Particle Size Analysis: Past, Present, and Paths Forward

CAD/PAD 2022 TEW
July 12-14

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CAPCO

EXTREME RELIABILITY
WHEN IT MATTERS MOST

Motivations for Understanding Particle Size:

1. Supply Variability
2. Obsolete military specifications

It is important to note that the preparation of a complex military specification involves much time and cooperation from many sources including military, federal, industrial and academic centers. As shown in Figure 3, the time period for the development of MIL-Z-46189 took over forty years from the initial work contributed by Harry Diamond Labs to the finalization of the military specification as noted above.

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A CASE STUDY OF THE DEVELOPMENT OF A MILITARY SPECIFICATION — ZIRCONIUM POWDER FOR THERMAL BATTERIES

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October 1987

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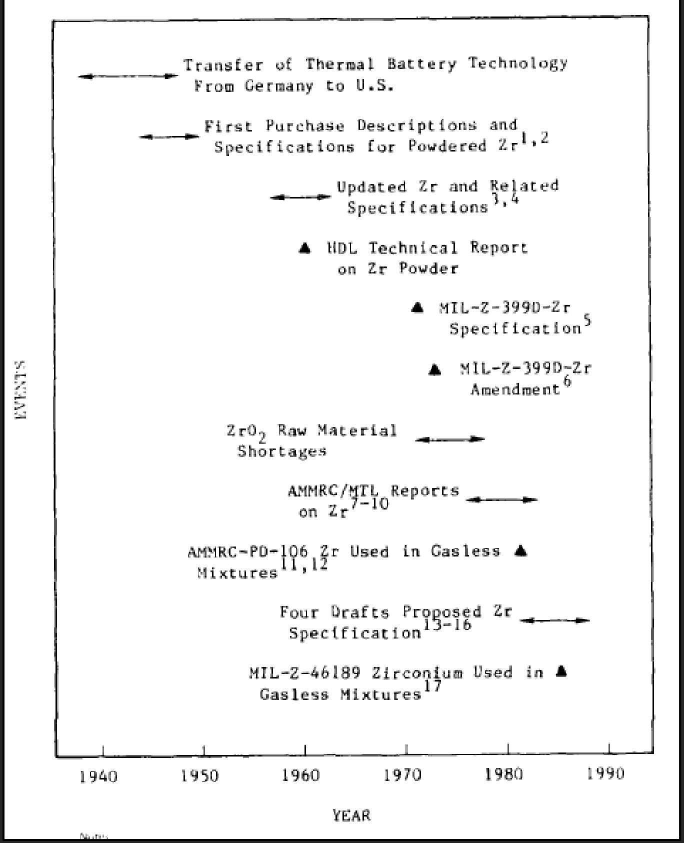
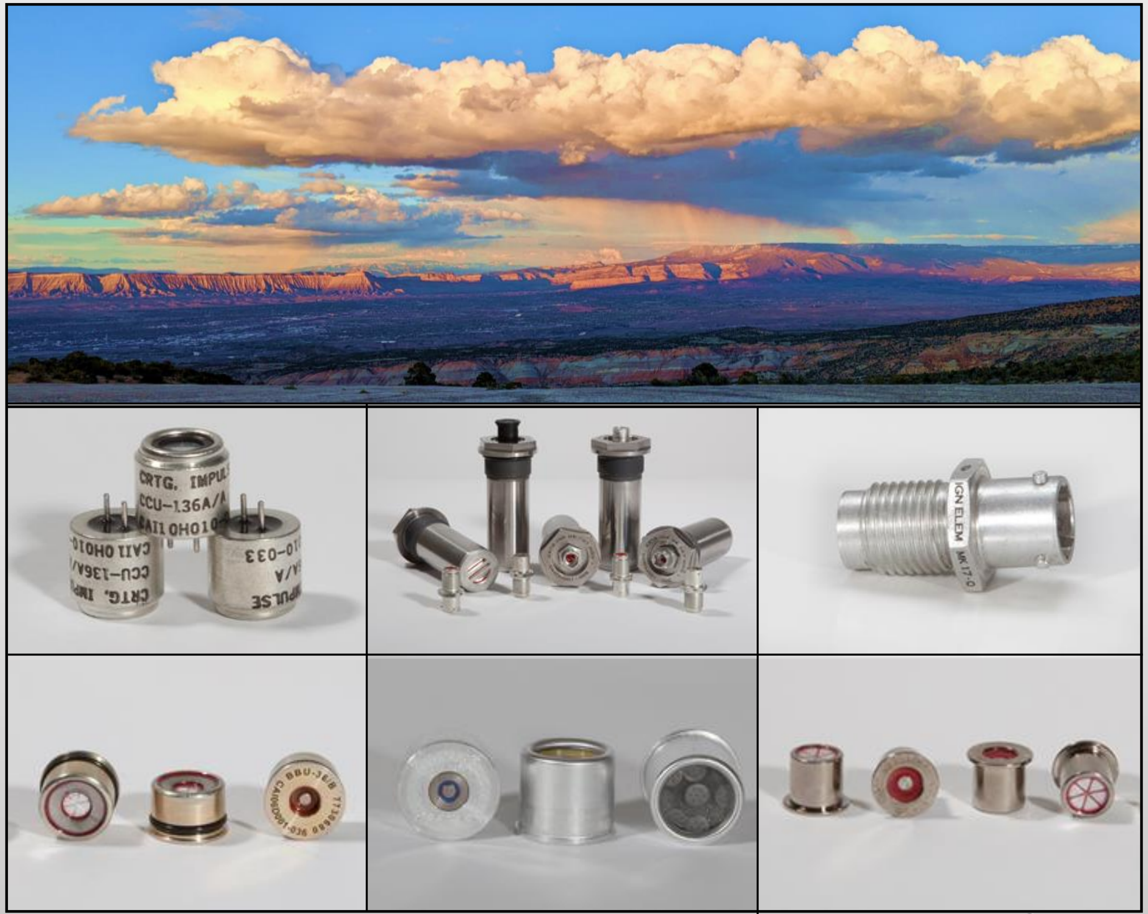


Outline

- Capco LLC Introduction
- Particle size and historical methods of subsieve measurements
- Impact of zirconium particle size on ZPP sensitivity
- Laser diffraction and considerations for pyrotechnics

Capco LLC Introduction

- Native American-owned small business in Grand Junction, CO
  - 144,000 sq. ft. facility
- 350+ Employees
- Prime DoD Contractor
- One of the largest US producers of impulse cartridges (ICs) for airborne expendable countermeasures
  - 1000s of cartridges produced daily
- US Navy, USAF, foreign militaries and commercial customers



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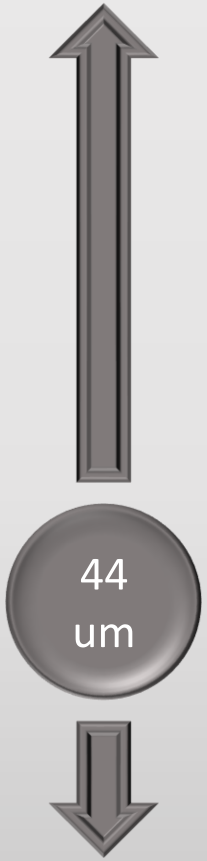
Capco LLC Introduction

- Explosives Capabilities:
  - 1.1,1.3, 1.4 storage magazines onsite
- Navy-approved LAT test facility
  - Ballistic testing
- 10k+ sq. ft of energetics manufacturing space
- Pyrotechnics / explosives characterization lab
  - DSC/TGA, Calorimetry, FTIR w/ gas cell and ATR
  - **Microtrac Bluewave S3500 Laser Diffraction Particle Size Analyzer**

Particle Size Specs in Energetic Constituents

- Military specifications govern particle size requirements
  - Most materials require sieve fraction determination (e.g. 44 um or larger)
    - Oxidizers
    - Inerts
    - Granular Metals
  - Subsieve fraction measurements for metal fuels
    - **Fine metal particle size heavily drives powder sensitivity**
- Mil Spec Subsieve Measurements
  - Andreasen Pipet Method (sedimentation)
  - Eagle-Picher Turbidimeter (sedimendation)
  - Wet sieving with extremely fine meshes (625 mesh, 10 um)
  - **Fisher Sub Sieve Sizer ("FSSS", air permeability) (Ti, Zr, B, $KClO_4$)**
    - Modern version made by Micromeritics (ASTM B330)
- Main issues: obsolete military specifications, extinct equipment, coarse or no size distribution data, lengthy analyses

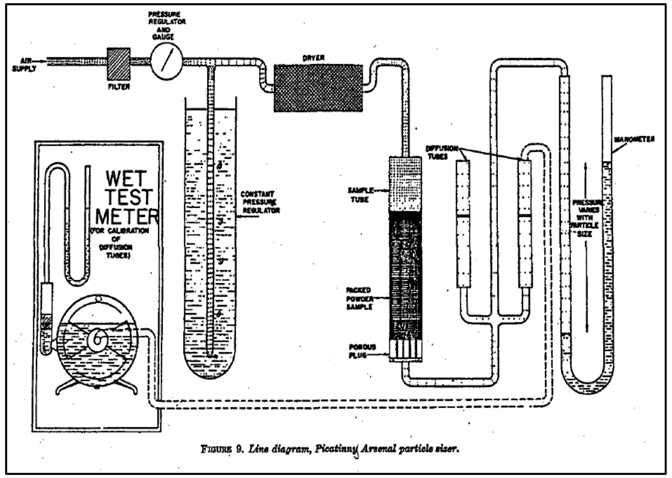


http://www.bangalorewiremesh.com/wp-content/uploads/2013/06/Test-Sieves3.jpg

Air Permeability and Sedimentation Methods

- Air Permeability
  - Still an established method for measurement of alumina, silica, metal powders, cements, ceramics, etc.
- Methods:
  - ASTM B330, C721-15
    - B859 deagglomeration method
  - ISO 10070
- Theory:
  - Gooden and Smith Equation
  - Stokes Equation
- **Both "Area Weighted" average diameters**
  - **"Fisher Number"**
  - Surface area-dependent measurement
  - Most relevant property for pyrotechnic reactivity

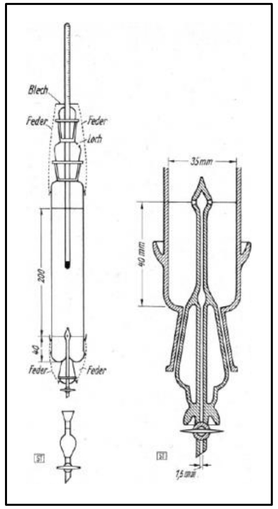
Air Permeability



Picatinny Arsenal (Modified FSSS) Apparatus
Gooden and Smith Equation

$$\mu = \frac{KHN}{(AH - N)^{3/2}} \cdot \sqrt{\frac{F}{P - F}}$$

Sedimentation



Andreasen Apparatus
Stokes Equation

$$V = \frac{d^2 g(\rho_p - \rho_s)}{18\eta}$$

https://www.researchgate.net/figure/Section-drawing-of-the-sedimentation-apparatus-used-in-the-Andreasen-pipette-method-to_fig4_230822038

Important Notes to Fisher Numbers

MIL-STD-1233
21 March 1962

Method 100

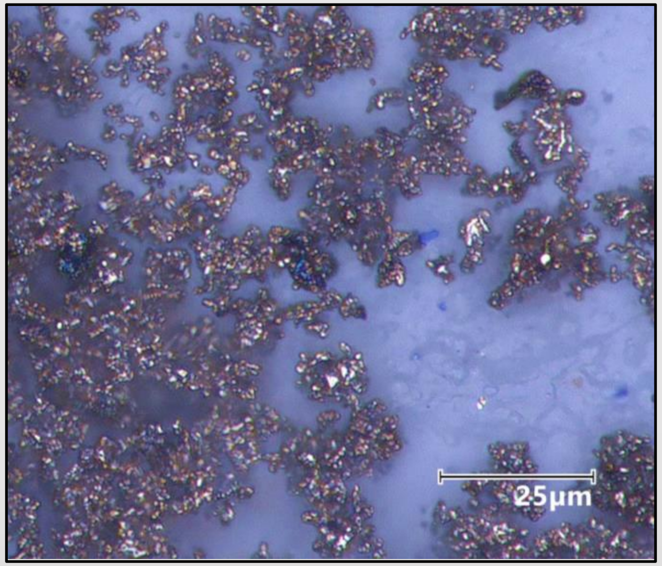
DETERMINATION OF AVERAGE PARTICLE SIZE,
2 to 100 MICRONS (FISHER SUB SIEVE SIZER)

- "Any deviation of the particles from sphericity would increase the surface per unit weight of material."
  - **Rougher particles translate to smaller Fisher Numbers**
- "The particle size obtained in not an absolute value. It is useful, however, for comparisons of average particle sizes based on surface area measurements."
  - **Results are technique-dependent**

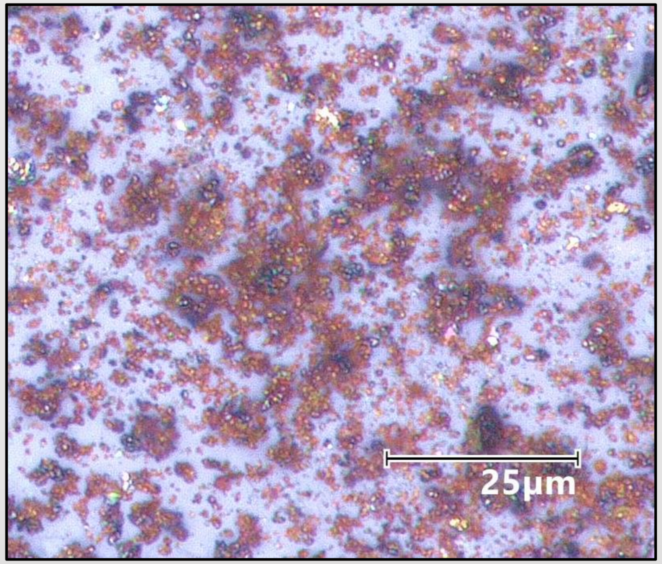
The average particle size of powdered ingredients, as determined by the air permeability method, is an average surface weighted diameter and, is a measure of the surface area per unit weight of powder. Any deviation of the particles from sphericity would increase the surface per unit weight of material. Thus, the addition of irregular particles to a sample of perfectly spherical particles would increase the average surface of the sample and consequently decrease the average particle diameter.

diameter. The Gooden and Smith equation is a rapid method for calculating the average particle size of powdered material (see 4.4.2.3). The paraticle size obtained is not an absolute value. It is useful, however, for comparisons of average particle sizes based on surface area measurements. The validity of the particle size comparisons based on the

Getting to Know Your Finely Divided Metals



A) Zirconium
B) Boron
C) Titanium



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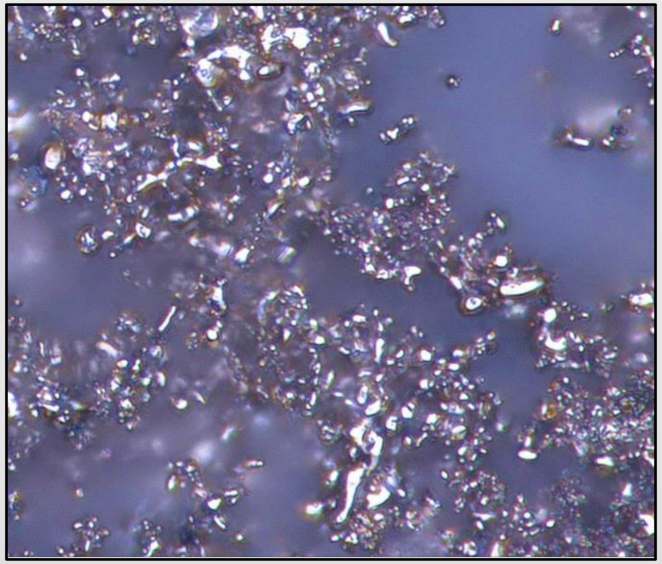
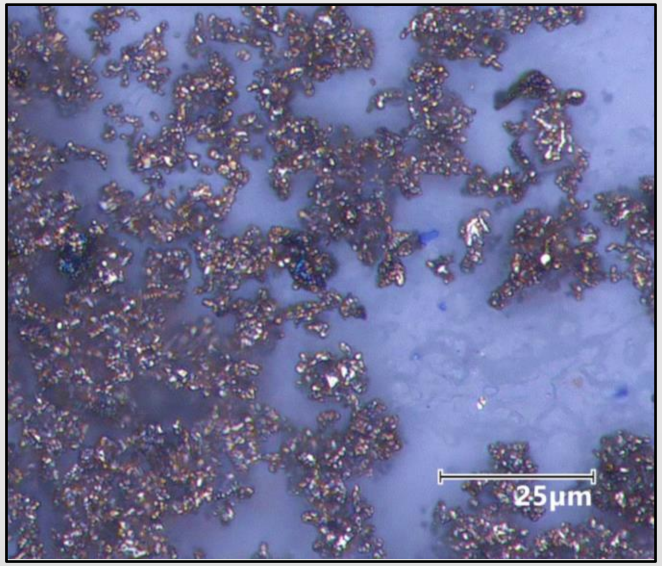


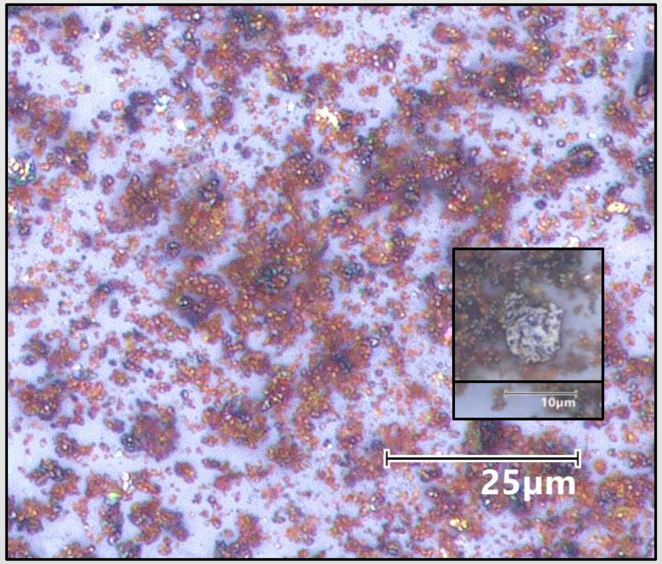
A) Zirconium
B) Boron
C) Titanium

Image source: Keyence VHX-7000, 2500x magnification

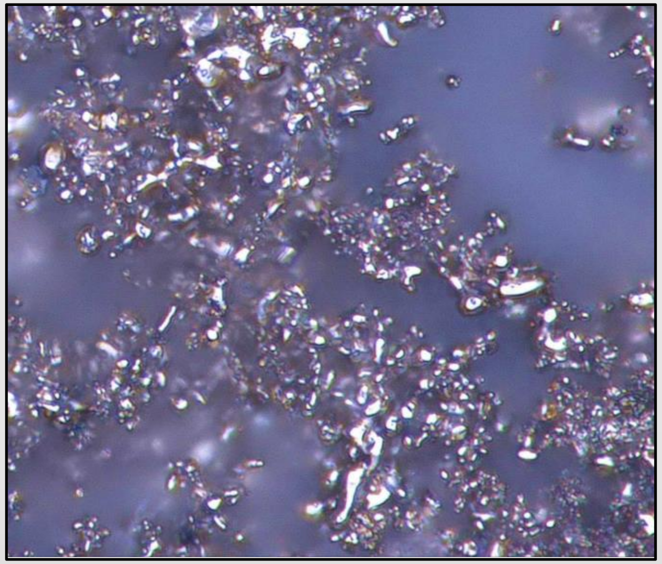
Getting to Know Your Finely Divided Metals



Zirconium
MIL-Z-399D
Type 2 Class 3



Boron
MIL-B-51092 Rev B



Titanium
MIL-T-13405
Type 1 (Grade E)

Not so spherical..

Image source: Keyence VHX-7000, 2500x magnification

Zirconium In Ignition Composition ZPP

- Zirconium Potassium Perchlorate (ZPP)
  - Ignition composition
  - Aka "Low Flash Primer" in Capco applications
  - Notorious for ESD sensitivity
- Zirconium Specification
  - MIL-Z-399D
  - **"Obsolete for new designs"**
  - How to define and measure Zr going forward?
- Particle size by MIL-STD-1233
  - 60+ year reign
  - 3.0±1.0 um zirconium by FSSS
- **Case study in zirconium sensitivity in ZPP**

MIL-Z-399D
1 October 1971
SUPERSEDING
MIL-Z-399C
19 February 1969

MILITARY SPECIFICATION

ZIRCONIUM (GRANULAR AND POWDERED)

Table II. Particle size requirements for type II zirconium

Sieve	Class 1	Class 2	Class 3
Thru No. 120 sieve (125 microns), percent by weight	100	100	99.5 min.
Thru No. 200 sieve (74 microns), percent by weight	99 min.	99 min.	
Thru Buckbee Mears No. 26 sieve, (20 microns), percent by weight	96 min.	96 min.	
Subsieve			
Less then 9 microns, percent by weight	85 min.	85 min.	
3 microns, percent by weight	70-90	70-90	
0.75 microns, percent by weight	12-30	12-30	
Average particle size, microns	2.5±1.0	2.0 ± 0.3	3.0 ± 1.0

MIL-STD-1233
21 March 1962

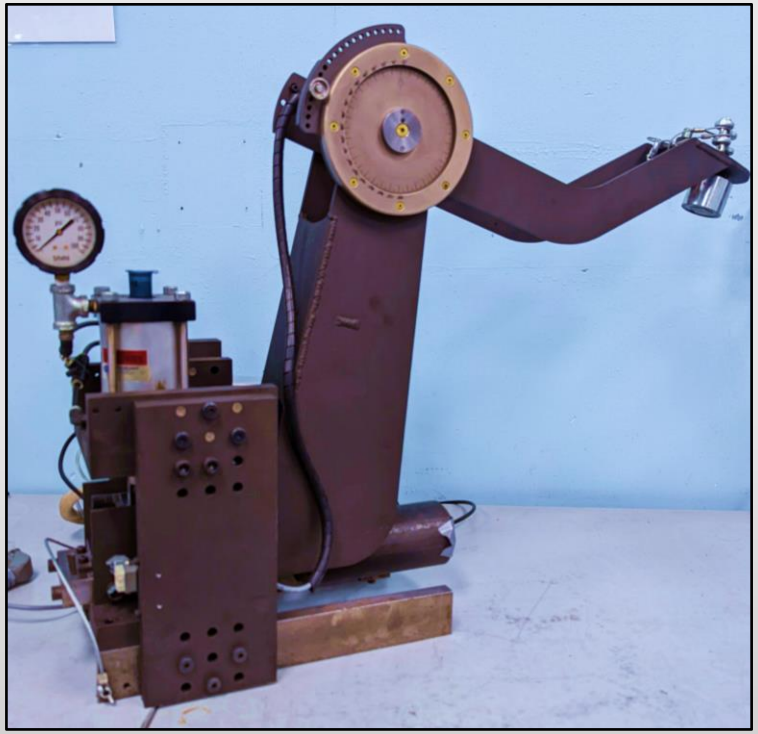
Method 100

DETERMINATION OF AVERAGE PARTICLE SIZE,

2 to 100 MICRONS (FISHER SUB SIEVE SIZER)

Testing Sensitivity of Zirconiums in ZPP

- Zirconium particle size study
  - Sizes: 1.5, 2.5, and 3.2 um
    - Supply variability
  - Determine impact on sensitivity
- Friction Tester
  - ABL-Style Friction Tester
  - Sliding plate, static wheel, and pendulum
  - Variable wheel force and impact velocity
- ESD Tester Configuration
  - Powder consolidated (10k PSI) in commercial header
  - Pin-to-case current path
  - "Human" Model Capacitor/Resistor
    - 500 pF, 500 Ω
  - Variable voltage (energy)
    - 1-30 kV (0. 3-225 mJ)



ABL-Style Friction Tester

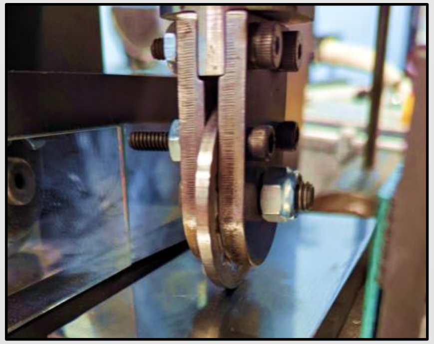
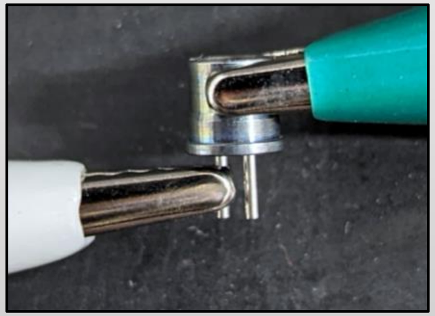


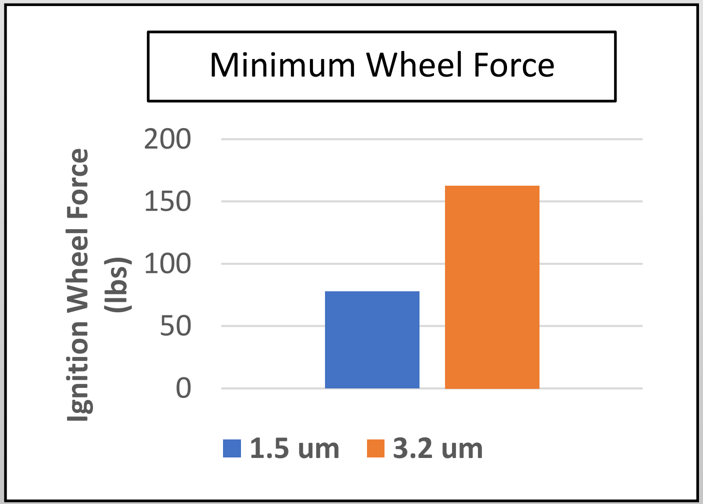
Plate and Wheel

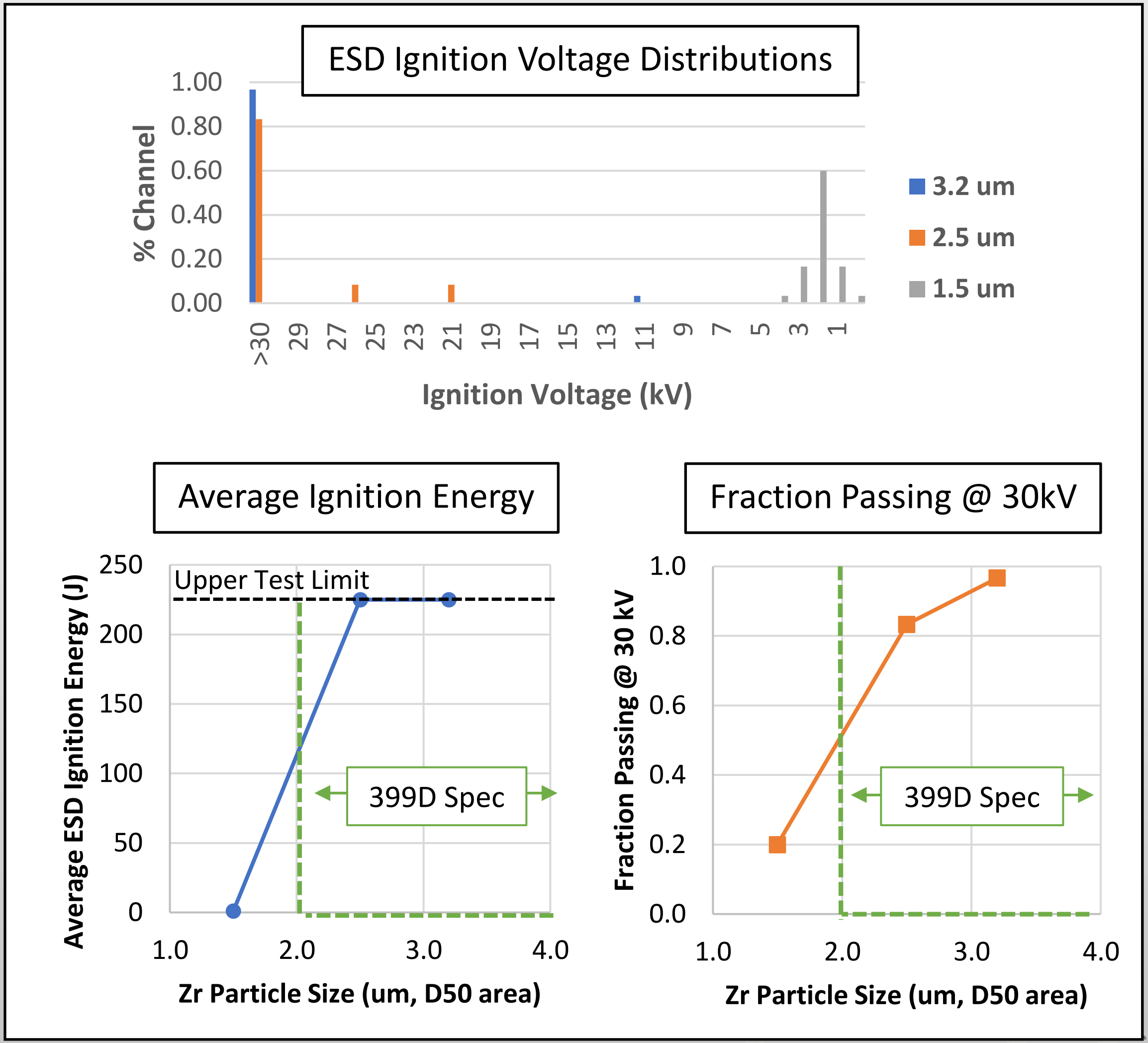


Pin-to-case current path

Testing Sensitivity of Zirconiums in ZPP

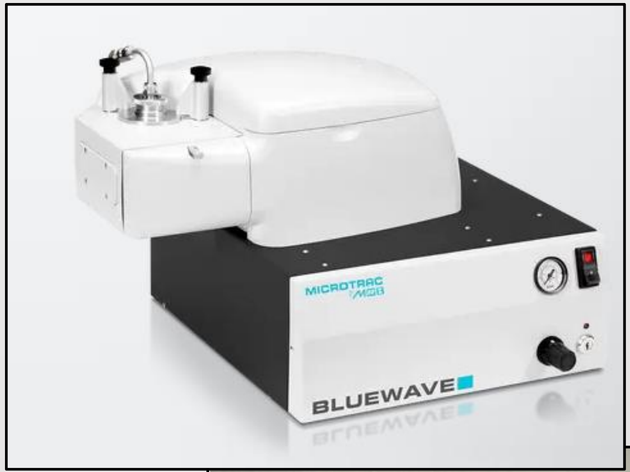
- Friction:
  - Wheel Force halved by smaller Zr
- ESD:
  - Orders of magnitude lower ignition threshold <2 um
- Zr particle size specifications clearly important to powder properties
- Obtaining suitable constituents can be a "back and forth" with manufacturer, but how to measure? And communicate sizes consistently?



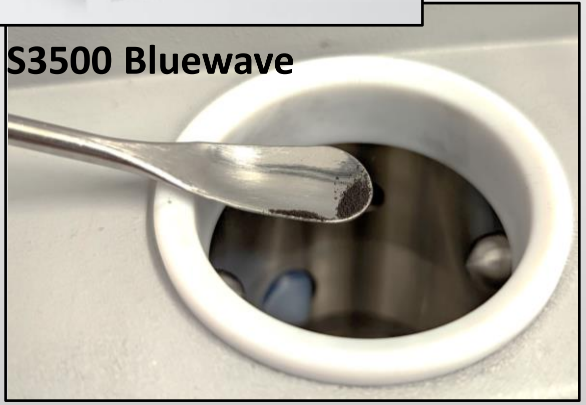


Laser Diffraction Particle Size Analysis

- Mainstream technique (Mid-90s)
- Wide measurement range (0.5-4000 um), fast, gives PSD, sample vehicle can be flowing air or solvent
  - We use isopropyl alcohol
- Standard Methods (**Guidelines**)
  - ASTM WK45140 still under development (Since 2014!)
  - ISO 13320:2020 (published guidance, not specific requirements)
- **Technique intrinsically "Volume-Weighted"**
  - Mie Theory of light scattering in 1908
  - Solution of Maxwell's Equations
  - Particles assumed as spheres
  - Requires knowledge of sample/solvent refractive indices
- Gives access to particle size distribution data



Microtrac S3500 Bluewave



Sample introduction

"..spherical cows in a vacuum.."

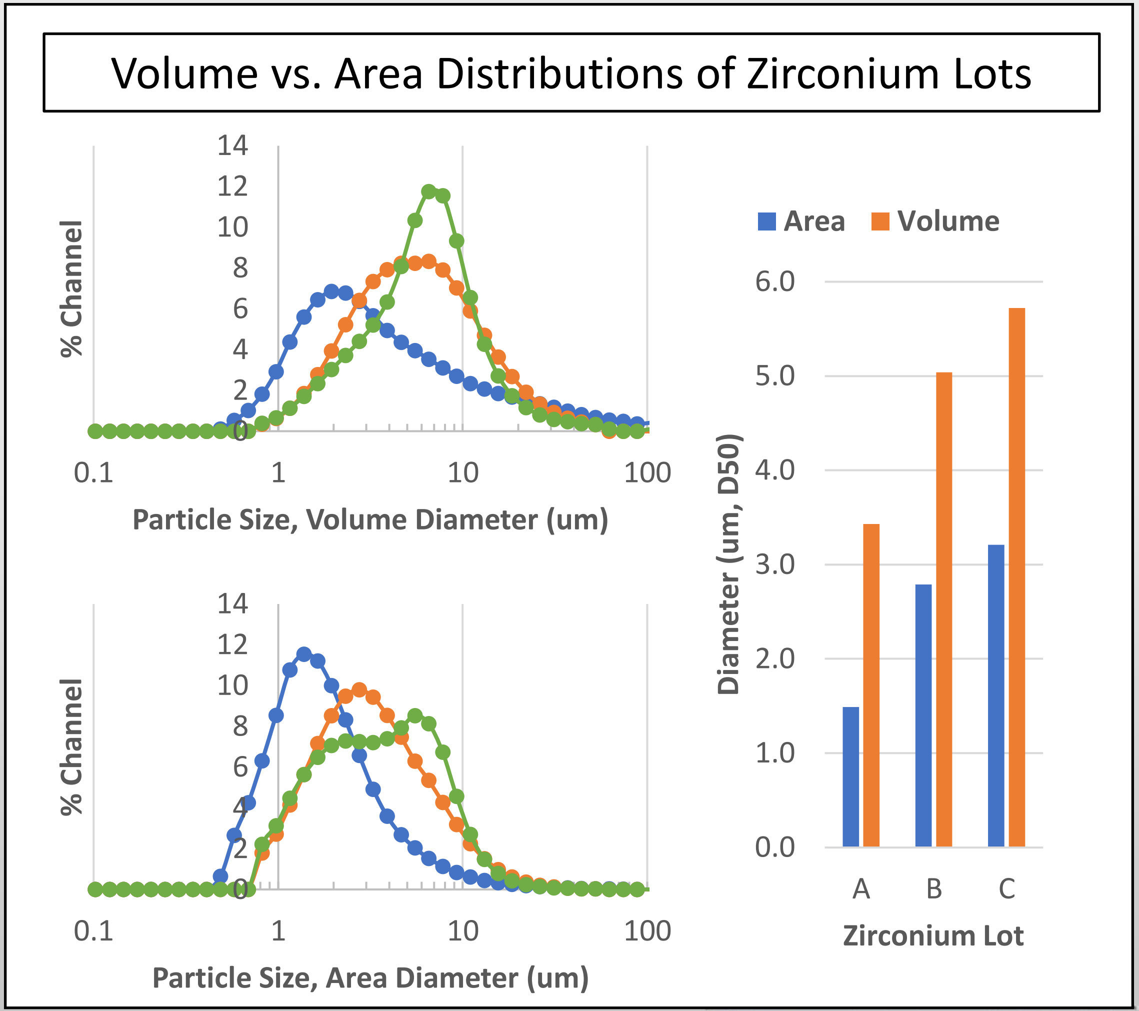
Gustav Mie

https://prabook.com/web/show-photo.jpg?id=2712382&cache=false

https://www.microtrac.com/products/particle-size-shape-analysis/laser-diffraction/s3500/

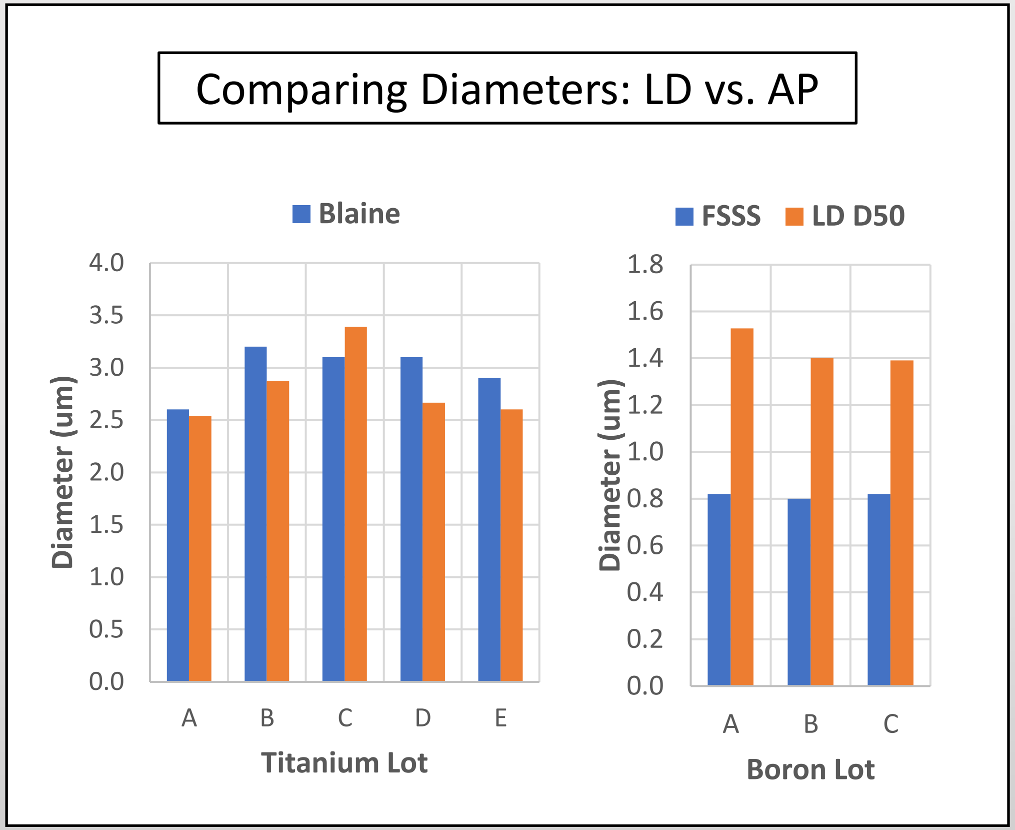
Discussing Laser Diffraction Results

- Data typically expressed as "Median Values"
  - D10, D50, D90
  - Percentage of particles above or below a Dx value
- Volume vs. Area Diameter Weighting
  - Weighted to larger (volume) or smaller (area) particles
  - Percentage of population at a given diameter
- Are bimodal distributions important?



Comparing Laser Diffraction to Air Permeability

- **"Area Weighting" most comparable to Air Permeability results**
- Comparability sample/metal dependent
  - Boron agglomeration (mfg. advised)
  - Sample preparation?
- Irregular particles
  - Instrument manufacturers offer "proprietary" methods of irregular shape interpretation
  - **How does "roughness" impact LD vs AP?**
- Conversion to Area Weighting ideally only applies to "normal" particle size distributions
- **Moving forward with LD for size specifications requires transference of experience with Fisher Numbers**



EXTREME RELIABILITY WHEN IT MATTERS MOST

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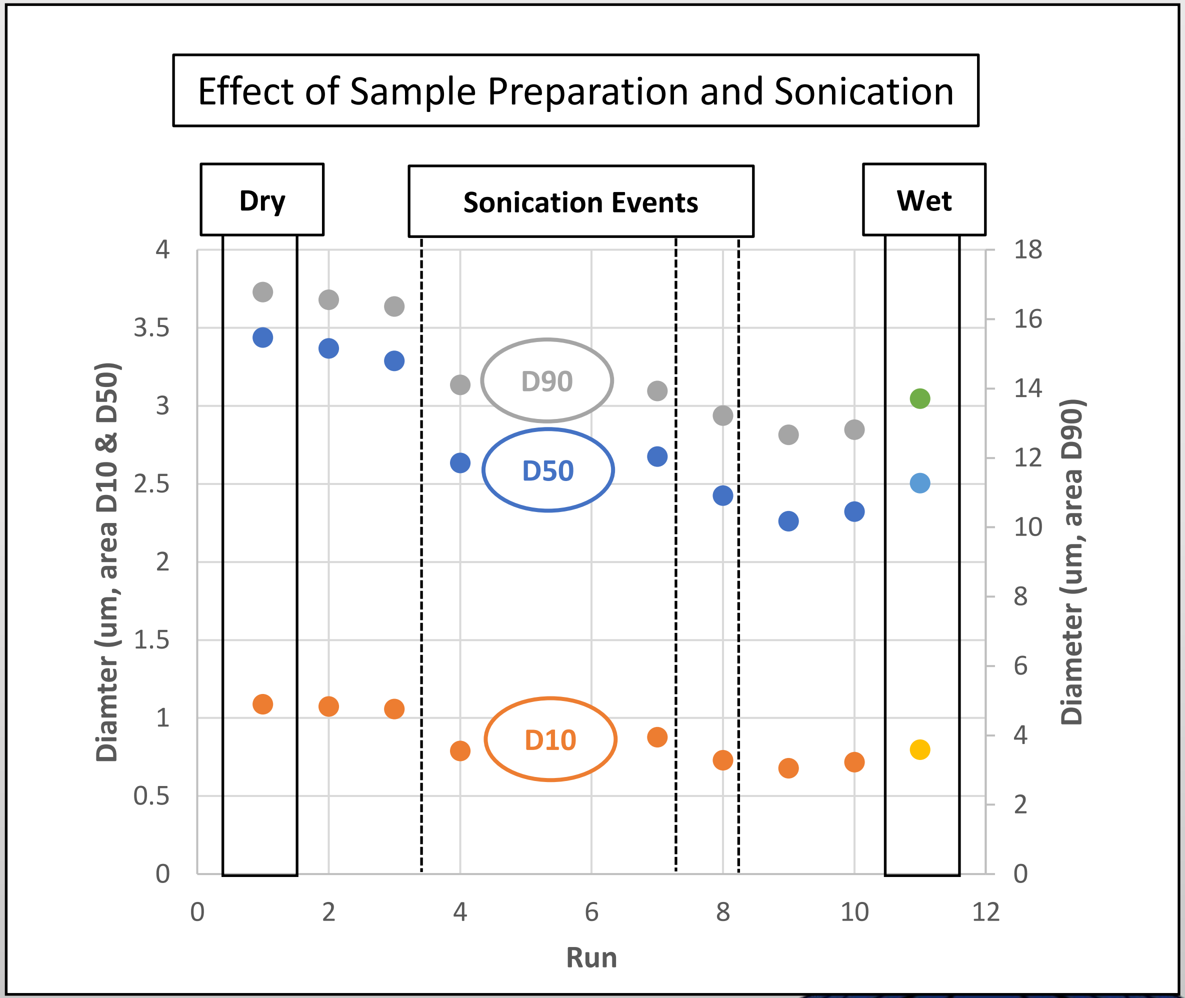
Titanium Sample Preparation Considerations

- Titanium stored in Ethanol
- Samples introduced dried or wet as "slurry"
  - Aggregation during drying
  - Sonication desegregates particles
  - Attrition possible in softer materials
- High rate of settling in slurry
  - "Representative" sampling method?
- Sample preparation SOP must be specified for reproducible results



EXTREME RELIABILITY WHEN IT MATTERS MOST

CAPCO

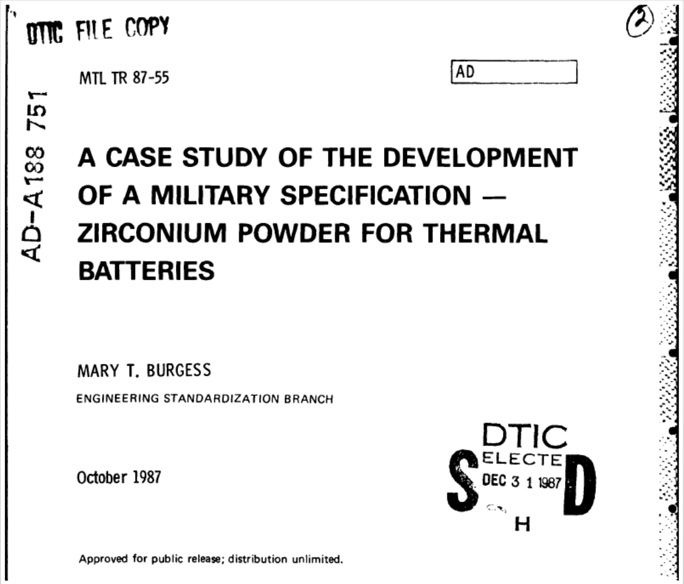
Considerations for Laser Diffraction

- Requires you know something about the sample
  - Absorb/reflect/shape
  - Agglomeration during drying
  - Desegregation by sonication/solvent forces
- Irregular particle shape math is proprietary to LD manufacturers
- May be variations in detector design that give differences even in spherical analysis, conversion to area diameter technically only valid for symmetric distributions, "roughness" in LD data
- ISO and in-progress ASTM standards for use are "guidelines"
- How does constituent behave during a blend? What characterization is most representative? Consistent? Useful?
  - Is everyone blending wet? Anyone drying metals before blending?
- How many MFGs run Laser Diffraction? Fisher? Blaine? Others?

Conclusions and Closing Thoughts

- Obsolete military specifications and standards pushing adoption of modern particle size analysis
- Laser diffraction: fast, versatile distribution data
  - "Area distributions" most relevant to pyrotechnic development!
  - Separate intrinsic measurement and caveats versus air permeability
- How to specify but not overcontrol requirements for constituent, powder blend, and assembled cartridge?
  - Is distribution data necessary? Is a D50 sufficient?
- What testing methods to use? Old with existing information or move into new domain?

Thank you!



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