LA-UR-02-6475

Approved for public release; distribution is unlimited.

Title: Materials Characterization Using Micro X-Ray Fluorescence Elemental Imaging

Author(s): George J. Havrilla
Thomasin Miller
Martha Joseph

Submitted to: Federation of Analytical Chemistry and Spectroscopy Societies Conference (FACSS)
Providence, RI October 13 - 18, 2002

LOS ALAMOS NATIONAL LABORATORY
3 9338 01045 9492

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Form 836 (8/00)

MATERIALS CHARACTERIZATION USING MICRO X-RAY FLUORESCENCE ELEMENTAL IMAGING

George J. Havrilla, Thomasin Miller and Martha Joseph
Los Alamos National Laboratory, Los Alamos, NM 87545

Materials characterization continues to be a key challenge in a variety of programs. Although bulk elemental composition provides overall concentration of both major and trace elements, the distribution of these elements both on micro and macro scales can determine the performance and ultimately the physical properties of the materials. Hence elemental imaging can provide a new level of information for major and in some cases bulk trace concentrations of elements.

Micro X-ray fluorescence (MXRF) offers unique capabilities in terms of elemental imaging. This approach is based on a meso scale level of resolution around 50 micrometer X-ray spot size. When coupled with a moveable stage, specimens several inches on a side can be imaged with surprising detail. In most instances, qualitative images are sufficient to illustrate the elemental heterogeneity. This information can then be used to determine if the material meets the desired physical characteristics and whether this is due to the observed heterogeneity or in spite of it.

Several examples of elemental imaging will be presented. These will include the aging of polymers and the effects of residual organotin catalyst. The tin can be imaged using MXRF and has been show to be mobile within the polymeric material over time. Corrosion is a serious issue throughout the industrial world. A specific example of chloride attack on a metal, which creates problems in waste storage. Finally, MXRF used in high throughput screening in the development of novel peptide receptors will be shown. The advantage of MXRF is that no fluorescent tags need be added to the target molecules. This insures the unhindered interaction of the target molecules and allows for additional characterization using molecular spectroscopic techniques.

Materials Characterization Using Micro X-ray Fluorescence Elemental Imaging

George J. Havrilla, Thomasin C. Miller, Martha R. Joseph

Los Alamos National Laboratory, Analytical Chemistry Science, Los, Alamos, 87545

CHEMISTRY

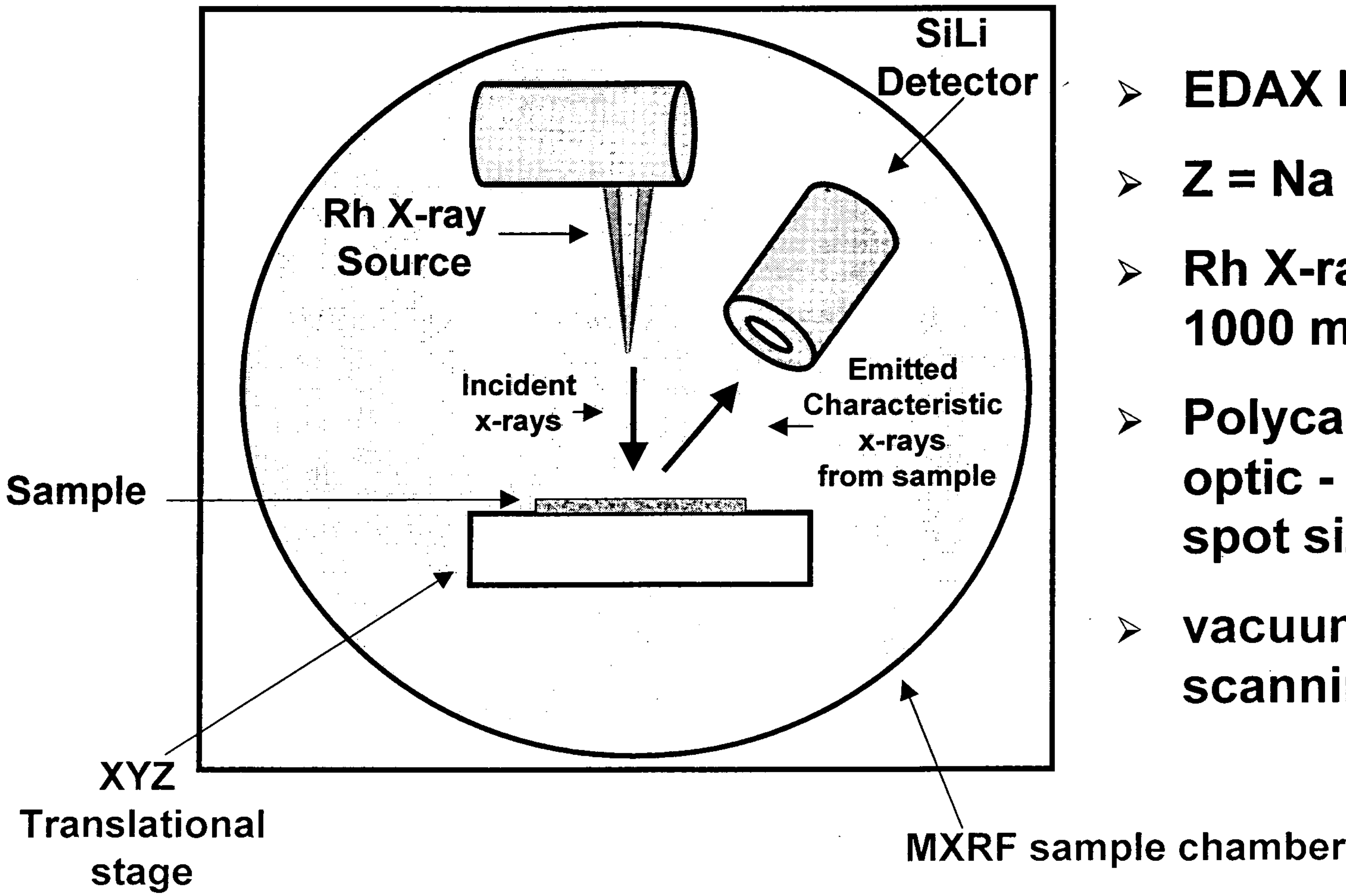
Los Alamos

Micro X-ray Fluorescence (MXRF)

MXRF provides the analytical scientist with a powerful tool to solve a variety of materials-based problems

- MXRF is an elemental analysis technique
- Elemental mapping shows the distribution of both major and trace elements in a sample
  - Variations in color rapidly convey the presence or absence of an element or highlight the correlation of one or two elements in a sample
  - Indication of sample heterogeneity or elemental associations
- Performance and physical properties of materials can be determined (3 systems will be explored in this study)
  - Aging of PDMS Silicone Foams
  - Corrosion of Waste Storage Container Filters
  - Screening of Combinatorial Libraries for Catalytic Activity

MXRF Instrumentation



- EDAX Eagle
- Z = Na through Pu
- Rh X-ray tube, 40 kV, 1000 mA
- Polycapillary focusing optic - 30 μm minimum spot size
- vacuum, dynamic scanning

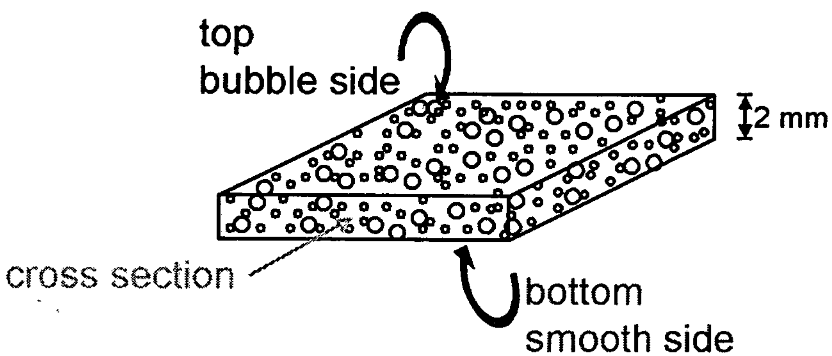
Introduction: Aging Study of PDMS Foam

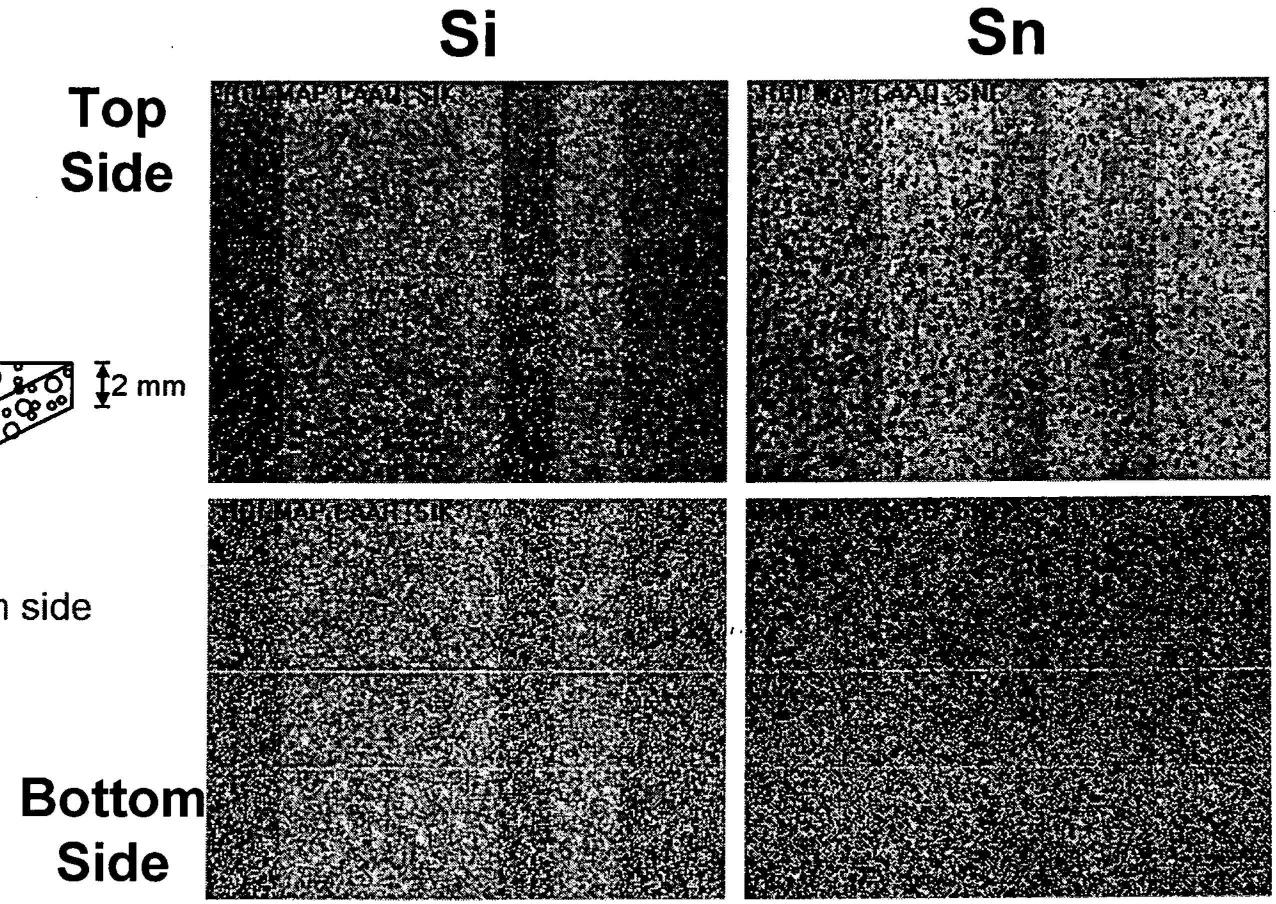
- Compression set is a key characteristic, which is being studied and how it is affected by the aging of PDMS silicone foams.

- MXRF was used to help identify and characterize the fundamental aging mechanisms of stress relaxation in the foams.

- Aging of the foams was accelerated enough to cause measureable changes, but not create irrelevant aging mechanisms.

Elemental Images of Virgin Foam

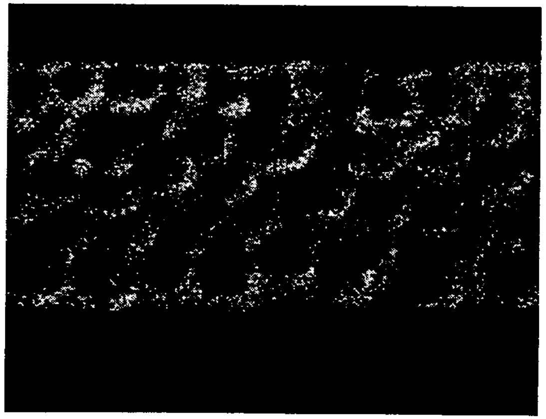




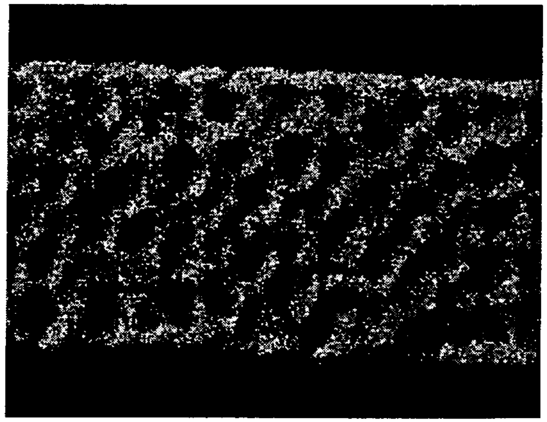
The major component of PDMS foam is Si, which is present throughout the body of the foam material. The foams also contain an organo-Sn catalyst in varying amounts in the foam. MXRF was used to study what happens to these components as the foam is aged.

Sn Maps of Virgin and Aged Foam Cross Sections

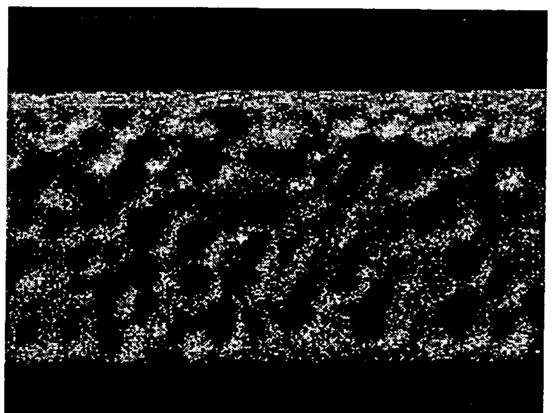
Virgin: no aging



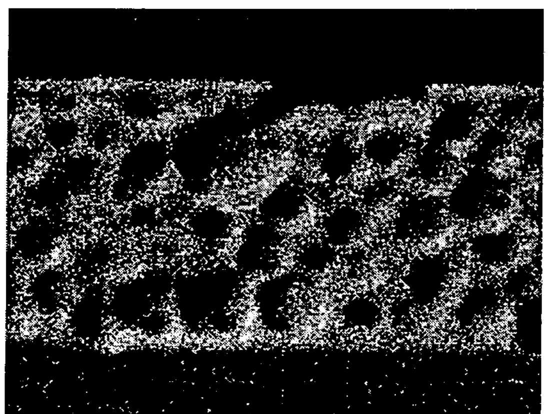
Aged 1 week



Aged 1 month



Aged 6 months



MXRF provides evidence that the Sn compound is volatile and migrates through the foam during aging. As the foam ages, the Sn concentrates at the top of the foam in a layer that is 50 - 75 μm thick. As aging continues, the Sn diffuses back into the bulk of the foam.

Si (not shown) tends to form a thin layer < 50 μm thick at the bottom of the foam.

Foams were aged at 50°C.

Introduction: Corrosion study of Waste Drum Storage Filters

- Several thousand 55-gallon drums of residue material, both aqueous and organic, are stored at Rocky Flats Environmental Technology Site.

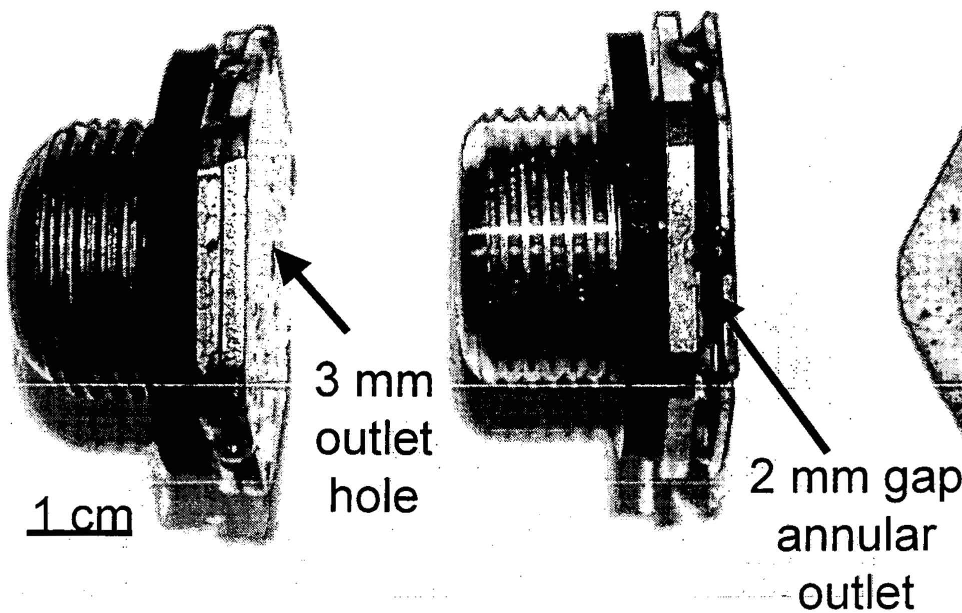
- Drum vent filters are used to reduce pressure buildup within the waste storage containers.

- A monitoring program was established to insure operability of vent filters.

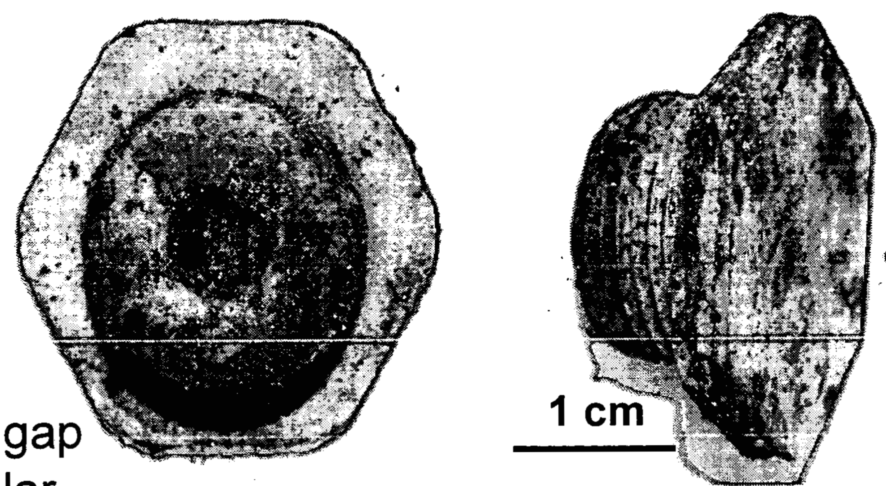
- MXRF is one of the tools being used to identify failure mechanisms in the filters.

White Light Images of Unused Filters and Corroded Filters

Unused Filters



Corroded Filters



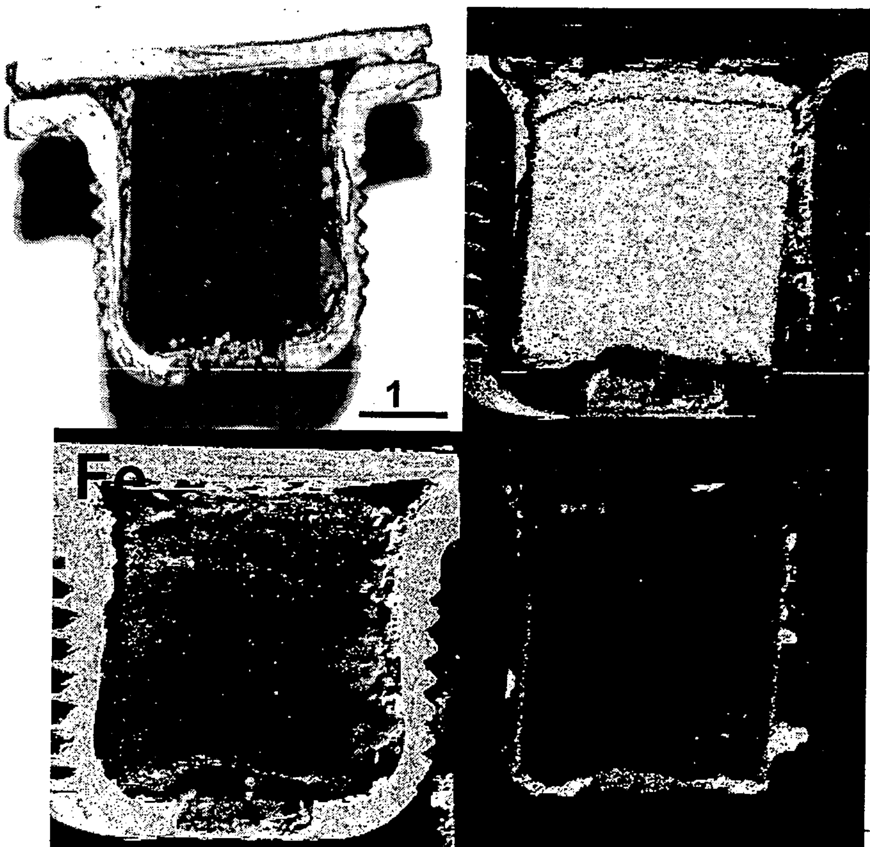
Two modes of failure have been identified:

1) Plugging of the filters resulting in reduced air flow

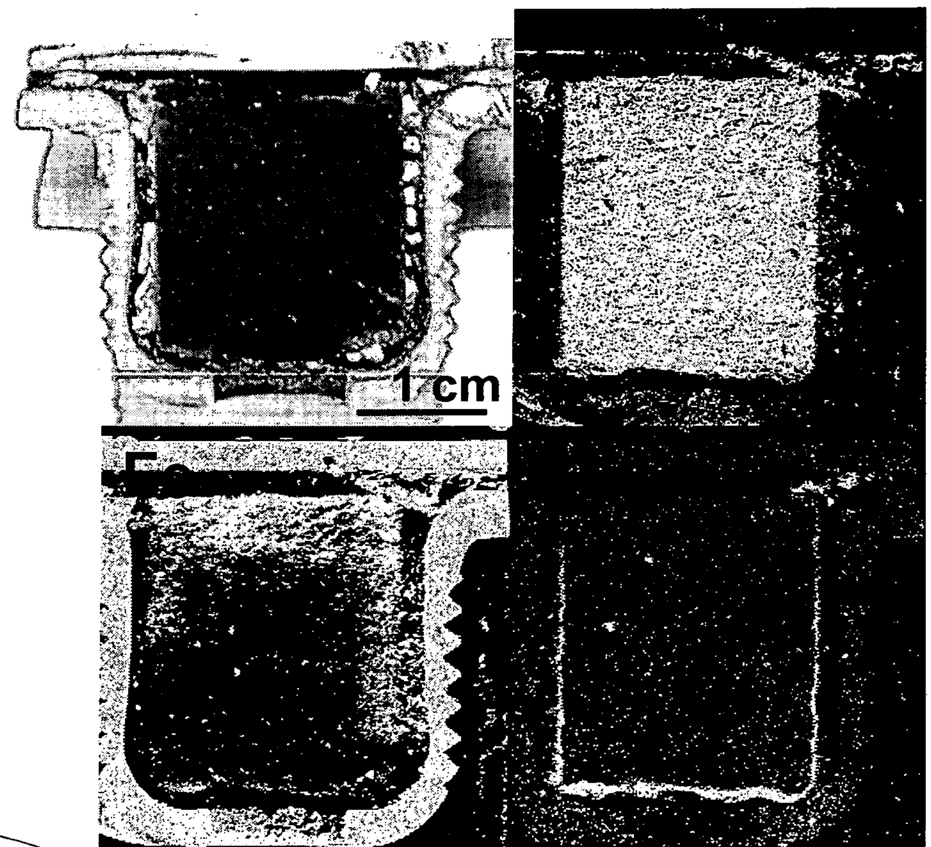
2) High air flow from the filters

Elemental Images Failed Filter Cross Sections

Low Flow/Plugged Filter



High Flow Filter

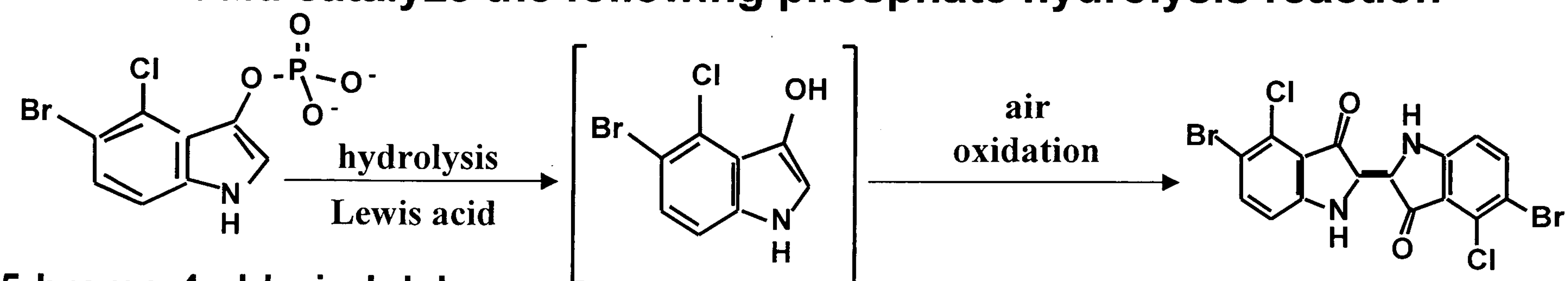


Proposed Filter Failure Mechanisms

- Both filters display high chlorine intensities within the body of the filter
  - Chlorine is not present in unused filter material
  - Chlorine based species are responsible for steel corrosion plugging inlet and outlets
- Si maps show that the Si layer in the filter is discontinuous
  - RTV sealant in the filter is degrading resulting in loss of filter integrity
- Manufacturing defects appear to be basis for aqueous filter failures

Introduction: Screening of Combinatorial Libraries

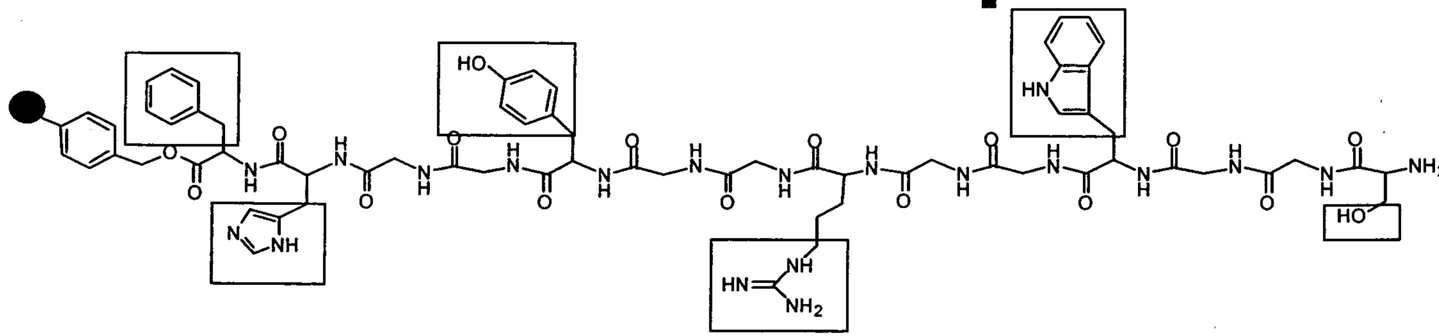
- **New means of reliably and rapidly screening activity and selectivity of combinatorial library components are needed**
- **Feasibility of MXRF as a screening technique is demonstrated by analyzing a library of bead-bound oligopeptides for catalytic activity**
  - **Specifically, MXRF was used to find peptide sequences that would catalyze the following phosphate hydrolysis reaction**



5-bromo-4-chlorindolyl Phosphate (BCP)

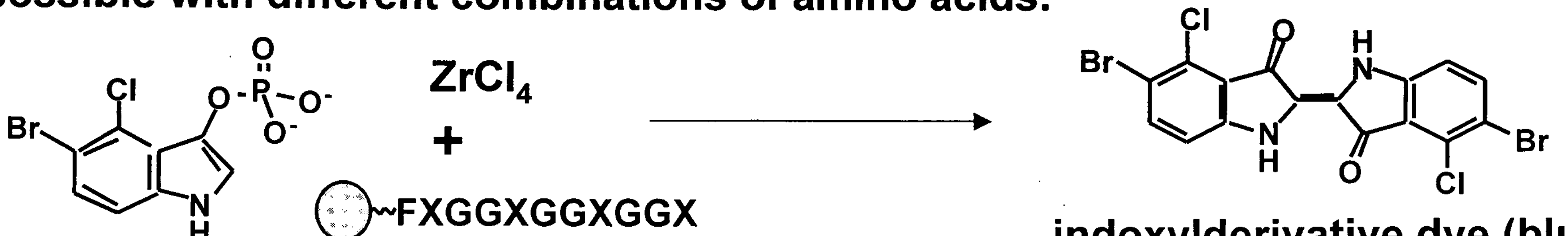
indoxylderivative dye (blue)

Exposure of Oligopeptide Library to Reaction Components



~~The~~ oligopeptide library is immobilized on polystyrene beads and is obtained commercially. Each sequence is 11 amino acids long varying 4 positions with 5 different amino acids yielding 625 unique peptides. Catalytic activity may be possible with different combinations of amino acids.

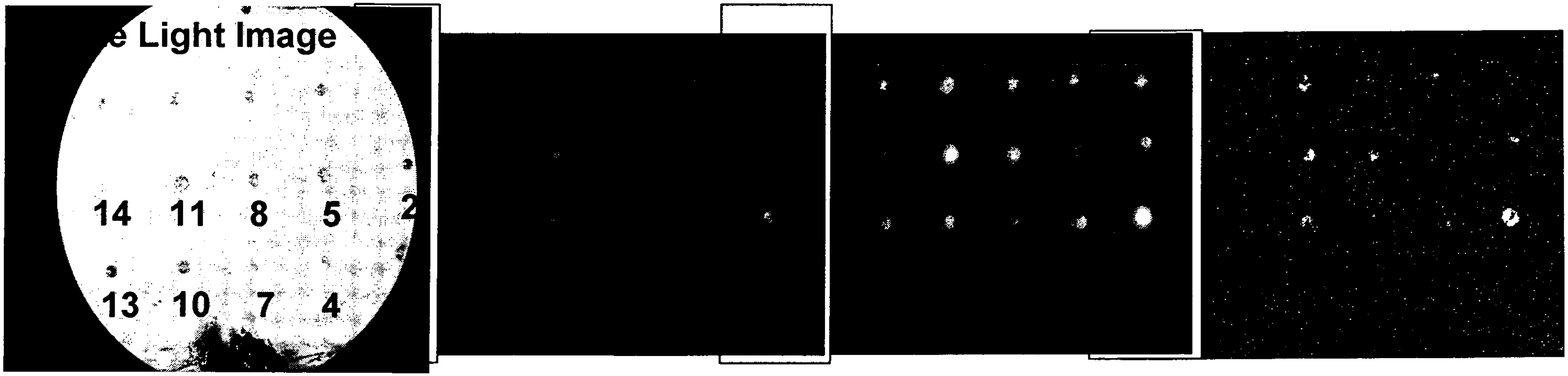
100 µm



indoxylderivative dye (blue)

Library is exposed to phosphate hydrolysis reagents with $ZrCl_4$ Lewis acid. Exposed beads are immobilized on a Tacky Dot™ microscope slide array for MXRF screening. Good catalyst beads will be blue in color and will have significant Br intensities with low P.

MXRF Screen of Exposed Library



White light image beads 10 and 13 are blue in color and signify catalytic sequences. MXRF maps show both beads are high in Br intensity, but low in P further indicating catalytic activity.

Unlike the white light image, MXRF can give an indication of the degree of catalytic activity of a particular sequence. Bead 13 is a good catalyst with little Zr. However, bead 10 has distinct Zr intensity, therefore only moderate catalyst.

14

MXRF can also give information about the non-catalytic beads. For example, beads 1, 8, and 11 have significant Br and P intensities, indicating that these bead sequences have bound the BCP starting material.

Summary of MXRF Combinatorial Library Screening

- MXRF was successfully used as a screen for phosphate hydrolysis catalyst discovery, with the ability to establish degree of catalytic activity
  - Catalytic beads could be isolated and their sequences determined for use in further analyses
  - Elemental images can bring out details not observable with white light
- MXRF is unique compared to other HTS screening techniques such as UV-VIS and fluorescence. Only the native elemental fluorescence is required for detection. No chromogenic tags are required
  - Tags are often bulky and can interfere with combinatorial library-target chemical interactions

Conclusions

- MXRF imaging provides elemental information useful in understanding the performance and physical properties of different materials

- MXRF is non destructive and preserves the integrity of the sample

- MXRF has sufficient sensitivity and spatial resolution for the determination of the distribution and heterogeneity of major and trace elements in materials