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Title: Trace Element Analysis by DC Arc

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Trace Element Analysis by DC Arc

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The Actinide Analytical Chemistry group (C-AAC) within Chemistry Division at Los Alamos National Laboratory works with the Plutonium Manufacturing & Technology Division on several non-proliferation projects. One of these projects involves processing Pu-238 to be used in heat source and radioisotope thermoelectric generator development technology. The Pu-238 program is required to meet project specifications for the amount of trace elements to be allowed in the final product. Due to the Pu-238 final product being heat treated to very high temperature to form a ceramic, this material is not easily dissolved in our typical acid mixtures. Therefore, we utilize a DC Arc solid-sampling method of analysis to measure a wide variety of analytes in the high-fired Pu-238 material. However, the equipment used in this DC Arc method is greater than 30 years old and is no longer made. We are not able to buy parts or get any professional service to maintain or fix the DC Arc stand, spectrograph, or micro photometer should this equipment fail. In order to maintain our solid-sampling analysis capability, we endeavored to update our method using newer equipment and technology. In conjunction with Teledyne Instruments Leeman Labs, we will interface a Prodigy spectrometer with a glovebox DC Arc stand separated by an optical, quartz window. This report describes the existing method of DC Arc and the actions that are currently being taken to develop this method using this newer equipment and technology to meet the project specifications for the Pu-238 program.

Trace Element Analysis by DC Arc

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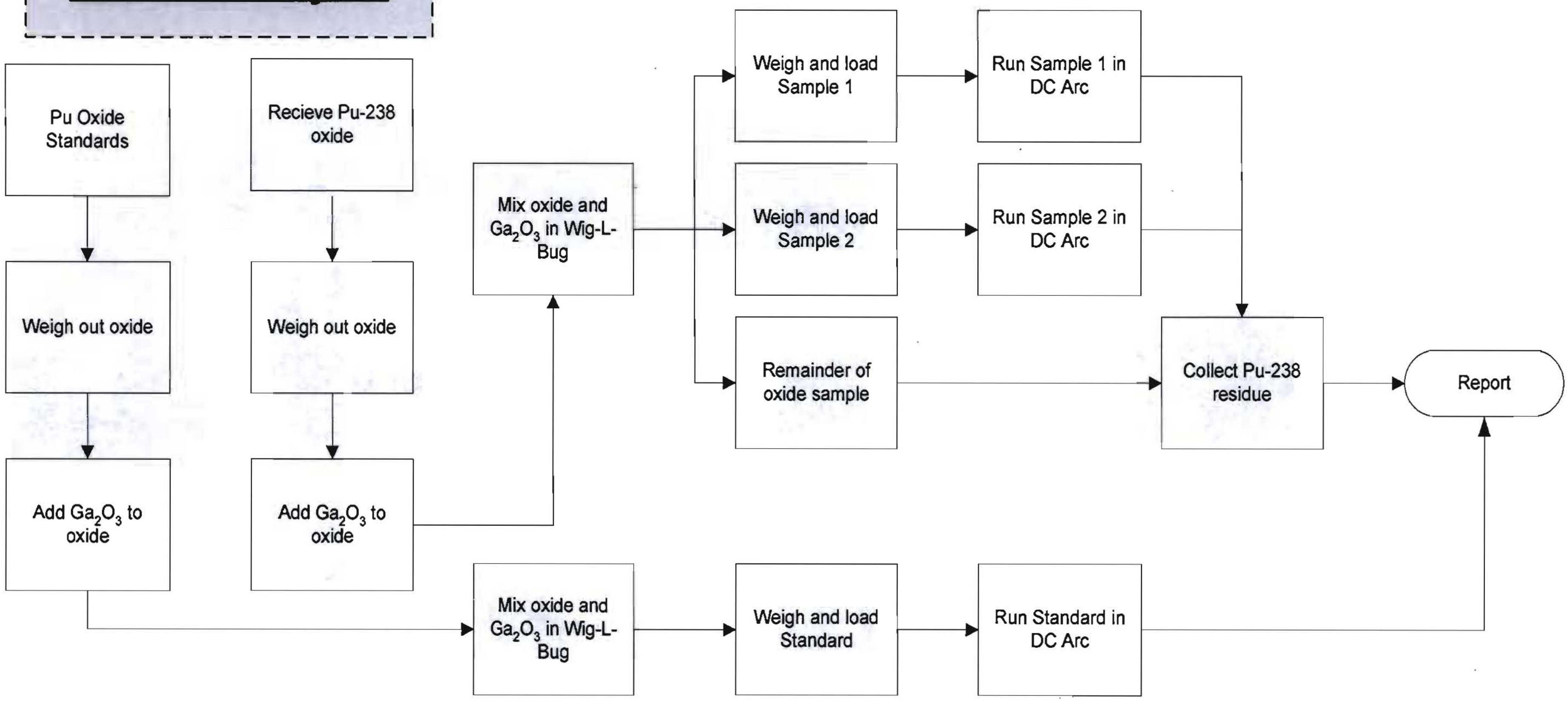
Trace Element Analysis by DC-Arc

DC Arc Analysis



Existing DC Arc Method for Pu-238 oxide

Carrier Distillation Technique

- Modification of Scribner and Mullins method[1] for U oxide
- Ga_2O_3 carrier, Co internal standard
- O_2 atmosphere
- 3.4 m Ebert spectrograph, grating ruling 30,000 grooves/inch
- Three Kodak SA-1 plates, 249.6 nm to 405.7 nm wavelength
- Full set of PuO_2 matrix standards for each sample batch
- Laboratory control sample (LCS) analyzed with each sample batch
- Samples analyzed in duplicate

Ref: 1) Scribner, Mullins, Spec. Acta.

Sample Receipt and Preparation

- Cut open tantalum vials and verify weight of each respective sample – this is typically 0.3 grams
- Using an analytical balance, tweezers and a platinum microspoon, accurately weigh 0.240 grams of the sample and 0.010 grams of a gallium oxide carrier with internal standard into a platinum weigh dish
- Mix the sample and carrier in a plastic vial using a Wig-L-Bug, or mixing mill
- Weigh 0.100 gram aliquots of each sample in duplicate and transfer each aliquot into it's respective graphite electrode
- This preparation process requires the highest level of analytical technique and patience – there is not enough sample for reanalysis

Sample Containers

Sample Preparation Tools

Sample Transfer and it's "Issues"

- Transfer the prepared sample aliquots from the glovebox in 7136 to the glovebox in 7134 for analysis by DC Arc
- The electrodes are placed upright in a wooden block, transferred into a plastic container and sealed with a lid. Since the glovebox train has doors in between each glovebox work station, the container with the electrodes are placed into successive plastic bags as they pass into each glovebox.
- Because of the "handling" of the samples in this fashion, there is a potential to lose some of the sample from the electrodes
- This transfer requires a respirator "Hot Job," therefore more personnel are needed to assist, and continuous RCT coverage is required
- In addition to the possibility of contamination from this transfer, ALARA in the form of time, distance, and shielding are used to minimize dose while handling the samples outside of the shielded confines of the glovebox
- This transfer process can take a significant amount of time due to these constraints

Airlock on Glovebox for Sample Transfer

Standard Preparation and Pre-Analysis Test

- Nine standards and a Laboratory Control Sample (LCS) reference are prepared in the same way as the samples (Note that we use Pu-239 for our standards)
- The samples and standards are packed and vented with a custom tantalum pack and vent tool for the electrodes
- The instrument is checked for appropriate current (Amps -- SC), gas flows, combustion chamber alignment, and instrument optical settings
- A test run using an iron reference is analyzed to ensure proper operation of the instrument and the photographic developing process

DC Arc Analysis and Photographic Developing

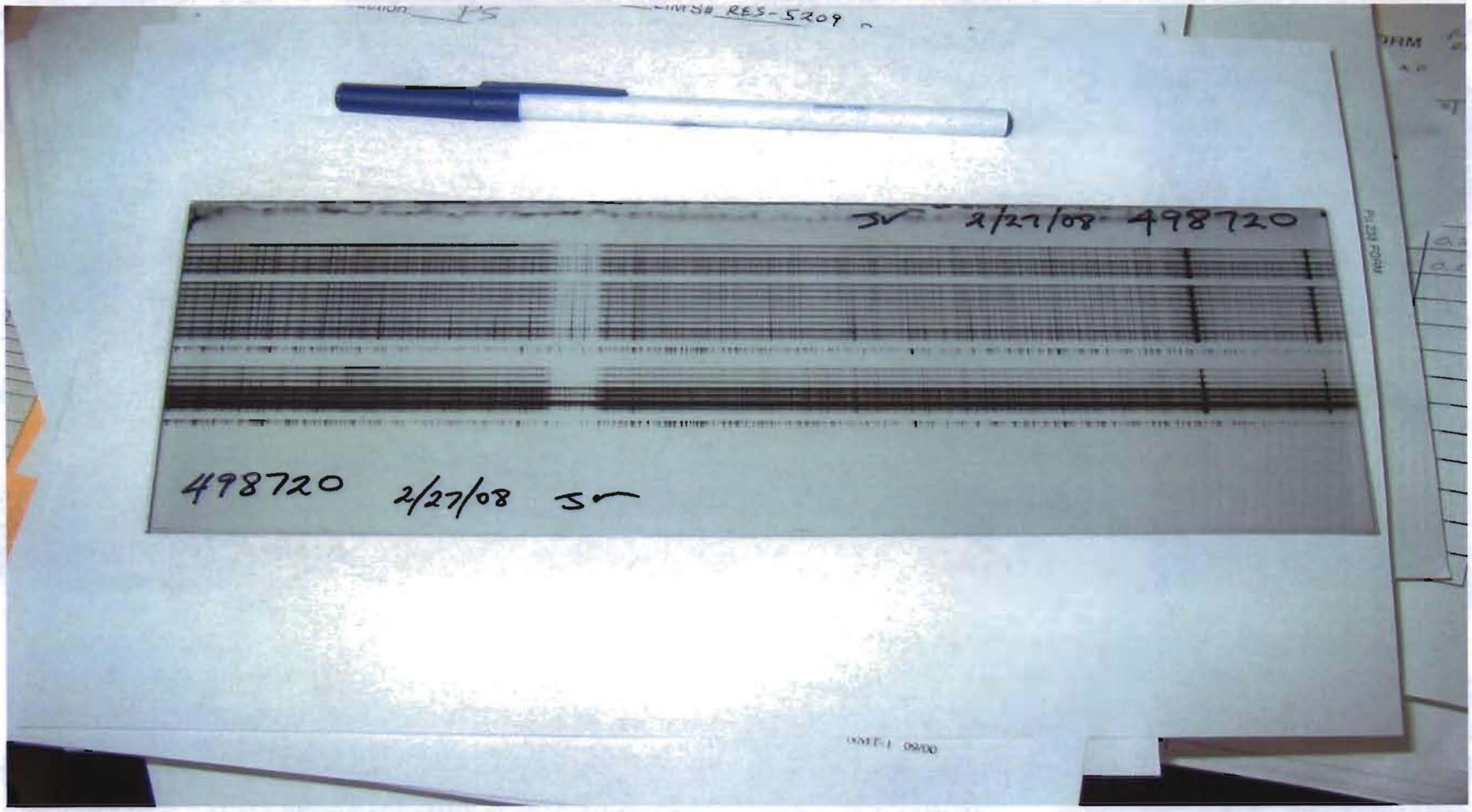
- The photographic plates are loaded into the camera in a dark room and the camera assembly is loaded into the Jarrell Ash Spectrograph for sample analysis
- The samples and standards are analyzed by DC Arc and the camera is advanced manually for each sample analysis. This requires a second person or repeated removal of hands from the glovebox. The auto advance no longer works and there are no replacement parts.
- The camera assembly is removed from the spectrograph and the photographic plates are developed in a Wing-Lynch automated photographic developer
- The plates are rinsed with water, dried, and surveyed for free release from the RCA

Existing DC Arc Stand Setup in Glovebox

Existing Jarrell Ash Spectrograph

Wing-Lynch Auto Developer

Photographic Glass Plate After Developing

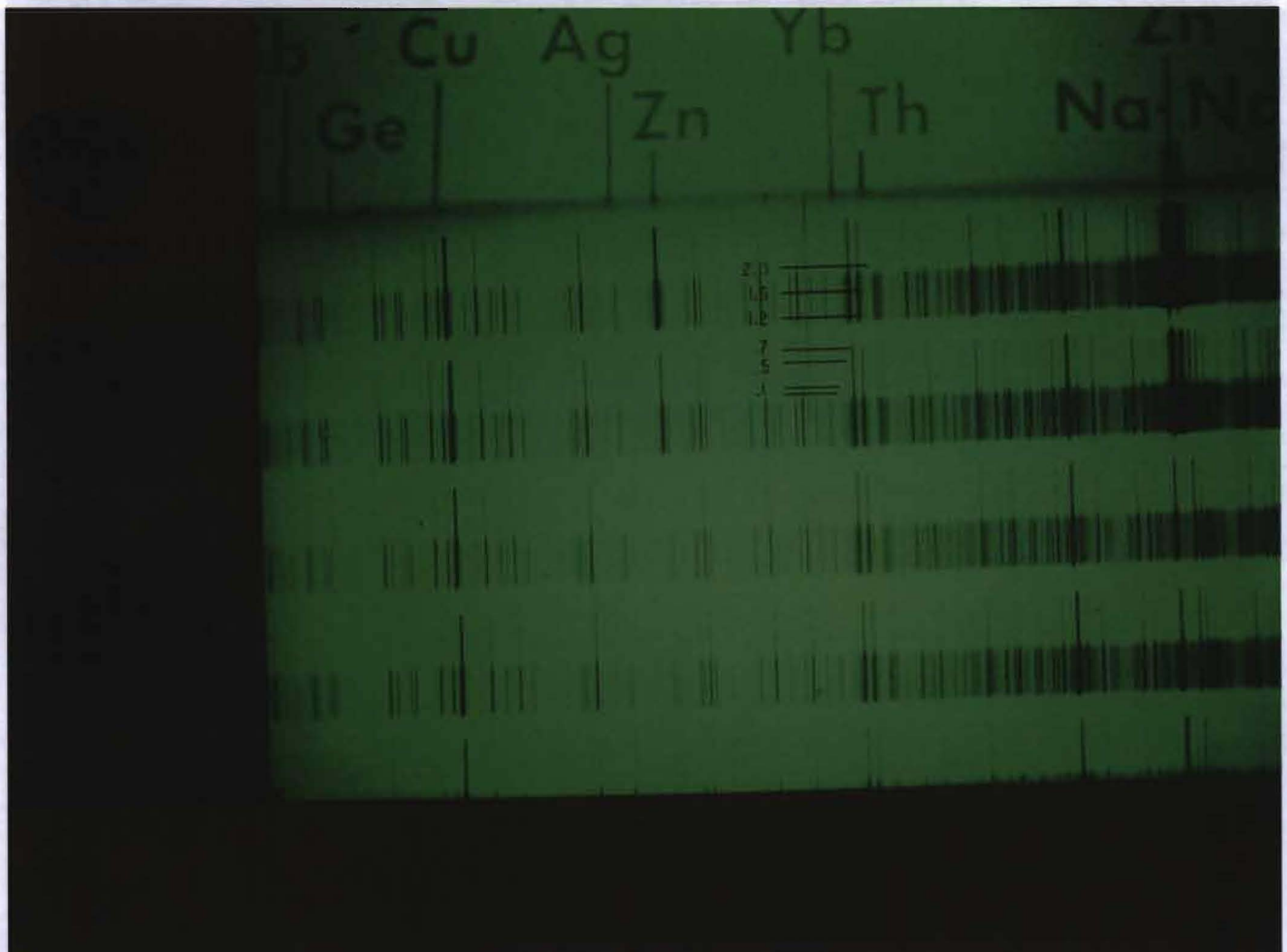


Processing Data

- The plates are read using a Jarrell Ash micro photometer. Each element for each sample aliquot is measured for its percent transmittance and recorded manually in a logbook
- All of the data is then manually entered into a computer using a BASIC program
- This computer program compares the sample data against the working standard curve of known concentrations (also analyzed in the same run batch) and determines a final concentration for each sample in ug/g (or ppm)
- Each sample aliquot concentration is then manually typed into an Excel spreadsheet
- The data is then uploaded into LIMS by using a macro – this eliminates one manual entry
- The data is checked by a second person for accuracy

Jarrell Ash Micro photometer

Measuring Percent Transmittance



Summary of Existing DC Arc Analysis

- The DC Arc stand, the Jarrell Ash spectrograph, and the Jarrell Ash micro photometer are 30 years old. We are not able to buy parts or get any professional service to maintain or fix the DC Arc stand or the spectrograph if a problem arises – the instruments are no longer made. **"We're on our own"**
- DC Arc is a "robust" method of analysis
- DC Arc gives us the capability of solid sample analysis
- The existing DC Arc stand does not allow for variable current settings, time-gating, background corrections, or interference corrections

Summary of Existing DC Arc Analysis – cont'd

- We can no longer procure any more photographic plates

- Some of the weaknesses with using these glass plates
  - The detection limits are limited
  - The linear dynamic range is limited by the amount of silver present
  - The background becomes darker over time due to degradation and exposure to humidity and room temperatures
  - The silver that comes off the plates during the developing process generates RCRA or mixed waste

Summary of Existing DC Arc Analysis – cont'd

- There is no data download capability for most of this process
- **MANY** hours of time are spent measuring percent transmittance data
- The data is manually manipulated in multiple steps which may lead to typos or handwriting mistakes
- The BASIC computer program is not very flexible for allowing the data to be processed
- The Pu-238 sample transfer from 7136 to 7134 is time consuming and a potential problem for contamination, dose, and sample loss

Objectives

- Interface a Prodigy spectrometer (Teledyne Leeman Instruments) with an arc stand similar to the existing one inside the glove box in 7136
- We can buy parts and have the instrument professionally maintained and serviced
- Eliminate the "hot job" transfer of samples from one room to another
- Eliminate the use of photographic glass plates – no RCRA or mixed waste, improved detection limits, and huge savings in labor
- New instrument will allow for variable current settings, time-gating, background corrections, and interference corrections
- Capabilities for computer download and processing of data
- This will be the prototype for future DC Arc analysis in PF-4

Prodigy ICP Spectrometer by Teledyne Leeman

Old vs. New

Old spectrograph:

spectrophotographic plate,

develop plate,

manual reading

New spectrometer:

Chips, digital,

computer

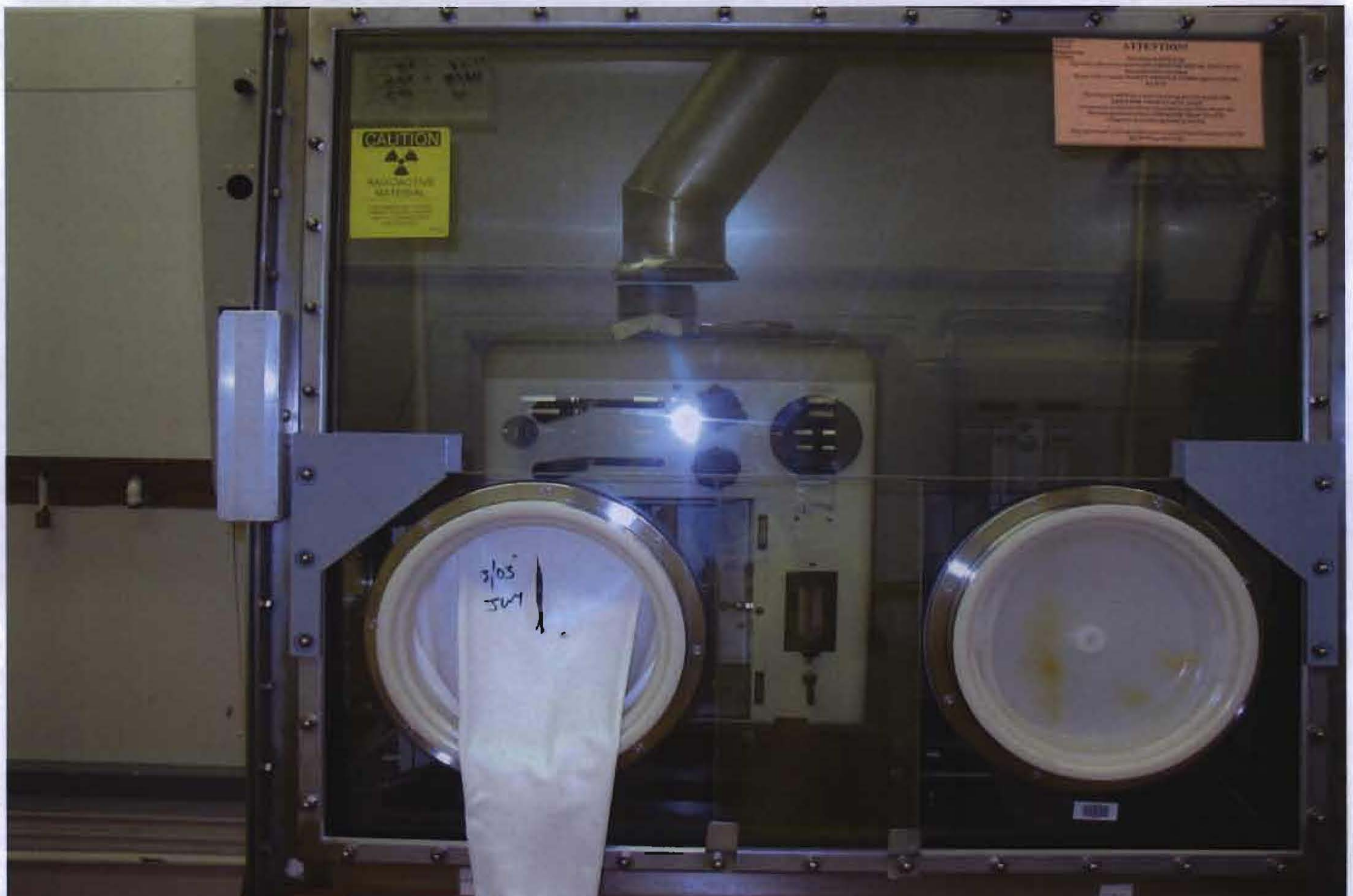
Same operation

Better quality

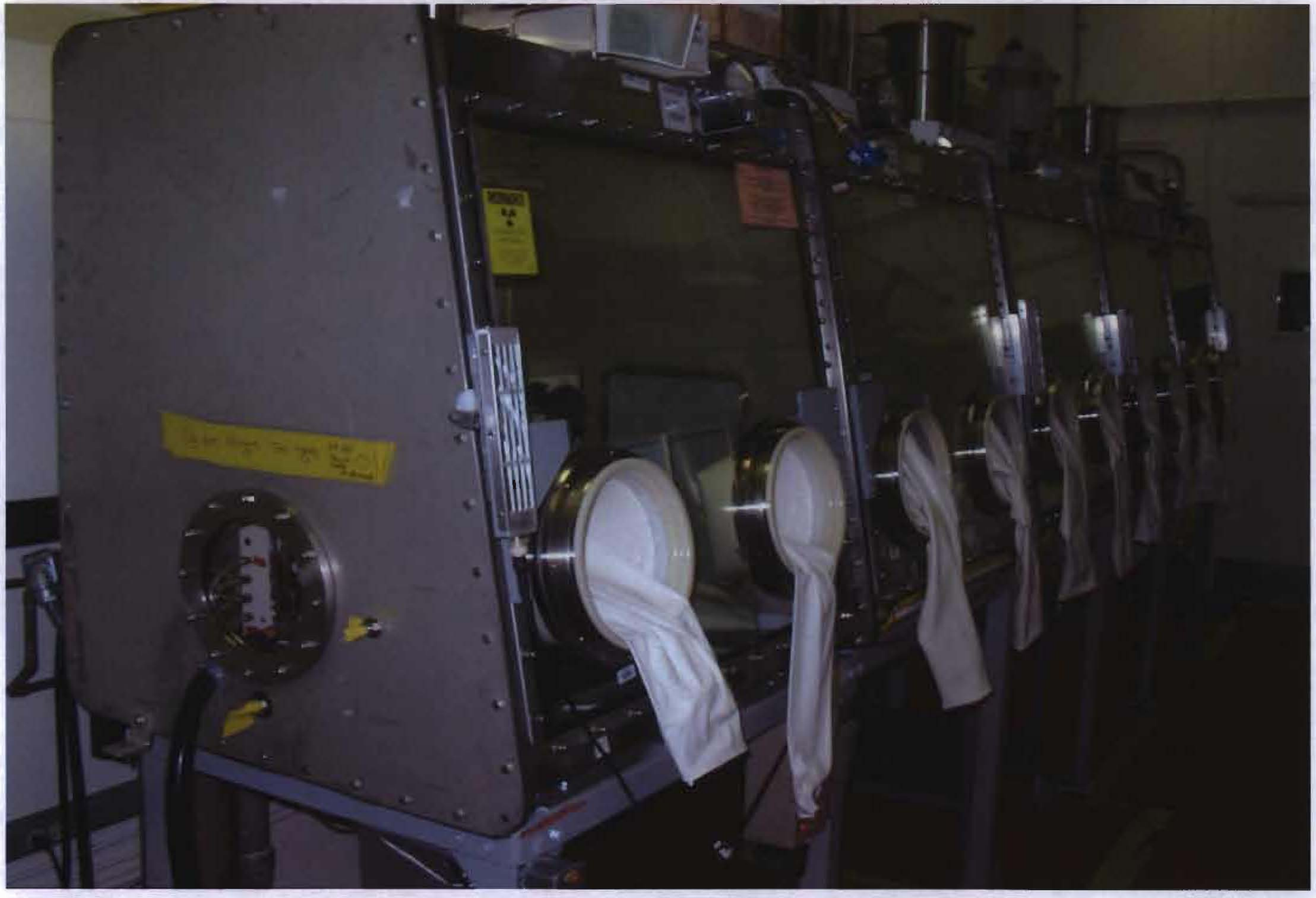
Safer

Teledyne Leeman Prodigy Spectrometer Interfaced with Glovebox Enclosure

Existing Arc Stand

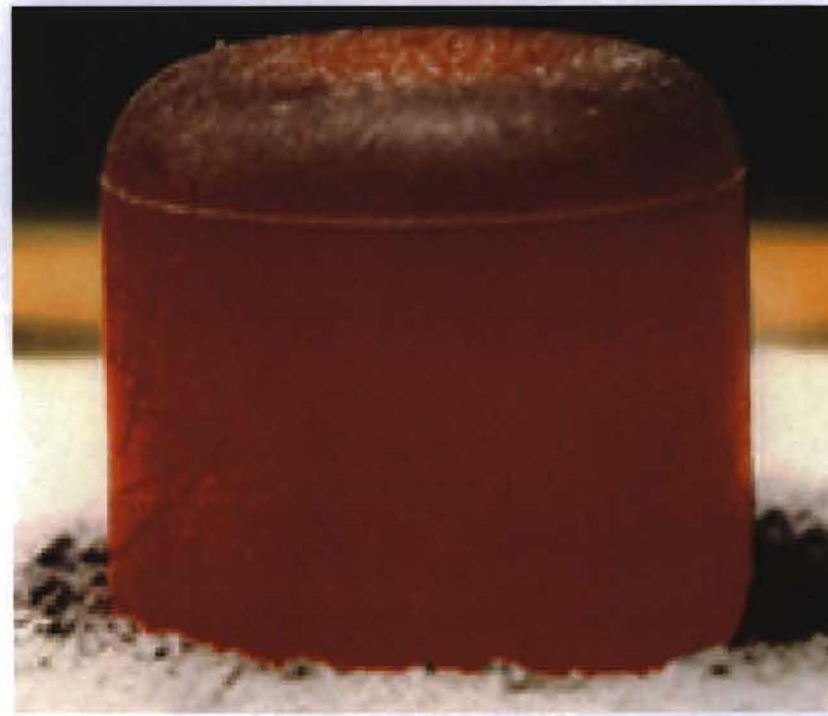


Glovebox for the New Modified Teledyne Leeman Prodigy Spectrometer

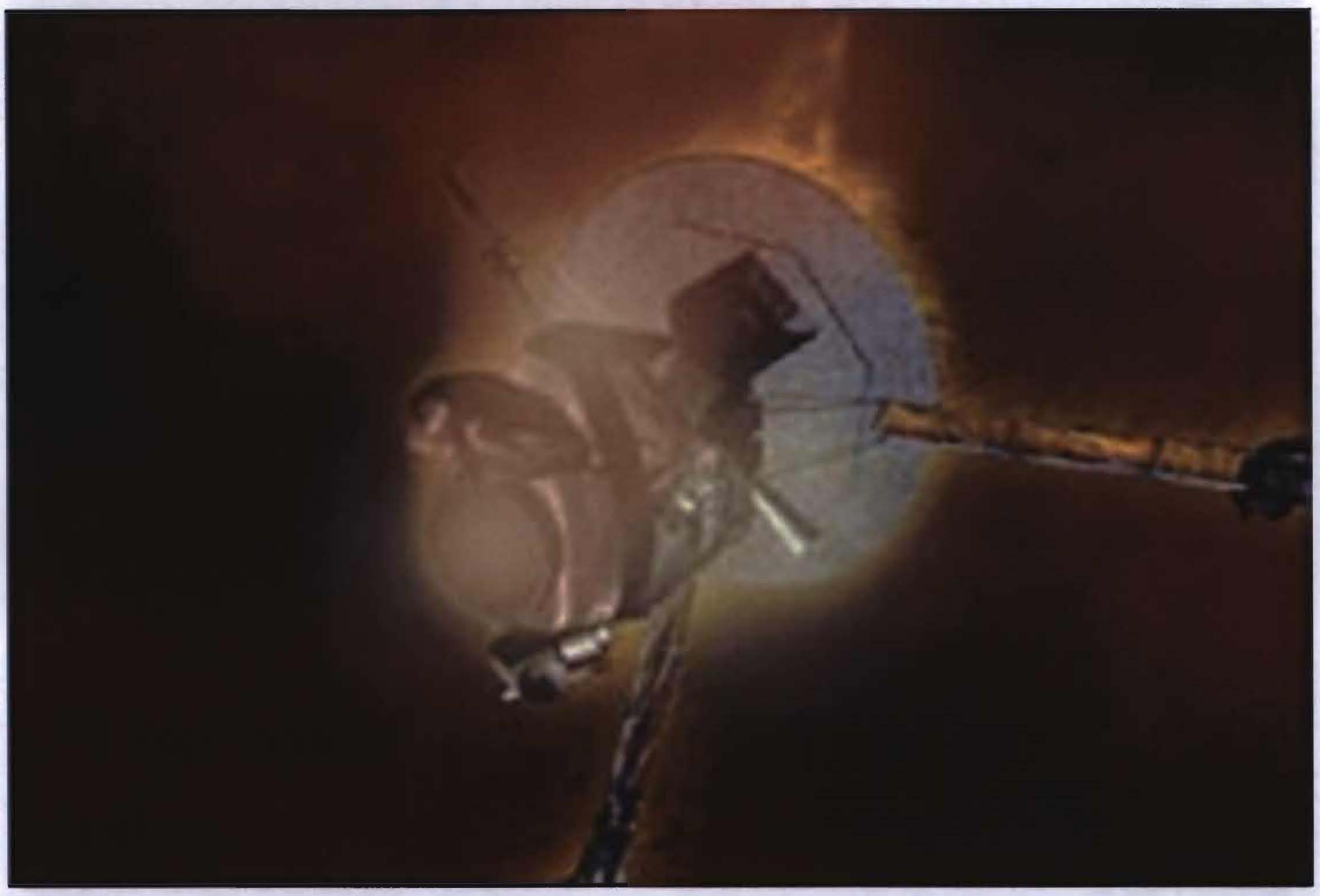


DC Arc Plasma

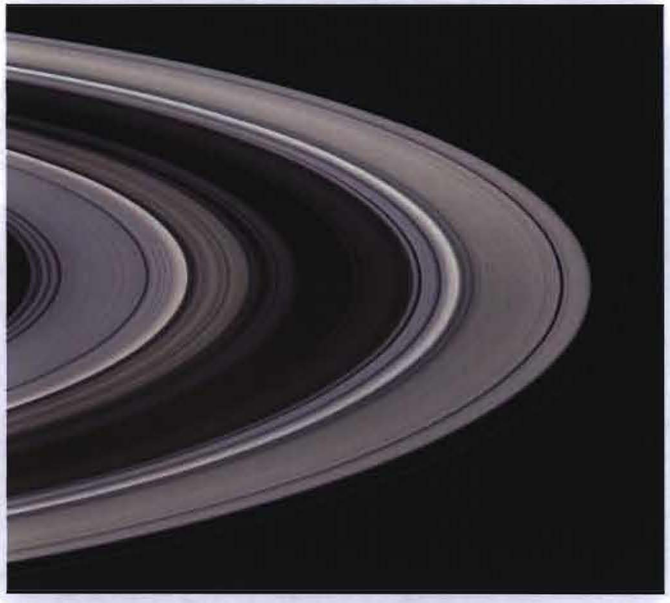
Plutonium – 238

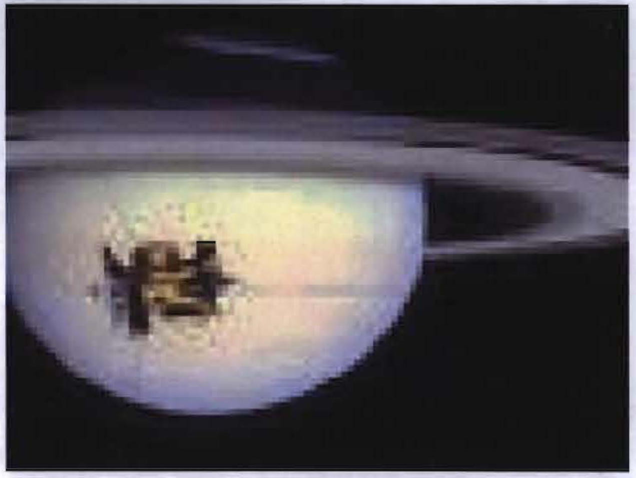


Galileo Spacecraft

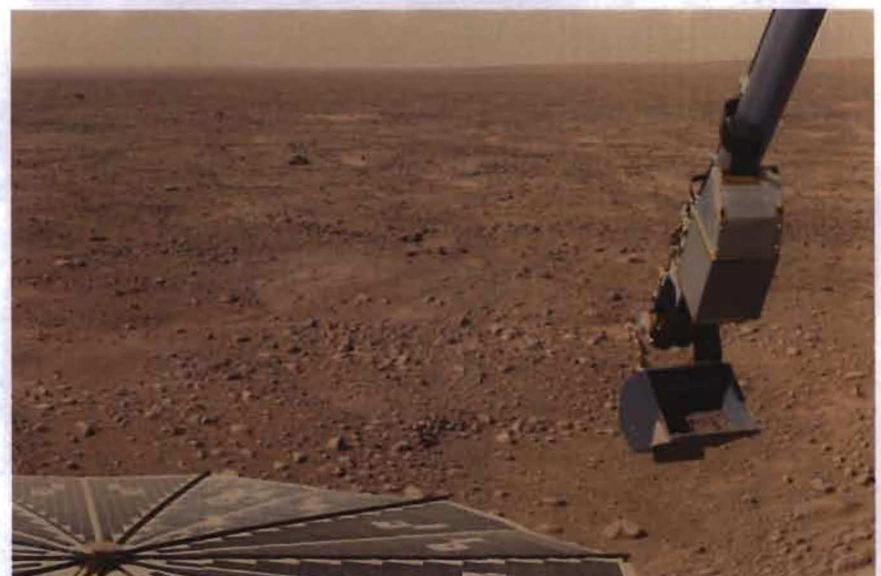


Cassini Spacecraft around Saturn





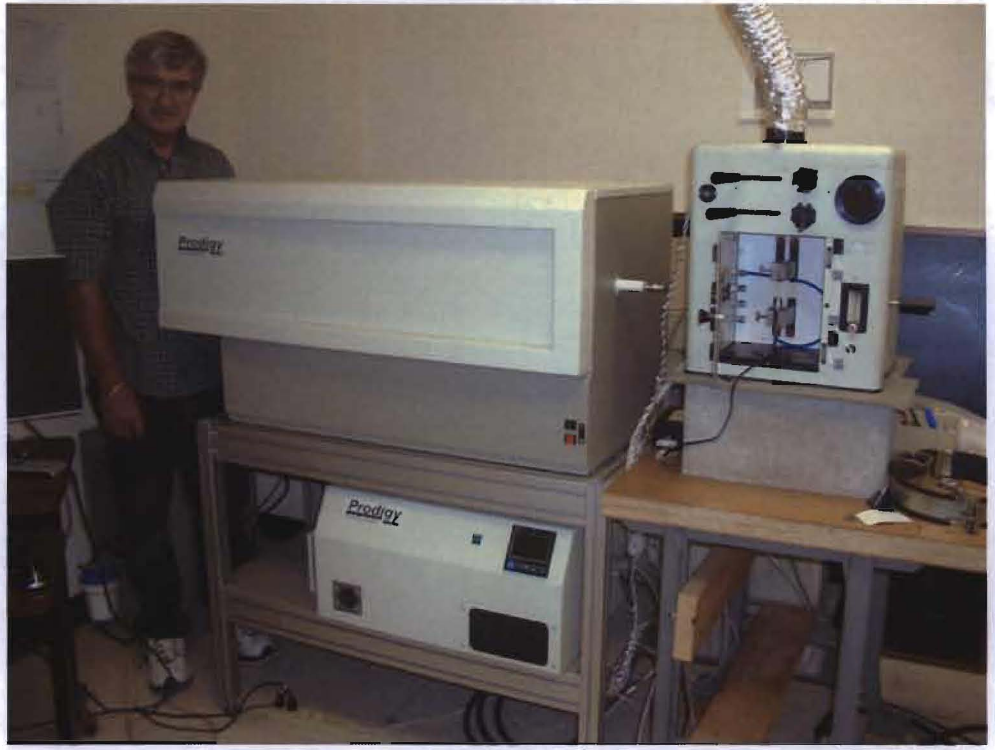
Mars Science Laboratory Rover



Proposed Time Schedule

- Instrument arrived in September, 2008
- Glovebox modifying, integrity testing, and installation of the DC Arc stand by January, 2009
- Instrument installation by March, 2009
- Instrument operational by April, 2009
- Instrument meets specification test by May, 2009

Acknowledgements



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of Teledyne Instruments Leeman Labs