Remote Raman technology for in-situ identification of nuclear tank waste

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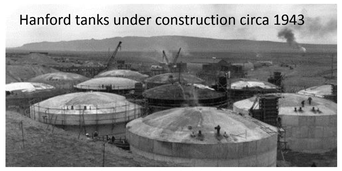
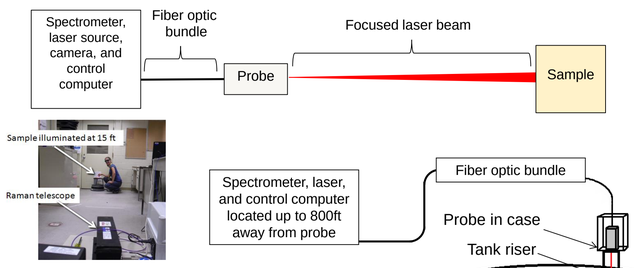
Introduction

- Hanford tank waste remediation is a focus of environmental clean-up efforts.
- Liquid wastes can be identified and removed from tanks, but solid wastes settled at the bottom of tanks (salt cakes) are difficult to identify and therefore difficult to remove.
- Safe, fast, and effective methods for identifying residual phases are needed.
- Novel long distance Raman spectroscopy, in which a laser beam is focused on samples at variable distances up to 50 ft away from the Raman probe can provide the remote and effective analysis needed in the tanks
- In conjunction with chemometric analysis this technique can be used to identify and quantify Raman-active compounds in the solid wastes.



http://www.brookings.edu/about/projects/archive/nucweapons/tanks

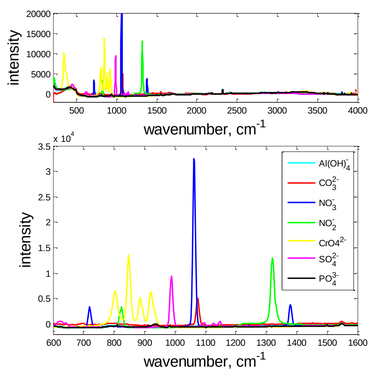
Telescopic Raman schematic



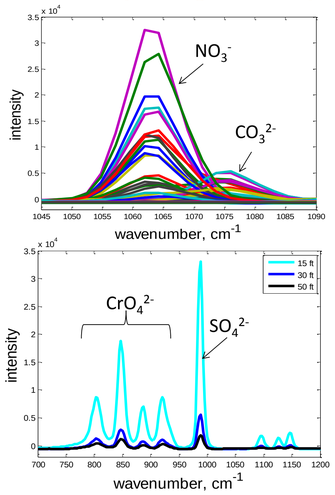
- Top: schematic presents the components of the telescopic Raman system. Laser beam can be focused using an onboard camera and the control computer
- Right: depiction of how probe will be mounted onto tanks. Fiber optic bundle is long enough to allow control equipment and personnel to be located 800 ft away from tanks

Library building of candidate tank waste compounds

- The list of possible tank waste species includes a substantial number of Raman active molecules
- Figure shows spectra of the seven salts chosen for testing probe response and modeling capabilities
  - Collected at 30'
- Top: full spectra
- Bottom: zoomed in to show majority of fingerprint region
- Bands not only show overlap but wide variety in Raman response, *e.g.* intensities of NO_3^- and PO_4^{3-} peaks



Laboratory testing of telescopic probe: variables to consider in building models



- **Variation of component weight fraction**
  - Samples were prepared to cover a large range of component weight fractions and compositions in pure to two-phase mixtures
  - Right: spectra from several samples containing varying weight fractions of $NaNO_3$ and Na_2CO_3 at a constant distance
- **Variation of sample distance from telescopic Raman probe**
  - Samples were measured at three distances from the Raman probe: 15', 30', and 50'
  - Shown here is a 55:45 weight ratio of Na_2CrO_4:Na_2SO_4 collected at all three distances

Chemometric modeling: The plan and points to consider

- **Step 1**: build PLS models using data collected at the different distances
- **Step 2**: build a model that is independent of distance

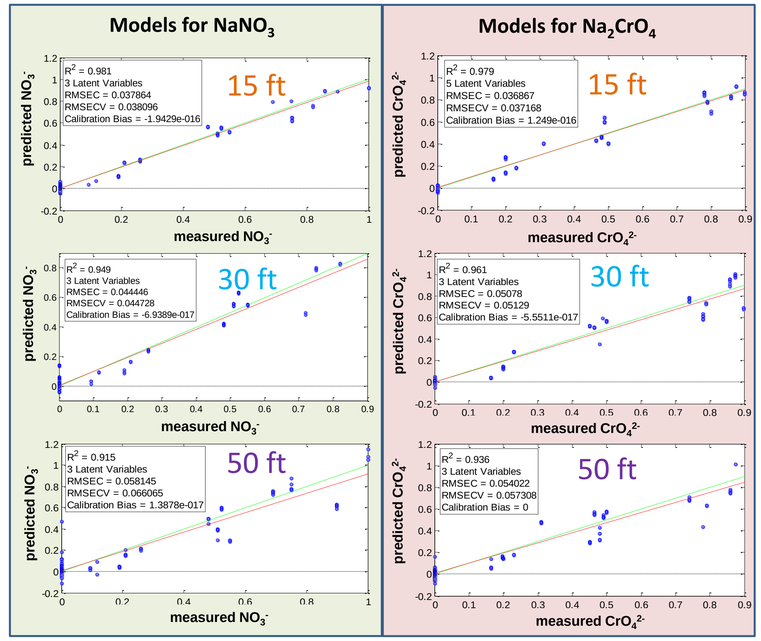
- Data presents a number of interesting factors that are useful to know when building a model:
  - Salts demonstrate a variety of Raman sensitivities with NO_3^- being the most sensitive while $Al(OH)_4^{2-}$ and PO_4^{3-} are the least sensitive
  - Salts also demonstrate variety in number of peaks ranging from one peak in the case of PO_4^{3-} to at least 5 major peaks in the case of CrO_4^{2-}
  - Fluorescence backgrounds also range for the samples, making background correction necessary

First steps: Using PLS modeling to build distance dependent models

- X block data consisted of 420 rows of Raman spectra (70 samples, 6 collections per sample)
  - Spectra were preprocessed using 1st derivative and mean center functions
- Y block data consisted of corresponding weight fraction values of salts in the sample
  - Values were preprocessed using the mean center function
- Venetian blinds cross validation was used with a split of 10
- Wavelength range was limited to 200 to 2000 cm^{-1}

	$Na_2Al(OH)_4$	Na_2CO_3	$NaNO_3$	$NaNO_2$	Na_2CrO_4	Na_2SO_4	Na_3PO_4
15'							
R^2 fit	0.823	0.962	0.981	0.930	0.979	0.958	0.928
latent variables	4	4	3	3	5	3	4
RMSEC	0.1186	0.0527	0.0379	0.0675	0.0369	0.0262	0.0719
RMSECV	0.1218	0.0527	0.0381	0.0680	0.0372	0.0263	0.0744
30'							
R^2 fit	0.504	0.933	0.949	0.864	0.961	0.936	0.787
latent variables	4	4	3	3	3	3	4
RMSEC	0.1382	0.0694	0.0444	0.0829	0.0508	0.0435	0.0921
RMSECV	0.1974	0.0706	0.0447	0.0833	0.0513	0.0430	0.1286
50'							
R^2 fit	0.457	0.870	0.915	0.768	0.936	0.866	0.656
latent variables	4	4	3	3	3	4	4
RMSEC	0.1666	0.0952	0.0581	0.1243	0.0540	0.0555	0.120
RMSECV	0.2164	0.1029	0.0660	0.1284	0.0573	0.0622	0.158

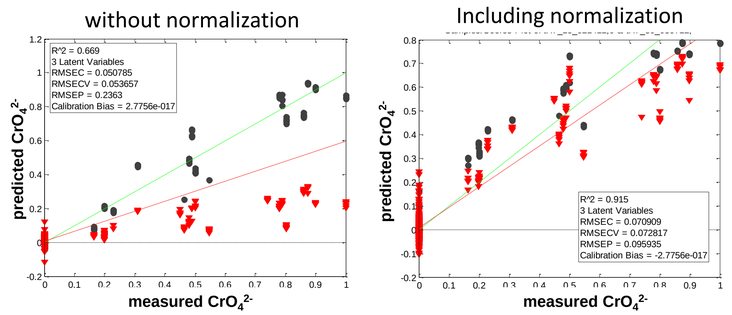
First steps: Using PLS modeling to build distance dependent models



- Even without significant amounts of optimization of preprocessing and modeling parameters, models created from data collected at all three distances are reasonable
- As expected, the best fitting models are obtained at 15'

Next steps: Using PLS modeling to build a distance independent model

- Determining appropriate normalization methods makes this difficult
- Current work suggests normalizing to area=1 is not appropriate but there is not a consistent feature that could be normalized to 1as an alternative
  - This is due to the wide variety of peaks present in the many mixtures
- Shown below is the 15' model for Na_2CrO_4 (shown above) predicting on data collected at 30' (left) and the results after adding normalization to the preprocessing (right)
- Modeling options will continue to be explored



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