 1:1 slope.)

### 3.3.2.1 Sampling Method—Crushed v. Intact

Analysis of drywall in homes using portable XRF analysis can be done three different ways. The first is to obtain measurements directly on the drywall *in situ* through paint/plaster, the second is to obtain measurements *in situ* but with the paper and paint/plaster removed, and the third is to first remove a sample of drywall with a coring tool or saw, and then analyze the sample. For the first method, we previously reported

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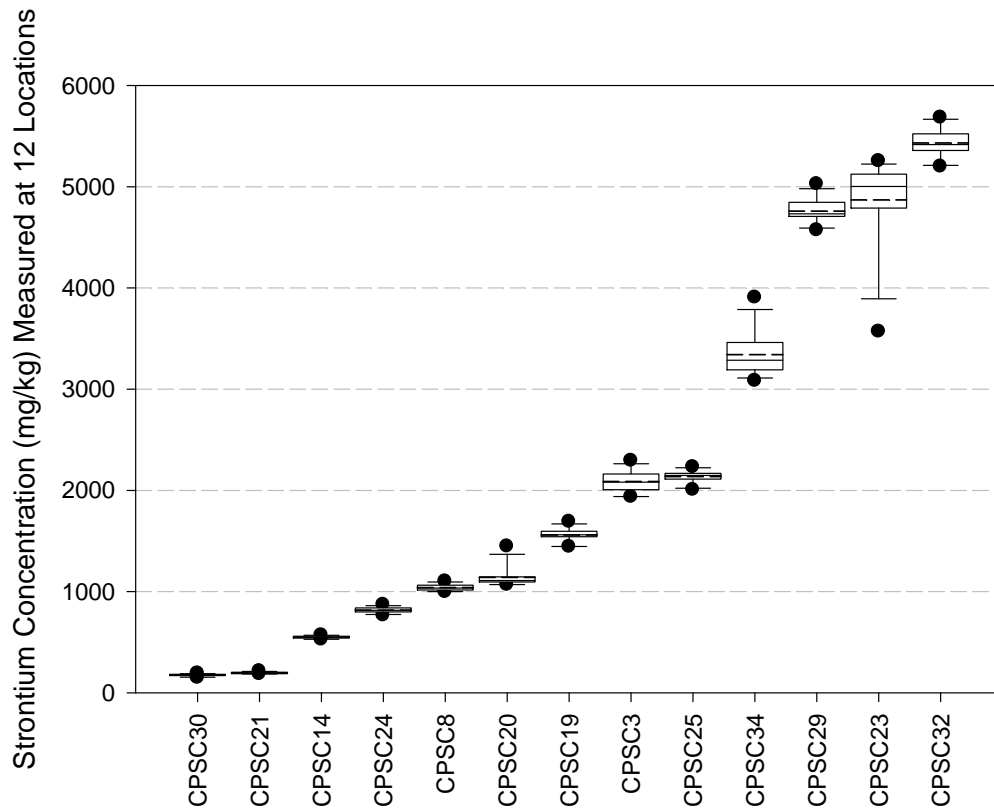
on the impact of surface coatings on obtaining accurate measurements of the drywall core using XRF (EH&E 2010). The second and third methods involve measuring the drywall core without interference from paint/plaster, but the latter method may provide a sample that is crushed and homogenized as opposed to intact, especially when using a coring tool. Therefore, we assessed agreement between measurements made directly on an intact core and then measurements made on the same sample after it was crushed. The results of this analysis are presented in Figure 3.4. There was a strong, positive, 1:1 relationship between strontium concentrations measured on an intact core and measurements made on a 2.5 gram, crushed sample (Spearman  $r = 0.99$ ,  $p < 0.0001$ ).



**Figure 3.4** Comparison of Strontium Measurements Made on Intact and Crushed Drywall Samples

### 3.3.3 Objective 3—Assessment of Strontium Intra-Board Variability and Sampling Methods

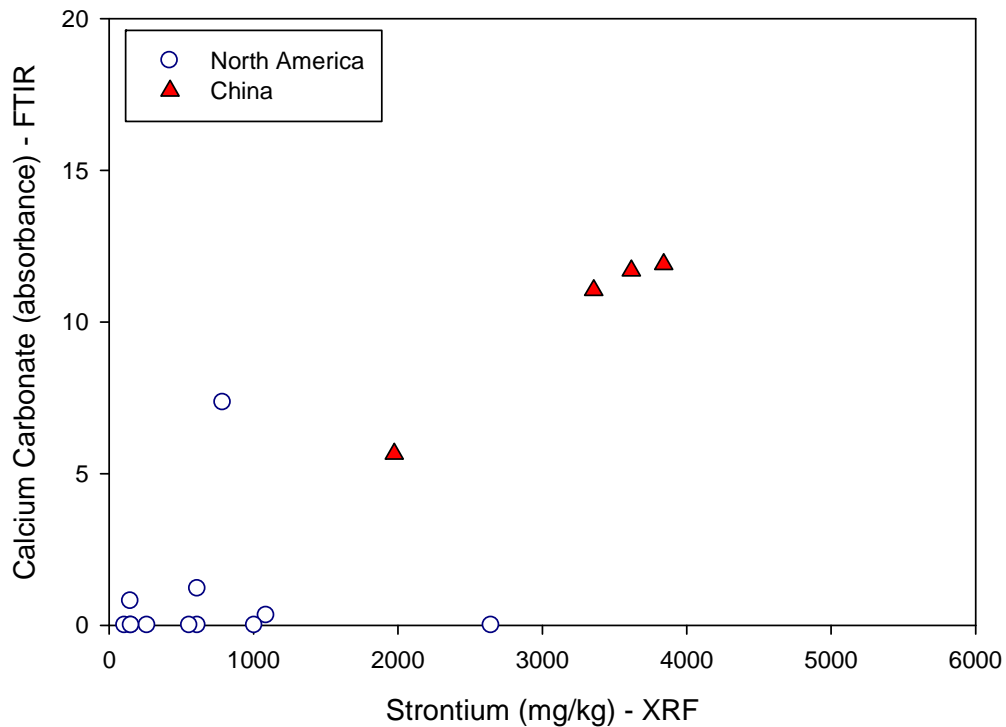
Results from strontium measurements made using an XRF analyzer (Innov-X) on twelve locations on each of the ten different drywall boards are presented in Figure 3.5. Similar results were observed for the Bruker and two Thermo/Niton brand XRF analyzers. Each box represents variability of the 12 measurements made from each of the 13 respective drywall boards. The results demonstrate intra-board variability is small for boards with strontium measurements nominally less than 3,000 mg/kg (coefficient of variation = 2 – 9%). The intra-board measurements demonstrated greater variation at concentrations greater than 3,000 mg/kg, although the overall precision in this range may not be as relevant.



**Figure 3.5** Distribution of Strontium Measurements Made at Twelve Unique Locations on Each Drywall Board

### 3.3.4 Objective 4—Review of the Two-Component Carbonate/Strontium Marker Using FTIR/XRF

During EH&E’s 51-home study, samples of known origin (‘catalog samples’) were measured to determine if there were unique markers of Chinese drywall. Based on testing of the catalog samples, it was observed that neither strontium nor carbonate alone were both sensitive and specific as a marker of “Chinese” drywall (i.e., testing by either method alone could produce some false positives and false negatives) (Figure 3.6). However, when strontium and carbonate were used in conjunction for analysis of samples, they were found to be a reliable marker of problematic drywall for that study.

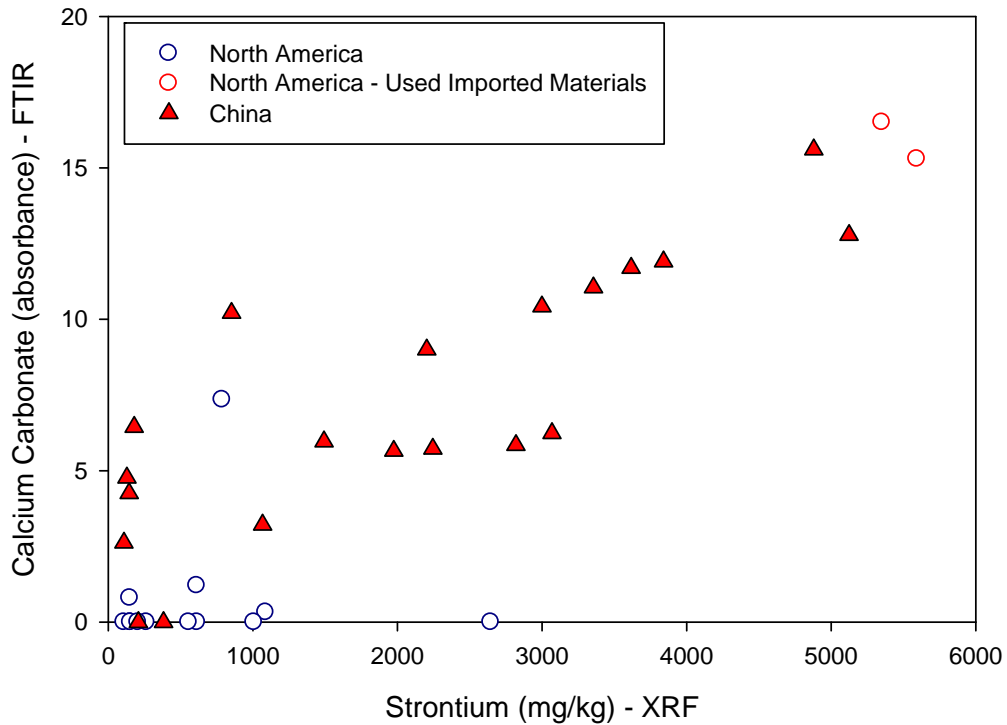


**Figure 3.6** Comparison of Strontium Concentrations (mg/kg) and Carbonate (Absorbance) Measured in Drywall Samples from Catalog Set at Time of EH&E’s 51-home Study

As a result, the 51-home study characterized homes based on whether or not drywall in the homes had the carbonate/strontium marker (‘FTIR/XRF marker’). This marker was found to be a significant predictor of hydrogen sulfide and elevated rates of corrosion in these study homes—homes which were qualified for the study based on their year of construction and self-reported occupant complaints.

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Carbonate and strontium results obtained on the full set of drywall samples of known origin ('catalog samples', identified in Table 3.2) are presented in Figure 3.7. When analyzing a more complete dataset, carbonate and strontium were found to be significantly and positively correlated, on average (Spearman  $r=0.72$ ,  $p<0.01$ ). However, the potential for false positives remained if only one marker was used.



**Figure 3.7** Comparison of Strontium Concentrations (mg/kg) and Carbonate (Absorbance) Measured in Drywall Samples from Full Catalog Set Used in this Study

The second aim of this task was to compare strontium concentrations to gas emissions and corrosion. This assessment of strontium concentrations as a marker of gases and corrosion is presented in Section 6.2, Source Markers and Corrosion.

## **4.0 SOURCE MARKER ANALYSIS—ORTHORHOMBIC SULFUR**

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### **4.1 INTRODUCTION**

Similar to the investigation of strontium as a source marker, there were two specific aims in evaluating orthorhombic sulfur as a marker of problematic drywall. The first aim was to evaluate the precision and accuracy of orthorhombic sulfur measurements. The second aim was to evaluate the sensitivity and specificity of orthorhombic sulfur as a marker of problematic drywall. This section focuses on the first aim—testing done to compare laboratory methods and evaluate the precision of orthorhombic sulfur measurements. The analysis of orthorhombic sulfur as a sensitive and specific marker of problematic drywall through comparison to gas emissions and corrosion rates is described in Section 6.

Elemental sulfur exists as three allotropes with the most stable and common being S<sub>8</sub>. S<sub>8</sub> has been proposed as a marker of suspect drywall by the EPA and other governmental and non-governmental groups.

EH&E conducted an evaluation of S<sub>8</sub> that included the following objectives:

#### *Objective 1*

Compare three analytical methods (EPA Environmental Response Team [ERT]/REAC SOP 1805, GC/MS [toluene-extraction] and GC/ECD) for analyzing orthorhombic sulfur in a subset of drywall samples from the CPSC 'catalog' drywall samples in this study

#### *Objective 2*

Assess intra-board variability to determine representativeness of using a single 'core' sample to characterize larger pieces of drywall

#### *Objective 3*

Determine orthorhombic sulfur concentrations in catalog drywall samples and archived drywall samples from the 51-home study

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## 4.2 METHODS

### 4.2.1 Study Design

#### 4.2.1.1 Laboratory Method Comparison—Catalog Samples

To evaluate agreement among the three analytic methods, a subset (n=13) of the catalog samples were analyzed using each of the three methods discussed previously (Table 4.1). A 15g sample was removed from each board, homogenized, and divided into three equivalent subsamples to ensure sample uniformity across methods.

<b>Table 4.1</b> Overview of Analytic Methods Used to Determine Orthorhombic Sulfur Concentrations		
<b>Analytic Method</b>	<b>Description</b>	<b>Number of Primary Samples</b>
EPA ERT/REAC SOP 1805	<ul style="list-style-type: none"><li>• Soxhlet extraction (dichloromethane:acetone)</li><li>• GC/MS</li></ul>	13
GC/MS (toluene extraction)	<ul style="list-style-type: none"><li>• Solvent extraction (toluene)</li><li>• GC/MS</li></ul>	13
GC/ECD	<ul style="list-style-type: none"><li>• Solvent extraction (toluene)</li><li>• GC/ECD</li></ul>	35
EPA	U.S. Environmental Protection Agency	
ERT/REAC	Environmental Response Team Response Engineering and Analytical Contract	
SOP	standard operating procedure	
GC/MS	gas chromatography mass spectrometry	
GC/ECD	gas chromatography electron capture detector	

Thirteen drywall samples were selected from the catalog samples for analysis by EPA's ERT/REAC SOP 1805 ('REAC SOP 1805') and a similar laboratory method that also uses GC/MS but with a toluene based extraction ('GC/MS (toluene extraction)'). While both methods rely on quantification of S<sub>8</sub> using GC/MS, the methods differ in the solvent extraction method and chromatographic column used to separate constituents of the sample. A complete description of the laboratory methods can be found in the Section 4.2.2.

In addition to the thirteen samples analyzed by both EPA REAC SOP 1805 and the GC/MS (toluene extraction) method, all of the catalog samples (n = 35) were analyzed for S<sub>8</sub> using a third method—GC/ECD. This method has been proposed as equivalent to

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the two methods that use GC/MS for determining  $S_8$  concentrations (Singhvi et al. 2009). Duplicate samples were prepared from six of the catalog boards and analyzed by GC/ECD to evaluate method precision.

### 4.2.1.2 Intra-Board Variability

Intra-board variability of  $S_8$  was assessed by analyzing multiple samples (n=3 to12) from eight separate catalog samples (Table 4.2). The boards were marked in evenly distributed sections and samples were taken from the mid-point of each location. Before sending the samples for  $S_8$  analysis, the samples were measured for strontium concentration by XRF.

<b>Table 4.2</b> Description of Samples Used for Intra-board Variability Tests		
<b>Catalog ID</b>	<b>Original Board Size</b>	<b>Number of Samples</b>
CPSC 3	1' x 1'	12
CPSC 10	9" x 6"	3
CPSC 14	9" x 6"	12
CPSC 15	1' x 1'	3
CPSC 25	9.5" x 16"	3
CPSC 32	1' x 1'	12
CPSC 34	1' x 1'	5
CPSC 35	1' x 1'	5

CPSC U.S. Consumer Product Safety Commission

### 4.2.1.3 Archived In-Home Samples

In addition to the catalog samples, archived samples from EH&E's 51-home study were analyzed for  $S_8$  concentrations by GC/ECD. During the 51-home study, samples were cored from the wallboard around electrical outlets in most rooms. These samples were typically <0.5 grams per core sample. Additionally, a larger piece (~1'x1') of drywall was obtained from each home and archived. The cored samples, not originally collected for this purpose, did not provide sufficient mass to provide detection limits in the 5 – 10 mg/kg range and therefore be comparable to the sensitivity anticipated for categorizing problematic drywall. Therefore, cored samples from the same room were composited to provide sufficient mass for analysis and provide a limit of detection (LOD) in the 5 mg/kg range. For these core composite samples, an equal mass from each of



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the individual core samples was combined to evenly represent the different wall boards sampled from a room. For the large wallboard piece, a 2 – 5 gram sample was removed and sent for analysis. The result was that each home had up to three total samples analyzed for  $S_8$  – two composite samples (one from each of two rooms), and one non-composite sample (n=153).

### 4.2.2 Laboratory Methods

Orthorhombic sulfur analysis was conducted by Columbia Analytical Services (Simi, California). The laboratory was provided an EH&E sample ID but were blinded to the origin of all samples. Three methods were used: EPA REAC SOP 1805, GC/MS (toluene extraction) and GC/ECD. Drywall samples were crushed by EH&E, homogenized, and divided into three equal subsamples to ensure uniformity. A negative control sample (known unaffected drywall) was prepared by Columbia Analytical Services and analyzed along with the various subsamples as an added check for quality control. A summary of each method was provided by Columbia Analytical Services and each is presented in the following sections.

#### 4.2.2.1 EPA REAC SOP 1805

Subsamples were extracted using EPA Method SW846 3541, “Automated Soxhlet Extraction” (Soxtherm). Samples were aliquoted, mixed with sodium sulfate to remove moisture, and surrogates (2-fluorophenol; phenol-d6; nitrobenzene-d5; 2-fluorobiphenyl; 2,4,6-tribromophenol; and terphenyl-d14) were added to evaluate extraction efficiency. Samples were then extracted per the method using a 4:1 mixture of dichloromethane:acetone. The samples were concentrated to a final volume of 1 mL and solvent exchanged into dichloromethane on an N-EVAP evaporator unit under nitrogen.

All samples contained sediment and therefore were filtered using a 0.45 micrometer ( $\mu\text{m}$ ) polytetrafluoroethylene (PTFE) syringe tip filter. The extracted samples were colored, which ranged from light yellow to dark brown. The darkest extract was analyzed at a 10 fold dilution.

A four point calibration was performed for the surrogate compounds. An EPA Method SW846 8270 internal standard mixture was added to an aliquot of the extracts. Sample

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extracts were analyzed on a GC/MS utilizing a DB-5 column (30m x 0.25mm x 0.25 $\mu$ m film thickness). Helium was used as the carrier gas in the analytical system. S<sub>8</sub> allotropes were identified based on the spectral match, comparing the mass spectra of the sample peak with mass spectra in a comprehensive mass spectral library. The concentration of S<sub>8</sub> was estimated using a response factor of one and the response of the associated internal standard (phenanthrene-d10). The results are reported as S<sub>8</sub> in mg/kg.

### 4.2.2.2 GC/MS (Toluene Extraction)

One gram (1g) aliquots of each subsample was solvent extracted with agitation for two minutes using toluene (5 mL). A 1.0 microliter ( $\mu$ L) aliquot of the sample extract is injected into the gas chromatograph by splitless injection where a fused silica capillary column separates S<sub>8</sub> from other species in the sample and a mass selective detector operated in the SCAN mode detected the S<sub>8</sub>. Helium was used as the carrier gas in the analytical system. The retention time and select characteristic ions of S<sub>8</sub> were used for identification. Quantitative analysis was performed by using an internal standard calibration procedure, which involves the comparison of instrument responses from the target compounds in the sample to the response of the internal standard that is added to the sample prior to analysis. The ratio of the peak area of the target compound in the sample to the peak area of the internal standard in the sample was compared to a similar ratio derived for each calibration standard.

Additional instrument quality control checks included daily tuning of the mass spectrometer using decafluorotriphenylphosphine (DFTPP), a five point calibration for S<sub>8</sub>, initial calibration verification standard analysis, and evaluation of extraction surrogate recovery.

The concentration of S<sub>8</sub> in the sample was reported in mg/kg, and was calculated using the analytical result, the sample weight and the final extract volume.

### 4.2.2.3 GC/ECD

One gram (1g) aliquots of the subsamples were solvent extracted with agitation for two minutes using toluene (5 mL). A 1.0  $\mu$ L aliquot of the sample extract was injected into

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the gas chromatograph by splitless injection where a fused silica capillary column separates  $S_8$  from other species and an ECD detects the  $S_8$ . Helium was used as the carrier gas in the analytical system. The identification of  $S_8$  was performed by comparing the retention time of  $S_8$  with the respective retention time of an authentic standard. Quantitative analysis was performed by using an internal standard calibration procedure, which involves the comparison of instrument responses from the target compounds in the sample to the response of the internal standard that is added to the sample prior to analysis. The ratio of the peak area of the target compound in the sample to the peak area of the internal standard in the sample was compared to a similar ratio derived for each calibration standard.

Additional instrument quality control checks included a five point calibration for  $S_8$ , initial calibration verification standard analysis, and evaluation of extraction surrogate recovery. The concentration of  $S_8$  in the sample was reported in mg/kg, and was calculated using the analytical result, the sample weight and the final extract volume.

### 4.3 RESULTS

#### 4.3.1 Objective 1—Analytic Method Comparison

Results of the  $S_8$  measurements of the catalog samples by three different methods are presented in Table 4.3.

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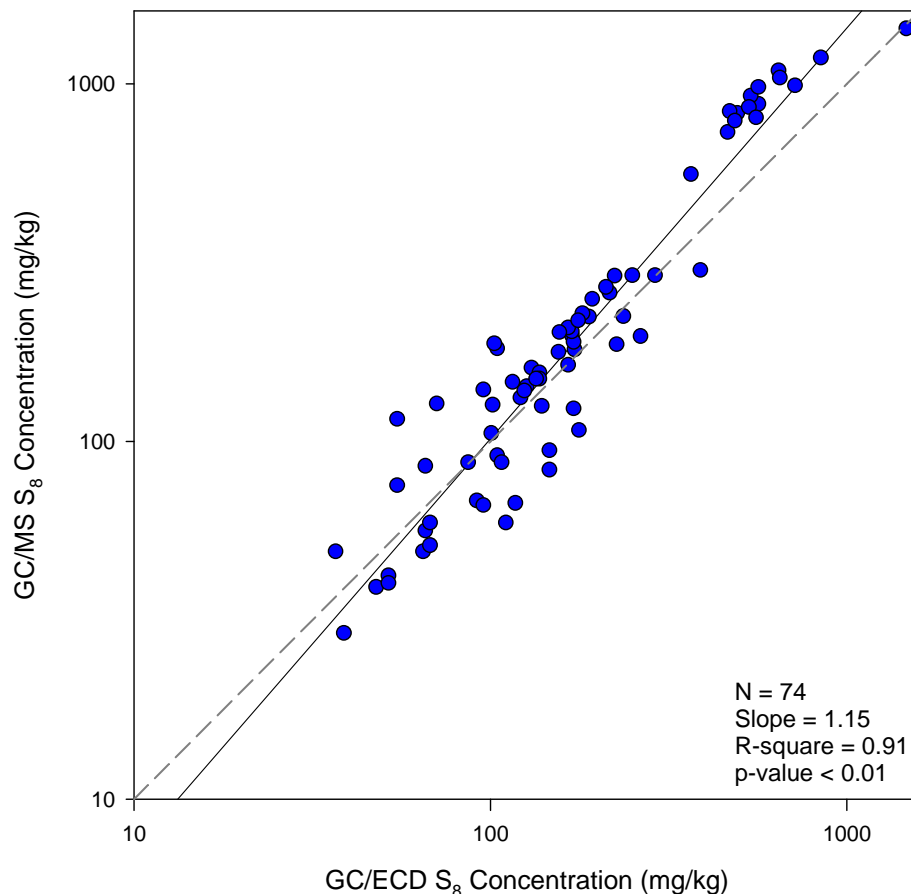
<b>Table 4.3</b> Comparison of Orthorhombic Sulfur Concentrations (mg/kg) Measured Using Three Different Methods			
<b>Catalog ID</b>	<b>REAC SOP 1805</b>	<b>GC/MS (toluene extraction)</b>	<b>GC/ECD</b>
CPSC1	ND	< 5	< 5
CPSC3	2.3	79	91
CPSC4	ND	< 5	< 5
CPSC5	ND	< 5	< 5
CPSC10	4.4	6	7.7
CPSC17	ND	< 5	< 5
CPSC19	ND	< 5	< 5
CPSC22	ND	< 5	< 5
CPSC23	ND	< 5	< 5
CPSC24	ND	< 5	< 5
CPSC26	ND	< 5	< 5
CPSC34	650	610	870
CPSC35	64	1,000	1,200

mg/kg milligrams per kilogram  
 REAC REAC SOP 1805  
 GC/MS gas chromatography mass spectrometry  
 GC/ECD gas chromatography electron capture detector

Laboratory limits of detection were 10 mg/kg for REAC SOP 1805, and 5 mg/kg for GC/MS (toluene extraction) and GC/ECD. Limits of detection are based on a 1 gram sample of drywall

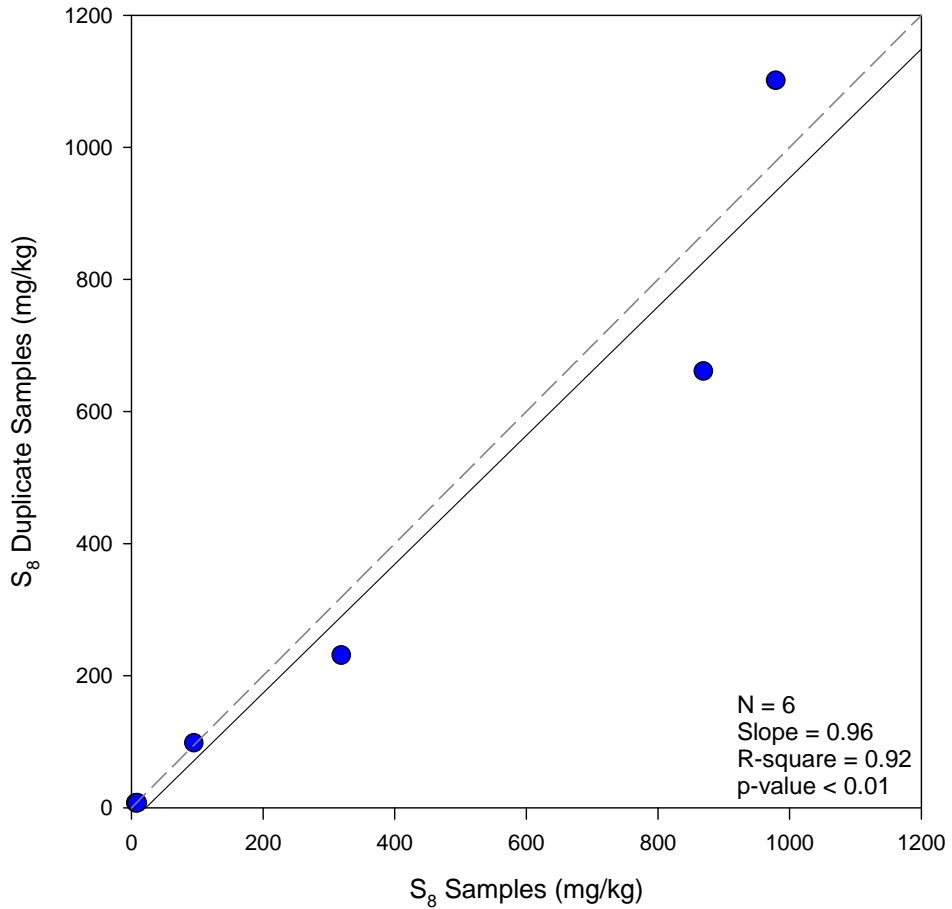
The three laboratory methods all showed 100% agreement on detect versus non-detect for S<sub>8</sub>. Results from the GC/MS and GC/ECD analyses were generally in good agreement with each other, although the GC/ECD results were consistently higher than the GC/MS results for samples with quantifiable S<sub>8</sub> concentrations. Although there are only four detectable samples available for comparison, concentrations of S<sub>8</sub> determined by the REAC SOP 1805 appear less consistent when compared to the other two laboratory methods.

In addition to the samples measured in this study, Columbia Analytic Services provided data obtained from analysis of drywall samples in other research not related to CPSC or EH&E. These additional data points show strong agreement between drywall samples analyzed by the GC/MS (toluene extraction) and GC/ECD methods (slope = 1.15; p<0.001) (Figure 4.1), consistent with the finding of strong agreement observed for the CPSC/EH&E samples presented in Table 4.3.



**Figure 4.1** Comparison of S<sub>8</sub> Concentrations Measured Using GC/MS and GC/ECD by Columbia Analytical (n=74). The regression line is represented by the solid line and the 1:1 slope is represented by the dashed line.

Determination of S<sub>8</sub> concentrations by GC/ECD was also found to be a reasonably precise method. Results of duplicate analyses (n=6) are presented in Figure 4.2 and show a 1:1 relationship between duplicate analyses. The mean relative standard deviation was 23%, and ranged from 1% – 43%, with stronger agreement observed at the lower end of the concentration distribution.



**Figure 4.2** Comparison of S<sub>8</sub> Concentrations (mg/kg) in Duplicate Samples as Measured by GC/ECD

### 4.3.2 Objective 2—Assessment of Intra-board Variability

Multiple measurements of S<sub>8</sub> by GC/ECD on the same drywall boards showed very low intra-board variability (Table 4.4). The average coefficient of variation was 8.5% and ranged from 0% to 23% across boards. Importantly, the presence or absence of S<sub>8</sub> was consistent across drywall boards. For example, when S<sub>8</sub> was determined to be less than the detection limit in one location, the remaining locations were all also less than the detection limit. Similarly, if S<sub>8</sub> was detected on one location of a drywall board, it was consistently detected in the remaining locations.

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<b>Table 4.4</b> Orthorhombic Sulfur Concentrations (mg/kg) at Multiple Locations Per Board												
<b>Sample ID</b>	<b>Sample Number</b>											
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>
CPSC3	130	130	110	110	120	120	100	110	140	130	150	130
CPSC14	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
CPSC32	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
CPSC34	870	700	740	750	700							
CPSC35	690	980	1200	980	870							
CPSC10	9.9	7.9	7.7									
CPSC15	99	96	110									
CPSC25	<5	<5	<5									

mg/kg milligrams per kilogram

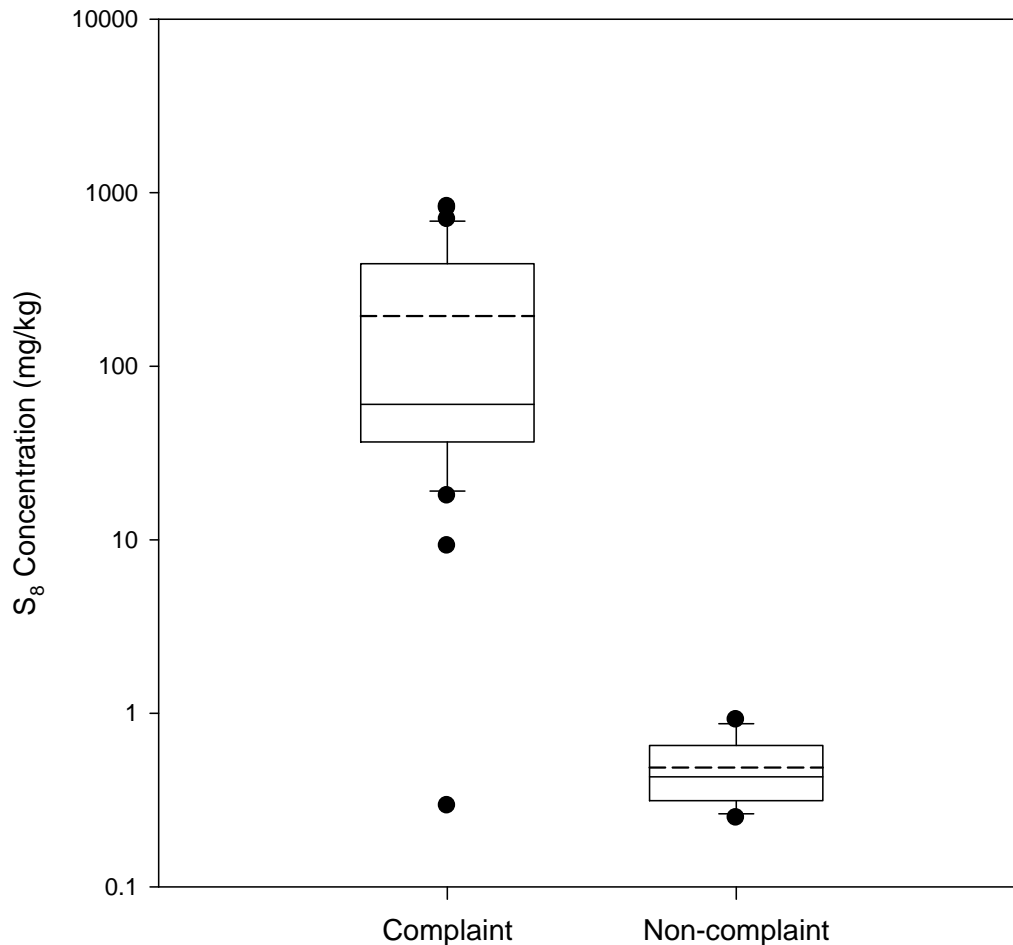
**4.3.3 Objective 3—Determination of Orthorhombic Sulfur Concentrations in Catalog Samples and Archived Samples from the 51-Home Study**

*4.3.3.1 Orthorhombic Sulfur Concentrations in Catalog Samples*

S<sub>8</sub> concentrations were determined for the full set of catalog samples by GC/ECD. S<sub>8</sub> concentrations of Chinese imported drywall boards ranged from <5 to 1,200 mg/kg in the catalog samples, with a median value of <5 mg/kg (mean = 191 mg/kg). All of the North American drywall board S<sub>8</sub> concentrations were <5 mg/kg. The S<sub>8</sub> concentrations measured by GC/ECD provide the basis for comparing the S<sub>8</sub> concentrations against measurements of gases and corrosion (see Section 5).

*4.3.3.2 Orthorhombic Sulfur Concentrations in Archived Samples from the 51-Home Study*

In the 51-home study, houses were identified as ‘complaint’ or ‘non-complaint’ based on homeowner reports to the CPSC that included information on corrosion and odor in the home, as well as possible health effects (EH&E 2010). House-average S<sub>8</sub> concentrations ranged from <5 to 830 mg/kg in CPSC complaint homes, with a median concentration of 54 mg/kg (mean = 180 mg/kg). For the non-complaint homes, house-average S<sub>8</sub> concentrations were all <1 mg/kg. House-average S<sub>8</sub> concentrations were significantly (p<0.01) higher in complaint homes compared to non-complaint homes (Figure 4.3).



**Figure 4.3** Comparison of S<sub>8</sub> Concentrations Measured In Drywall Samples from Complaint and Non-complaint Homes in the 51-home Study

Additionally, of the three drywall samples measured for S<sub>8</sub> in each of the 10 non-complaint homes (n=30), none of the individual samples had detectable levels of S<sub>8</sub> (detection limit range for individual samples <1 mg/kg – 33 mg/kg; median <10 mg/kg). An assessment of these S<sub>8</sub> results as a marker of gases and corrosion in the home is presented in Section 6.2, Source Markers and Corrosion.



## **5.0 CHAMBER-BASED CORROSION**

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### **5.1 INTRODUCTION**

Several methods have been utilized to identify Chinese drywall (e.g., XRF/FTIR, S<sub>8</sub>, housing characteristics and corrosion potential). The extent to which these markers identify all Chinese drywall or, more importantly, only problematic drywall, is unknown. This section outlines the results of a chamber-based study designed to aid in the identification of markers of problematic drywall as it relates to a primary dependent characteristic of problematic drywall, corrosion.

The objectives of this chamber-based study were:

#### *Objective 1*

Conduct pilot testing to identify an appropriate chamber testing scenario to address Objective 2

#### *Objective 2*

Identify the potential of drywall in the catalog samples to cause corrosion

### **5.2 METHODS**

During the initial study design phase, the chamber environment was designed to maintain 77 °F and 50% RH. Preliminary results indicated low rates of corrosion under these conditions in the test chambers during the eight day exposure period. The chamber environment was altered, in a second set of tests, to conditions that more closely reflected outdoor conditions during the 51-home study (90 °F; 50% RH). These conditions were found to induce corrosion to occur over a time frame of approximately eight days. The methods for the elevated temperature test are described in detail as follows. The lower temperature tests were performed in a similar manner.

#### **5.2.1 Chamber Testing**

The chamber testing lasted a total of nine days, which included a 23-hour conditioning phase followed by the silver and copper coupons being exposed for approximately eight

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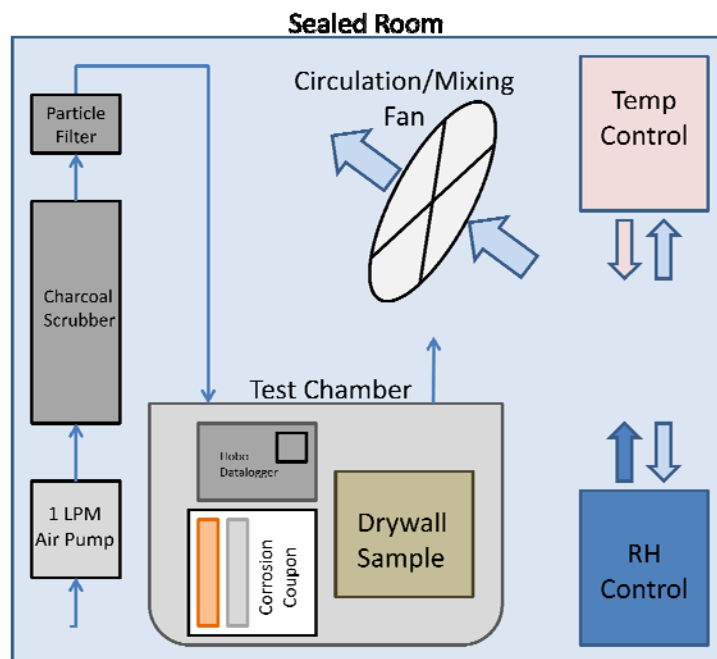
days. Chamber corrosion testing was carried out in a temperature and RH controlled room (12' x 9.25' x 7', with a 2' plenum). The room was maintained at 90 °F (32 °C) +/- 5 °F using a heater and a thermostat, and 50% RH +/- 8% RH using a water bath filled with deionized water. Air was constantly flowing above the surface of the water bath. The whole room was kept in a well mixed condition by a large, suspended box fan.

Each test consisted of placing a drywall sample into a 6L stainless steel chamber that also included a temperature and RH datalogger. An air pump and a charcoal scrubber were used to condition the stainless steel chamber. The air pump was housed inside the larger temperature and RH conditioned chamber to avoid condensation in the tubing (any heat generated by the pumps was shown to not adversely impact temperature control). The stainless steel chamber was equipped with clamps and a non-volatile organic compound-emitting Tygon<sup>®</sup> gasket that allowed the lid to be sealed in place, and 2 threaded Swagelok<sup>®</sup> ports to permit conditioning of the chamber.

Each test consisted of three phases. In the first phase, a 3-inch by 3-inch gypsum sample with all four cut edges exposed and the two large faces having intact paper sheathing was placed on top of a small glass jar inside the stainless steel chamber. The datalogger was also placed in the chamber at this time. The chamber was then clamped shut, and the pump, charcoal scrubber, and particle filter were connected to one of the Swagelok<sup>®</sup> ports. The other port was left open as an exhaust. For 23 hours the pump drew temperature and RH controlled air from the chamber, passed it through the scrubber, and into the stainless steel chamber at a rate of approximately 1 liter per minute (LPM).

After 23 hours, the test moved into the second phase. The lid of the chamber was briefly opened and a corrosion classification coupon containing one strip each of pre-cleaned copper and silver was placed inside, oriented so that the individual metal strips extended from near the bottom of the chamber to near the top. The coupon was approximately 2.5 inches from the drywall sample. The chamber was again clamped closed, and the pump continued to deliver conditioned air at 1 LPM (Figure 5.1).

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**Figure 5.1** Schematic of the Chamber Testing Equipment

After one hour, the test moved to the final phase. The pump, scrubber, and filter apparatus was disconnected from the Swagelok<sup>®</sup> port, and both Swagelok<sup>®</sup> ports were sealed closed. The chamber was then left in the temperature controlled chamber for eight days, at which point the chamber was opened, the coupon removed, packaged, and sent to the laboratory for analysis. The temperature and RH datalogger was also downloaded and the data checked for temperature or RH variation during the exposure period. Prior to re-using the system, each chamber was thoroughly cleaned with an Alconox solution, rinsed with deionized water, and carefully dried.

The corrosion classification coupons were used to determine the integrated corrosion rate. The corrosion coupons used in this study contained copper and silver metal and were supplied by Purafil, Inc., Research and Development Laboratory in Doraville, Georgia. At the end of the sampling period, the corrosion coupons were collected, placed in sealed containers and returned to Purafil for analysis. The laboratory measured the thickness of several copper and silver compounds including silver sulfide (Ag<sub>2</sub>S), silver chloride (AgCl), Ag 'unknown', copper sulfide (Cu<sub>2</sub>S), copper oxide (CuO), and Cu 'unknown' present in the sample corrosion coupons. The laboratory normalized the data using the actual period of exposure and reported the result in units of "angstroms per 30 days of exposure." This rate is not directly comparable to in-home

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measurements because the samples were not taken in ambient conditions. However, the corrosion rates are directly comparable between samples because they were all obtained under identical test conditions. Corrosion rates were compared with reference values contained in the Instrumentation, Systems, and Automation Society (ISA) Standard ISA-71.04-1985, *Environmental Conditions for Process Measurement and Control Systems: Airborne Contaminants*.

### 5.2.2 Quality Assurance/Quality Control

For corrosion monitoring, blank and duplicate samples were obtained during each round of testing to estimate the background rate of corrosion for this sampling design. Additionally, five replicate samples were obtained (Note: duplicate samples refer to repeat testing using a different piece of drywall from the same larger piece, while replicate samples refer to repeat testing of the exact same drywall sample that was originally tested). Temperature and relative humidity were recorded as 5-minute averages using a HOBO datalogger in each stainless steel test chamber and remained stable during testing. Over 95% of Temperature and relative humidity readings remained between 89 and 92 °F, and between 45 and 56% RH, over the 9-day period. Minimum and maximum temperature and RH recorded were 86 °F, 96 °F, 44%, and 60% respectively.

Each chamber was given a unique number and samples were randomly assigned to a specific chamber to reduce the potential for systematic bias. Corrosion rate data were analyzed for trends by chamber and no systematic bias found.

### 5.3 RESULTS

The initial study design had a chamber maintained at 77 °F and 50% RH. A total of 13 tests (includes one blank and one duplicate sample) were run under this scenario. Test results indicated that these chamber conditions were not conducive to generating measurable corrosion in a short test period (nine days).

Silver and copper corrosion rates were subsequently determined from the final chamber design (90 °F and 50% RH) for all 'catalog' samples and ranged from 94 angstroms per

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30 days (A/30d) to 1473 A/30d, and <32 A/30d to 589 A/30d, respectively. The results from this chamber testing were compared against the S<sub>8</sub> and strontium source marker concentrations, described in the following section of this report (Section 6). Individual corrosion rate results can be found in the summary table in the Discussion section of this report (Section 7).

Analysis of blank samples (n=4) showed a low rate of background corrosion. All blank samples had Cu<sub>2</sub>S copper corrosion rate of <32 A/30d. For Ag<sub>2</sub>S, the mean corrosion rate was 181 A/30d with a standard deviation of 104 A/30d. The method limit of detection for Ag<sub>2</sub>S was defined as three times the standard deviation of field blank results (104\*3 = 312 A/30d). Duplicate and replicate tests showed strong agreement and are presented in Table 5.1.

<b>Table 5.1</b> Comparison of Corrosion Rates (A/30d) between Sample and Duplicate Samples						
<b>Catalog ID</b>	<b>Cu<sub>2</sub>S</b>			<b>Ag<sub>2</sub>S</b>		
	<b>Sample</b>	<b>Duplicate</b>	<b>Replicate</b>	<b>Sample</b>	<b>Duplicate</b>	<b>Replicate</b>
CPSC2	<32	<32	–	156	109	–
CPSC3	227		<32	673	–	592
CPSC5	<32	<32	–	324	302	–
CPSC6	<32	–	<32	131	–	218
CPSC7	<32	–	<32	94	–	128
CPSC8	<32	<32		203	90	–
CPSC15	265	–	<32	686	–	624
CPSC16	<32	–	<32	187	–	125
CPSC18	<32	–	<32	842	–	857
CPSC33	<32	–	<32	156	–	150
CPSC34	589	–	<32	1,473	–	935
CPSC35	530	–	<32	1,052	–	1,017

Cu<sub>2</sub>S    copper sulfide  
 Ag<sub>2</sub>S    silver sulfide

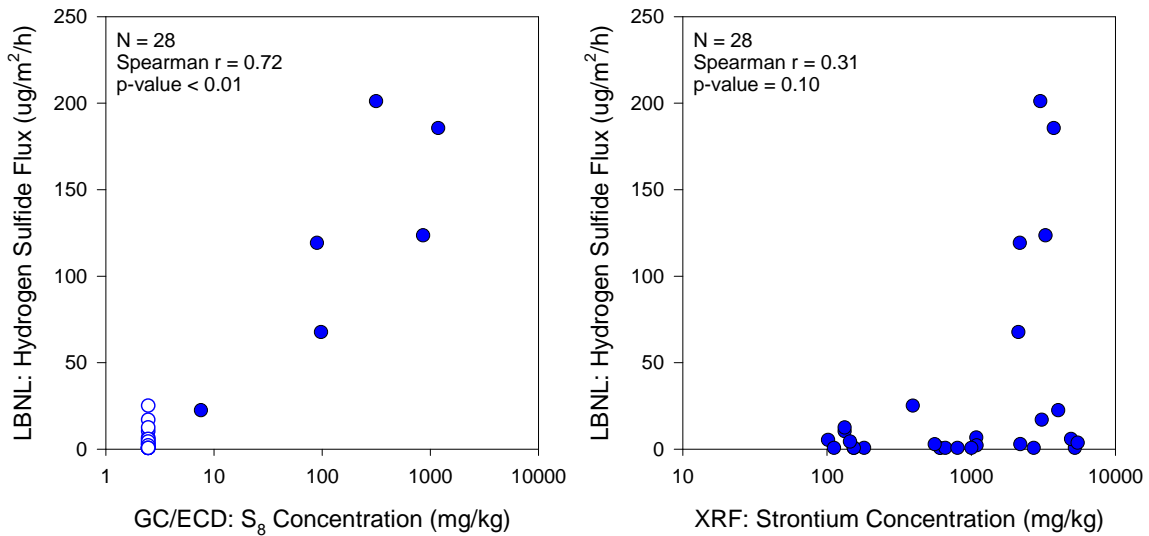
## 6.0 SOURCE MARKERS AND EFFECT

### 6.1 SOURCE MARKERS AND GAS EMISSIONS

#### 6.1.1 Source Markers and Gas Emissions—Chamber Testing

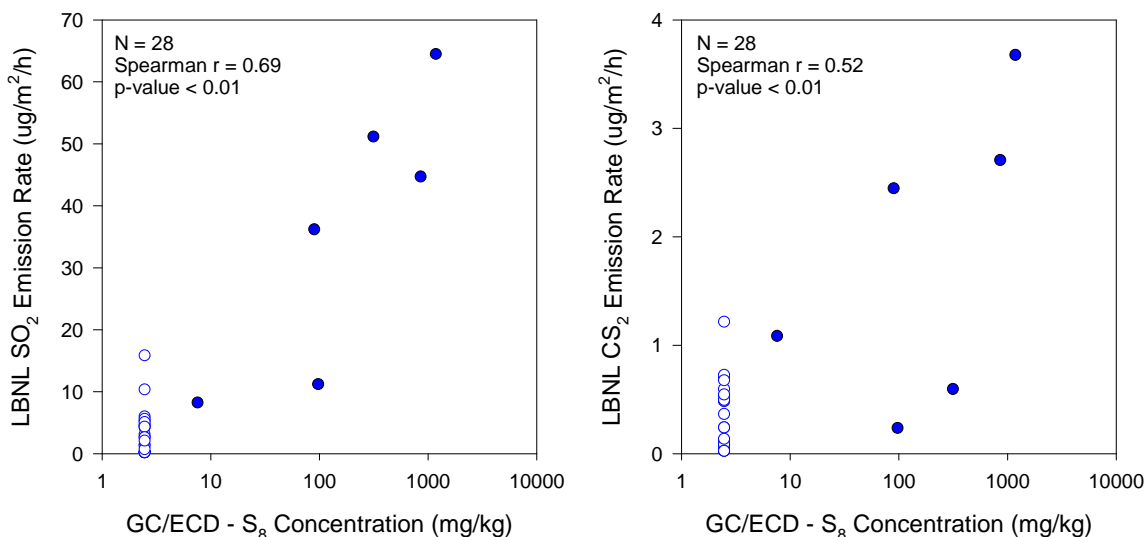
In a recent report, Lawrence Berkeley National Laboratory (LBNL) reported reactive sulfur compound emissions data for a number of drywall samples. Most of these drywall samples overlapped with drywall samples received by EH&E, which were analyzed for  $S_8$  and strontium and provide the basis for comparing gas emissions to source marker concentrations.

$S_8$  measured in drywall samples in this study was found to be strongly associated with hydrogen sulfide ( $H_2S$ ) emissions, while strontium levels, taken alone, were generally found to be a poor predictor of  $H_2S$  emissions when evaluating all North American and Chinese samples (Figure 6.1).



**Figure 6.1** Scatterplot Showing the Relationship Between a)  $S_8$  Concentration (mg/kg) and Hydrogen Sulfide Flux and b) Strontium (mg/kg) and Hydrogen Sulfide Flux. Open circles represent points where the  $S_8$  concentration was <LOD

In addition to hydrogen sulfide,  $S_8$  concentrations were also found to be moderately associated with carbon disulfide ( $CS_2$ ) and sulfur dioxide ( $SO_2$ ) emission rates (Figure 6.2).



**Figure 6.2** Scatterplot Showing the Relationship between  $S_8$  Concentration (mg/kg) and a) Sulfur Dioxide Emission Rate and b) Carbon Disulfide Emission Rate. Open circles represent points where the  $S_8$  concentration was <LOD.

**6.1.2 Source Markers and Gas Emissions—51-Home Study**

Consistent with the associations observed between  $S_8$  and chamber-based  $H_2S$  emissions,  $S_8$  and  $H_2S$  were associated in the 51-home study. House average  $S_8$  concentrations in drywall, obtained by averaging the two room composite samples and one large bulk sample (see Methods for details) were significantly associated with house average  $H_2S$  concentrations, controlling for dew point and outdoor hydrogen sulfide concentrations (Table 6.1).

<b>Table 6.1</b> Regression Model Results Showing Predictors of House Average Hydrogen Sulfide Concentrations (Natural log-transformed) in Indoor Air			
<b>Parameter</b>	<b>Estimate</b>	<b>Standard Error</b>	<b>p-value</b>
Intercept	-3.98	0.96	<0.01
Orthorhombic Sulfur ( $S_8$ ) (natural log)	0.08	0.03	0.03
Dew Point	0.05	0.02	0.01
Outdoor Hydrogen Sulfide ( $H_2S$ )	0.18	0.11	0.09
Model $R^2=0.37$			

To explore the potential for interaction, the  $S_8$  concentration was dichotomized based on a cutoff of 10 mg/kg and the regression analyses were re-run. The presence of  $S_8$  in

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concentrations greater than 10 mg/kg was significantly associated with house average hydrogen sulfide, similar to the results using  $S_8$  as a continuous variable ( $p < 0.01$ , model  $R^2 = 0.41$ ). There was also significant interaction observed between the dichotomized  $S_8$  variable and dew point. The effect of dew point on hydrogen sulfide was dependent upon the presence of  $S_8$  ( $p < 0.05$ ).

In similar regression analyses used to identify predictors of  $H_2S$ ,  $S_8$  concentrations from the 51-home study were not associated with  $CS_2$  or  $SO_2$  concentrations in the homes ( $p = 0.25$ ,  $p = 0.13$ , respectively).

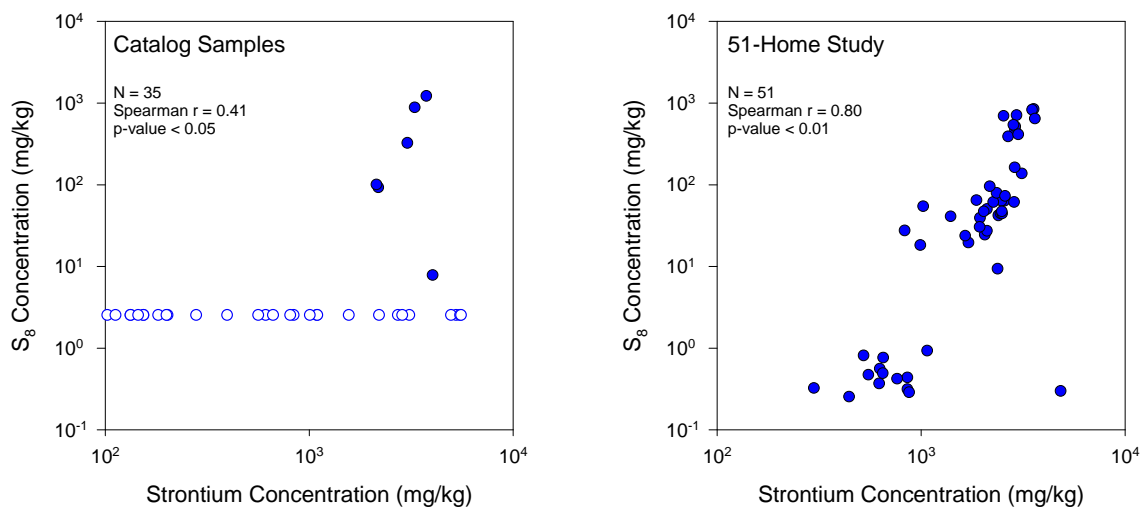
For strontium, house average strontium concentrations from the 51-home study were significantly associated with  $H_2S$  concentrations in the home. These results differ from the analysis of catalog samples where strontium concentrations were not associated with  $H_2S$  emissions. This difference is discussed in more detail below.

Parameter	Estimate	Standard Error	p-value
Intercept	-6.28	1.20	<0.001
Strontium (natural log)	0.32	0.13	0.01
Dew Point	0.05	0.02	<0.01
Outdoor Hydrogen Sulfide ( $H_2S$ )	0.18	0.11	0.10

Model  $R^2 = 0.38$

The evidence presented here suggests that  $S_8$  is directly associated with  $H_2S$  emissions, and thus is a desirable marker for problematic drywall. Strontium was significantly associated with  $H_2S$  in homes from the 51-home study, but not  $H_2S$  from the chamber tests of catalog samples. This may be because  $S_8$  and strontium are correlated in problematic drywall, as evidenced in the results from the in-home study (Figure 6.3), but they are not correlated in the catalog samples, which represent a more diverse cross-section of drywall samples (e.g., imported, domestic, year of production, etc.). As noted previously, the strontium marker appears to be useful when used as part of a multifactor screening process that includes additional information including age of installation and corrosion potential, among other factors.





**Figure 6.3** Correlation of  $S_8$  and Strontium in a) Catalog Samples and b) Homes in the 51-home Study. Open circles represent points where the  $S_8$  concentration was <LOD.

## 6.2 SOURCE MARKERS AND CORROSION

### 6.2.1 Source Markers and Corrosion—Chamber Testing

A summary of source marker concentrations and corresponding corrosion rates for all catalog samples is presented in Table 6.3.

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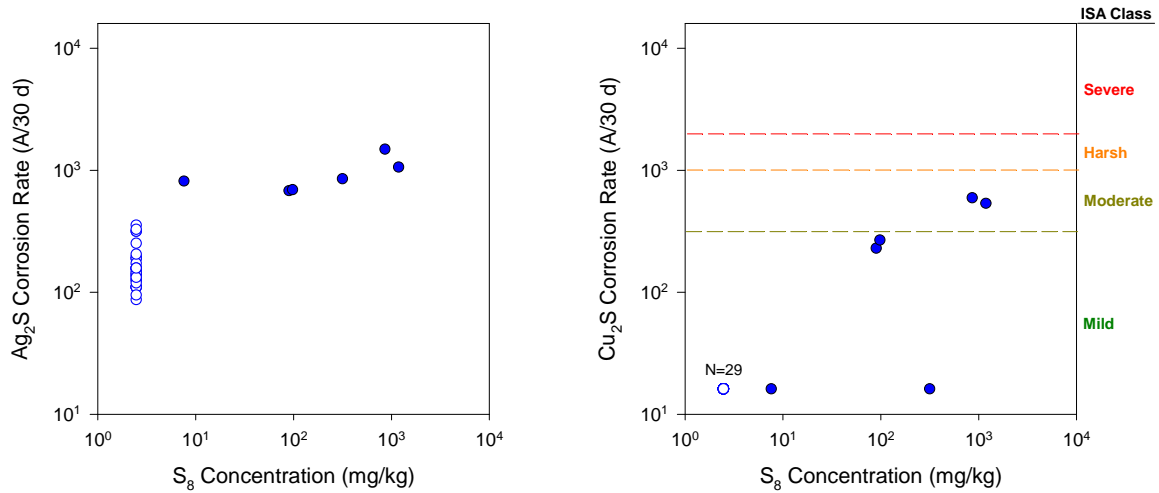
<b>Table 6.3</b> Summary Table						
<b>Catalog ID</b>	<b>CPSC ID</b>	<b>Country of Origin</b>	<b>Strontium (mg/kg)</b>	<b>S<sub>8</sub> (mg/kg)</b>	<b>Cu<sub>2</sub>S (A/30 days)</b>	<b>Ag<sub>2</sub>S (A/30 days)</b>
CPSC1	09-302-1429-02	Canada	273	<5	<32	150
CPSC2	09-840-9139-05	US	2,580	<5	< 32	156
CPSC3	09-302-1379-09	China	–	91	227	673
CPSC4	09-840-9858-01	US	946	<5	<32	118
CPSC5	09-810-7932-05	US	–	<5	<32	324
CPSC6	09-810-7639-06	US	–	<5	<32	131
CPSC7	09-840-9961-03	US	–	<5	<32	94
CPSC8	09-840-9962-08	US	–	<5	<32	203
CPSC9	09-810-8213-02	US	119	<5	<32	156
CPSC10	09-810-7069-06	China	3,740	7.7	<32	807
CPSC11	09-810-8235-03	US	–	<5	<32	187
CPSC12	09-810-8036-05	US	–	<5	<32	193
CPSC13	09-810-8037-01	US	–	<5	<32	137
CPSC14	09-810-8236-07	US	570	<5	<32	140
CPSC15	09-840-9672-07	China	2,350	99	265	686
CPSC16	09-302-2636-03	China	–	<5	<32	187
CPSC17	09-840-9707-05	China	351	<5	<32	125
CPSC18	09-840-9673-08	China	–	320	<32	842
CPSC19	09-302-1487-02	China	1,500	<5	<32	109
CPSC20	09-302-2634-01a	China	–	<5	<32	125
CPSC21	09-302-1492-02	China	–	<5	<32	109
CPSC22	09-302-1493-02a	China	–	<5	<32	109
CPSC23	09-302-2631-02b	China	5,890	<5	<32	156
CPSC24	09-810-7077-02	China	870	<5	<32	86
CPSC25	09-810-7078-05	China	2,200	<5	<32	312
CPSC26	09-302-2632-01	China	2,720	<5	<32	312
CPSC27	09-302-2633-02	China	2,810	<5	<32	171
CPSC28	09-302-2635-02	China	–	<5	<32	109
CPSC29	09-840-9667-01	China	–	<5	<32	249
CPSC30	09-302-2637-02a	China	–	<5	<32	133
CPSC31	09-302-1484-02a	US	195	<5	<32	143
CPSC32	09-840-9175-05	US: Used Imported Materials	6,540	<5	<32	351
CPSC33	09-840-9174-01	US: Used Imported Materials	6,410	<5	<32	156
CPSC34	09-810-7339-10	China	–	870	589	1,473
CPSC35	09-810-8357-01	China	273	1,200	530	1,052

CPSC	U.S. Consumer Product Safety Commission
mg/kg	milligrams per kilograms
S <sub>8</sub>	orthorhombic sulfur
Cu <sub>2</sub> S	copper sulfide
A/30	Angstroms per 30 days
Ag <sub>2</sub> S	silver sulfide

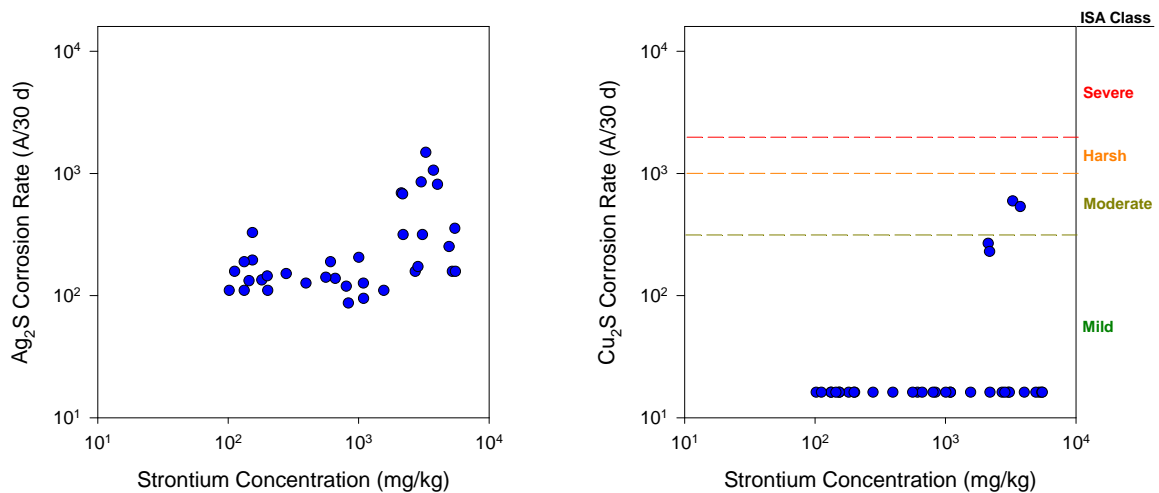
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S<sub>8</sub> concentrations in catalog drywall samples were associated with both silver ( $r = 0.66$ ,  $p < 0.01$ ) and copper sulfide corrosion ( $r = 0.82$ ,  $p < 0.01$ ) as determined in the chamber-based testing (Figure 6.4).



**Figure 6.4** Comparison of S<sub>8</sub> Concentrations (mg/kg) and Chamber-based Corrosion Rates (A/30d). Open circles represent points where the S<sub>8</sub> concentration was <LOD.

Strontium concentrations in the catalog samples were associated with copper and silver corrosion in the chamber testing, but only for catalog samples of drywall that were from China and produced during the timeframe when problematic drywall was imported (Figure 6.5).



**Figure 6.5** Comparison of Strontium Concentrations (mg/kg) and Chamber-based Corrosion Rates (A/30d)

6.2.2 Source Markers and Corrosion—51-Home Study

The house average  $S_8$  concentrations were generally associated with corrosion in the home, as measured by silver and copper corrosion classification coupons at the air handling unit (AHU) air register (Figure 6.6).

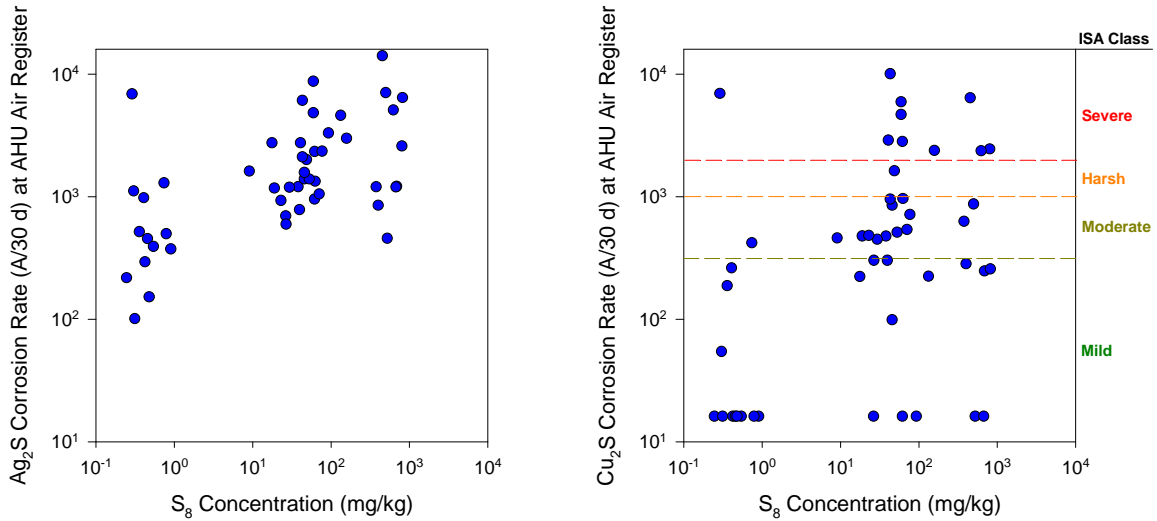


Figure 6.6 Comparison of House-average  $S_8$  Concentrations (mg/kg) and Corrosion Rates at the AHU Air Register from the 51-home Study

Multiple regression analyses showed that  $S_8$  concentration (mg/kg; natural log-transformed) was a significant predictor of silver and copper corrosion rates, controlling for region, outdoor corrosion rate and indoor temperature (silver –  $p < 0.001$ , model  $R^2 = 0.56$ ; copper –  $p < 0.001$ , model  $R^2 = 0.47$ ) (Tables 6.4 and 6.5).

<b>Table 6.4</b> Regression Model Results Showing Predictors of Silver Corrosion Rate at the AHU Air Register (Natural log-transformed)			
Parameter	Estimate	Standard Error	p-value
Intercept	5.23	1.25	<0.001
Orthorhombic Sulfur (natural log)	0.26	0.04	<0.001
Region – Florida East	1.46	0.35	<0.001
Region – Florida West	0.97	0.37	0.01
Region – Gulf Coast	0.68	0.34	0.05
Region – Virginia	--	--	--
Outdoor Silver Sulfide ( $Ag_2S$ )	<0.001	<0.001	0.20
Dew Point	<0.001	0.02	0.99
AHU air handling unit Model $R^2=0.56$			

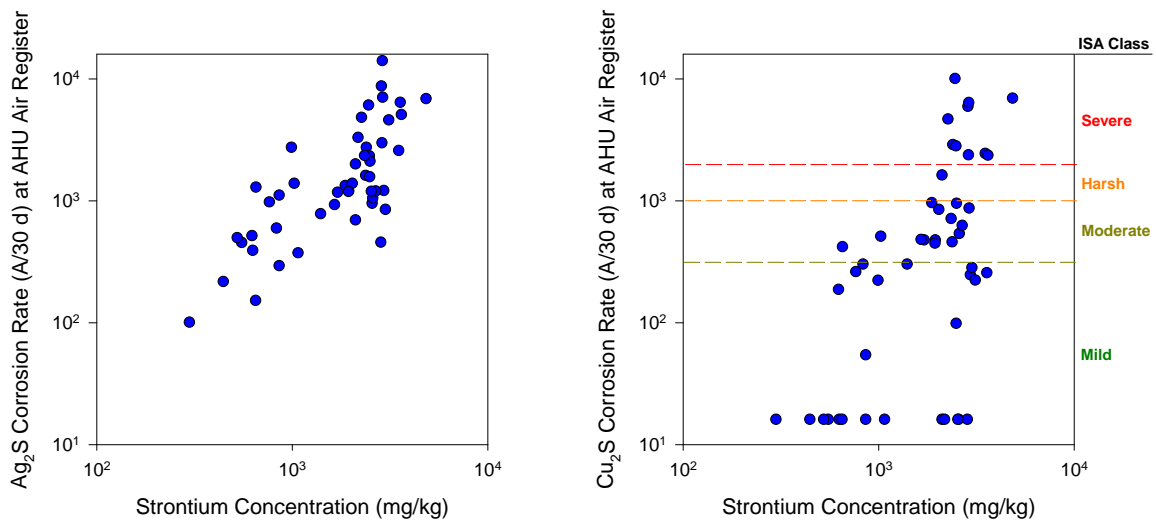
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<b>Table 6.5</b> Regression Model Results Showing Predictors of Copper Corrosion Rate at the AHU Air Register (Natural log-transformed)			
<b>Parameter</b>	<b>Estimate</b>	<b>Standard Error</b>	<b>p-value</b>
Intercept	3.94	2.60	0.1367
Orthorhombic Sulfur (natural log)	0.42	0.09	<0.001
Region – Florida East	2.25	0.76	<0.01
Region – Florida West	1.59	0.74	0.04
Region – Gulf Coast	1.15	0.70	0.11
Region – Virginia	--	--	--
Outdoor Copper Sulfide (Cu <sub>2</sub> S)	<0.001	<0.001	0.05
Dew Point	-0.021	0.04	0.62

AHU air handling unit  
 -- Referent group  
 Model R<sup>2</sup>=0.47

When the S<sub>8</sub> concentration was dichotomized based on a cutoff of 10 mg/kg this relationship remained, with the S<sub>8</sub> marker accounting for 49% and 46% of the variance in silver and copper corrosion, respectively. No significant interaction was found for the S<sub>8</sub> marker and environmental parameters such as temperature and relative humidity.

Analysis using the house average strontium concentrations yielded similar results. Strontium was significantly associated with both silver and copper corrosion at the AHU air register (p<0.01, R<sup>2</sup>=0.65; p<0.01, R<sup>2</sup>=0.46) (Figure 6.7).



**Figure 6.7** Scatterplot Comparing Strontium Concentrations (mg/kg) and Silver and Copper Corrosion Rates (A/30 days) at the AHU Air Register

## 7.0 DISCUSSION

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### 7.1 OVERVIEW

In an earlier study involving 51-homes (complaint and non-complaint) XRF and FTIR were evaluated as methods for identifying markers of imported drywall (EH&E 2010). Strontium and carbonate were identified as two markers that, if analyzed together, were useful in identifying imported drywall (EH&E 2010). In this previous study, homes with the carbonate and strontium marker determined by FTIR and XRF, respectively, were found to have significantly elevated concentrations of H<sub>2</sub>S and corrosion compared to homes without the marker present. While the 51-home study was being conducted, an allotrope of S<sub>8</sub> in the drywall was suggested as another potential marker of problematic drywall. Because of the critical need to have accurate means of screening for problematic drywall potentially impacted homes, a series of experiments were proposed to provide further insight. The objectives of this study, designed to provide information relevant to this inquiry, were to:

1. Determine the precision and accuracy of strontium concentration measurements in drywall made with field portable instruments.
2. Determine S<sub>8</sub> content in drywall samples from the CPSC inventory ('catalog drywall samples') and drywall samples archived from the 51-home study.
3. Characterize the potential of catalog samples to cause corrosion.
4. Identify source markers of problematic drywall by comparison of source marker concentrations to both chamber-based and in-home measurements of gases and corrosion.

### 7.2 STRONTIUM CONCENTRATIONS USING PORTABLE XRF ANALYZERS

Four different XRF units (three manufacturers) were compared to assess the consistency of results. The strontium concentrations measured with the four instruments were very highly correlated ( $r > 0.99$ ,  $p < 0001$ ). If the instruments were calibrated with a standard reference material containing the element being measured, the results were essentially interchangeable. XRF results were also compared to ICP-AES determinations of strontium. In paired samples the strontium concentrations measured by XRF were very consistent with concentrations from the ICP-AES analyses

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( $r$  0.85-0.95,  $p < 0.01$ ). This finding indicates that portable XRF analyzers can be reliably used to quantify strontium concentrations.

### 7.3 COMPARISON OF ANALYTICAL METHODS FOR ORTHORHOMBIC SULFUR

Three methods for analyzing  $S_8$  were used to measure  $S_8$  concentrations in samples of drywall. These drywall samples were obtained from known sources and contained products that were both domestically produced and, imported. The methods were REAC SOP 1805, an EPA method; GC/MS with a toluene-based solvent extraction, and GC/ECD. The GC/MS and GC/ECD methods generally were in agreement but the REAC SOP 1805 was not as consistent when compared to the results from the other two methods. There was 100% agreement between all three methods when the criteria was detect vs. non-detect for  $S_8$ . The GC/ECD method was selected as the method for analyzing  $S_8$  in the remaining catalog and in-home samples in this study. The GC/ECD method showed strong internal consistency, has been demonstrated to be useful for drywall analysis (Singhvi et al. 2009), and has a lower cost than the other two methods for laboratories with this capability.

### 7.4 INTRA-BOARD VARIABILITY OF STRONTIUM AND ORTHORHOMBIC SULFUR CONCENTRATIONS

When multiple measurements of strontium and  $S_8$  were made on the same drywall board, there was low intra-board variability. Importantly, the presence or absence of  $S_8$  was consistent across drywall boards. For example, when a  $S_8$  was determined to be less than the detection limit in one location, the remaining locations were all also less than the detection limit. Similarly, if  $S_8$  was detected on one location of a drywall board, it was consistently detected in the remaining locations. The results of this portion of the study indicate that there is little variability in sampling results by selecting different parts of the board, a finding that is consistent with previously reported results (Alessandroni, 2009). This should make in-home/field sampling more straightforward and efficient and increase confidence in results obtained with a few number of samples.

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### 7.5 EXPOSURE PATHWAY: SOURCE – EXPOSURE – EFFECT

Multiple lines of evidence were pursued to evaluate the robustness of associations between source markers (i.e., strontium and  $S_8$ ), exposure (i.e., gases), and effects (i.e., corrosion). This included assessing the relationships observed in controlled chamber studies, and also associations observed in homes.

Several of the drywall samples that had been analyzed by LBNL for reactive sulfur gases were from the same source sample materials that EH&E had analyzed for  $S_8$  and strontium. This subset of drywall samples and analytical data provide the basis for comparing gas emissions to source marker concentrations (sulfur and strontium). In this study  $S_8$  measured in drywall samples was found to be strongly associated with  $H_2S$  emissions, while strontium was found to be a good predictor of  $H_2S$  emissions in drywall samples suspected of being problematic due to both their origin and date of production. The results of the in-home study indicate that both strontium and  $S_8$  were both significant predictors of  $H_2S$  concentrations in homes. These homes were suspected of containing problematic drywall due to reports of odors, corrosion, health complaints, and, importantly, meeting the criteria of being constructed during the time when problematic drywall was imported. The comparison of markers and  $H_2S$  emissions in these samples indicates that  $S_8$  is a reliable predictor of  $H_2S$  emissions regardless of any pre-screening criteria. However, strontium measurements can be obtained rapidly, non-destructively, and *in situ*. Therefore, in-home screening conducted using XRF and analyzing for strontium is a useful tool in identifying problematic drywall provided that pre-screening criteria are met (e.g., odor, corrosion, health complaints). Confirmatory analysis using  $S_8$  as a marker could be used to verify the results.

Strontium and  $S_8$  concentration in drywall samples were also found to be associated with both chamber-based corrosion rates and corrosion rates measured in homes. Stronger associations were observed for  $Ag_2S$  corrosion compared to  $Cu_2S$  corrosion. One possible explanation for this observation is related to the mass increase rates. Copper and silver both have fast mass increase rates, but, in an experimental study, silver was shown to have a mass increase rate an order of magnitude faster than copper, showing mass responses within several minutes after  $H_2S$  was introduced (Forslund et al. 1997).



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In this study's chamber-based corrosion tests, corrosion was strongly associated with the sulfur concentration; however, the strontium concentration alone was found to be a poor predictor of corrosion (as measured in the chambers) without any information on the origin of the drywall samples. The lack of association with corrosion for strontium differs from that in the 51-home study. In that study strontium was associated with problem homes and corrosion in those homes. This apparent inconsistency may be the result of the aforementioned selection process for homes in the 51-home study. In the 51-home study, the homes were selected based on several criteria that helped identify them as 'problem' homes. In samples of drywall from those homes, strontium and  $S_8$  were highly correlated. As a result, they were both useful markers of problematic drywall for homes in that study. The catalog samples tested in this study contain a diverse mix of domestic and imported drywall, some manufactured during the period of prime interest and others after, and some of which is problematic and some of which is not. For this wide range of samples, without use of any additional characteristics, strontium was not a consistent predictor of problematic drywall.

### 7.6 SUMMARY

In the 51-home study, indoor  $H_2S$  levels were found to be associated with corrosion and the home being classified as a "problem home" (EH&E 2010). Although the mechanism responsible for the corrosion has not been elucidated, the strong relationship observed in this study between sulfur content of problem drywall and  $H_2S$  emissions is supportive of  $S_8$  being a reliable marker for problematic drywall. Further support for this conclusion is the finding that concentration of sulfur in the drywall is associated with corrosion in testing chambers and that in multiple regression analyses of corrosion measured in homes during the 51-home study, sulfur concentration in drywall was significantly associated with corrosion rate (while controlling for temperature, humidity, and region). This consistency with experimental studies, observations in the field and statistical analyses which control for potential effect modifiers/confounders, supports the use of  $S_8$  in drywall as a reliable indicator of problematic drywall. In addition,  $S_8$  and strontium concentrations were found to be correlated in problematic drywall and strontium was an equally strong predictor of  $H_2S$  and corrosion in problematic homes. Therefore, the ability to test for strontium concentration in the field instantaneously and non-

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destructively using portable XRF analyzers suggests that strontium is useful as a screening tool for problematic drywall when pre-screening criteria are utilized.

## 8.0 CONCLUSIONS

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The objective of the source characterization study was to evaluate proposed markers of problematic drywall, defined as drywall associated with elevated rates of copper and silver corrosion. In this study, we investigated two proposed markers—strontium and  $S_8$ . The robustness of each source marker was evaluated by first comparing different instruments/methods for quantifying each, examining parameters such as within-board variability and determining method precision. The source markers were then compared to both chamber-based and field-based measurements of gases and corrosion. The following observations were made during the course of this investigation:

- Strontium is a useful, but non-specific marker of problematic drywall when used in isolation

*Elevated strontium concentrations were observed in all problematic drywall, but also in some non-problematic drywall. Strontium concentrations were correlated with  $S_8$  concentrations in problematic drywall. Therefore, in the 51-home study where homes were pre-screened based on specific criteria contained in a CPSC questionnaire (EH&E 2010) strontium was found to be predictive of problematic drywall. Strontium content in drywall measured by XRF is non-destructive, field portable and nearly instantaneous, and, therefore, remains a useful marker of problematic drywall when used as part of a multi-level screening approach.*

- Analysis of strontium in drywall samples can be reliably performed using XRF  
*Strontium measurements using XRF were accurate when compared to strontium as determined by ICP-AES (inductively coupled plasma-atomic emission spectroscopy). Models from three different manufacturers yielded highly similar response factors and strongly correlated results (1:1 slope). Instrument method calibration specific to strontium is necessary to ensure accuracy of the measurements.*
- $S_8$  is a sensitive and specific marker of problematic drywall  
 *$S_8$  concentrations in drywall were associated with chamber-based measurements of hydrogen sulfide and corrosion. Consistent findings were observed when this*

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*relationship was evaluated using archived samples of drywall and measurements of hydrogen sulfide and corrosion in the 51-home study.*

- $S_8$  was not detected in any drywall samples from the non-complaint homes in the 51-home study

*Three drywall samples from each of the 10 non-complaint homes in the 51-home study were analyzed for orthorhombic sulfur.  $S_8$  was not detected in any of these samples. In contrast,  $S_8$  concentrations in the complaint homes ranged from <5 mg/kg to 830 mg/kg (median = 54 mg/kg), and were significantly higher than the levels in the non-complaint homes.*

- $S_8$  determined using two toluene-based extraction methods showed strong agreement

*$S_8$  concentrations determined using the GC/MS (toluene extraction) and GC/ECD methods showed excellent agreement. Results using EPA's REAC SOP 1805 did not show consistent agreement when compared with the other two methods, in a limited number of samples. GC/ECD appears to be an attractive option for future analysis of drywall samples due to its potentially lower cost for laboratories with this capability.*

- $S_8$  and strontium both exhibited low intra-board variability

*Repeat measurements of  $S_8$  and strontium on different locations of the same drywall board showed strong consistency.*

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