3rd NIST Workshop on Cement Materials Characterization

XRF ANALYSIS

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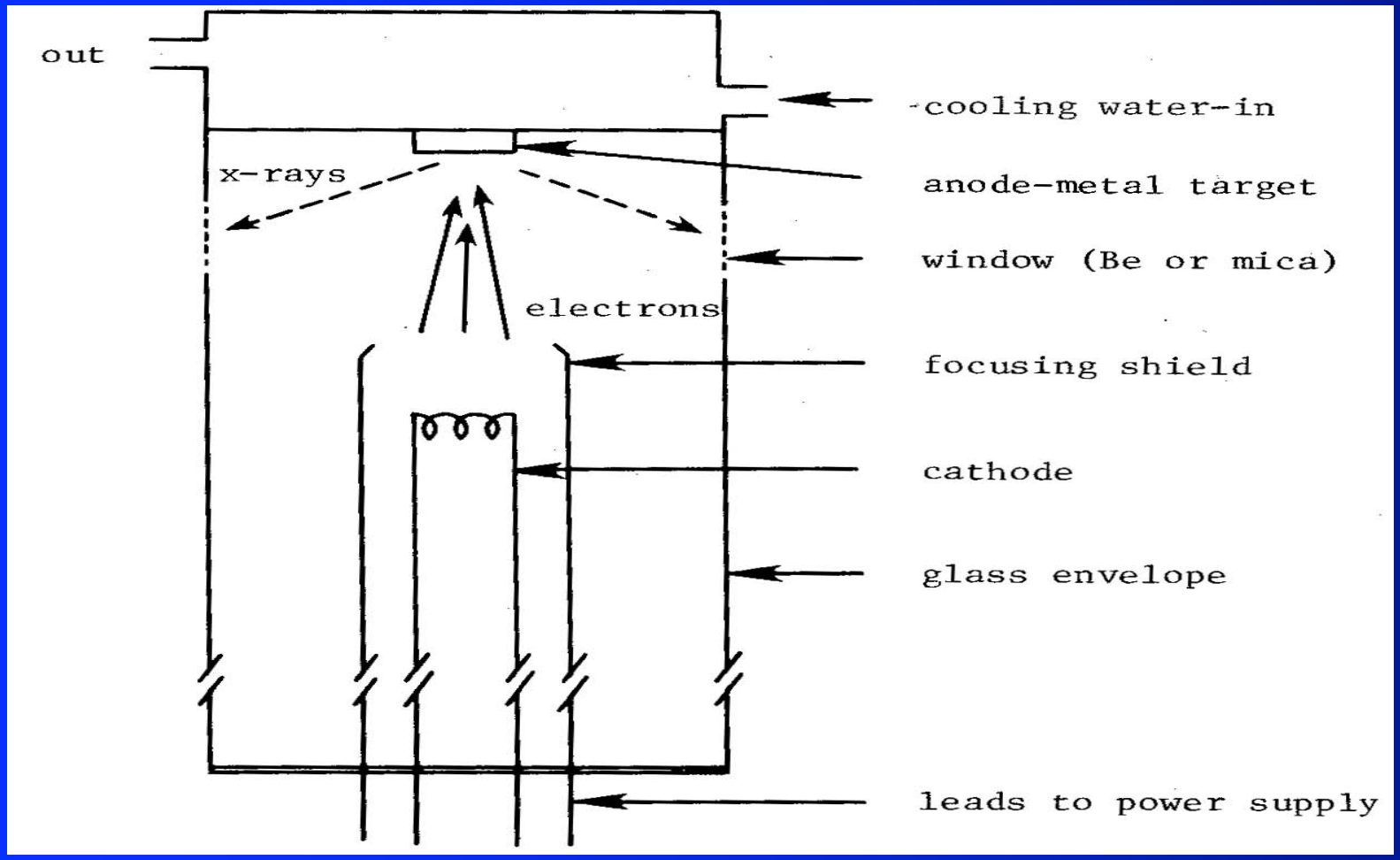
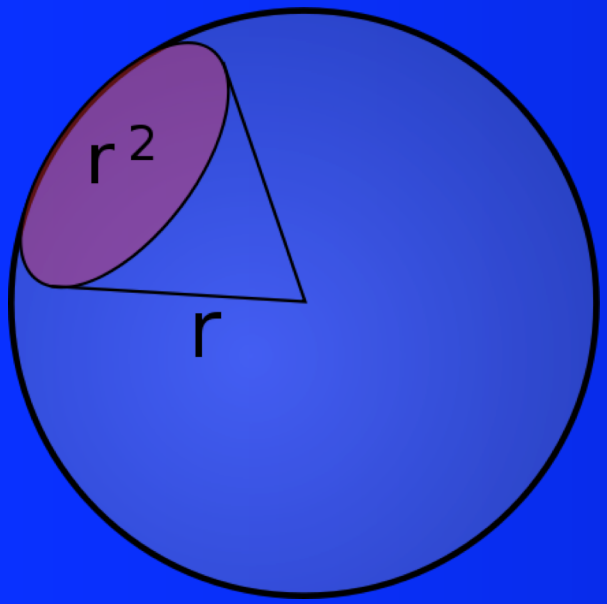
X-ray Analysis

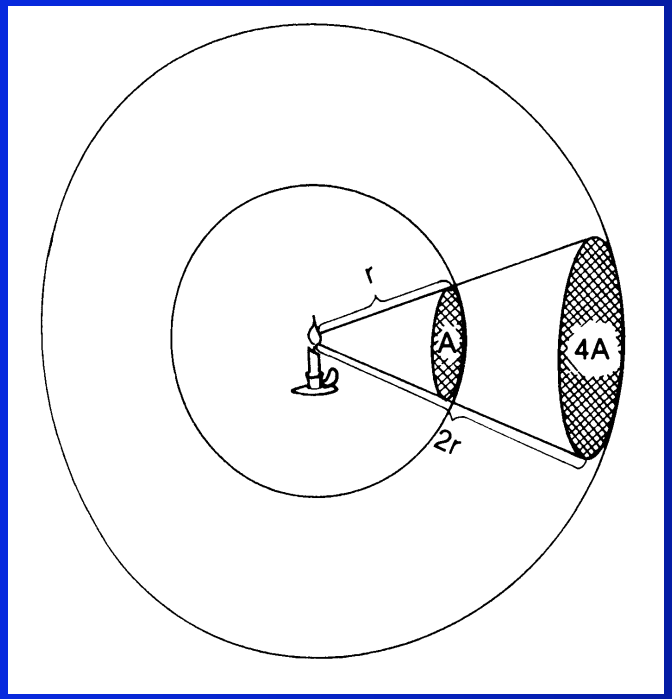
- XRF is elemental composition, fast, accurate
- Perfect for production
- Alternate C114 wet methods too time consuming
- We report as the oxide by convention
- We can run solids or liquids
- Metals reported as the element

Schematic Diagram



Steradian





X-ray tube spectrum

- Electrons accelerated towards target
- hits target and gives up energy step wise which gives rise to the continuum
- More Kv shifts short wavelength limit to the left thus exciting higher atomic number elements
- Higher energy/shorter wavelengths
- Lower energy/longer wavelengths

Ionization

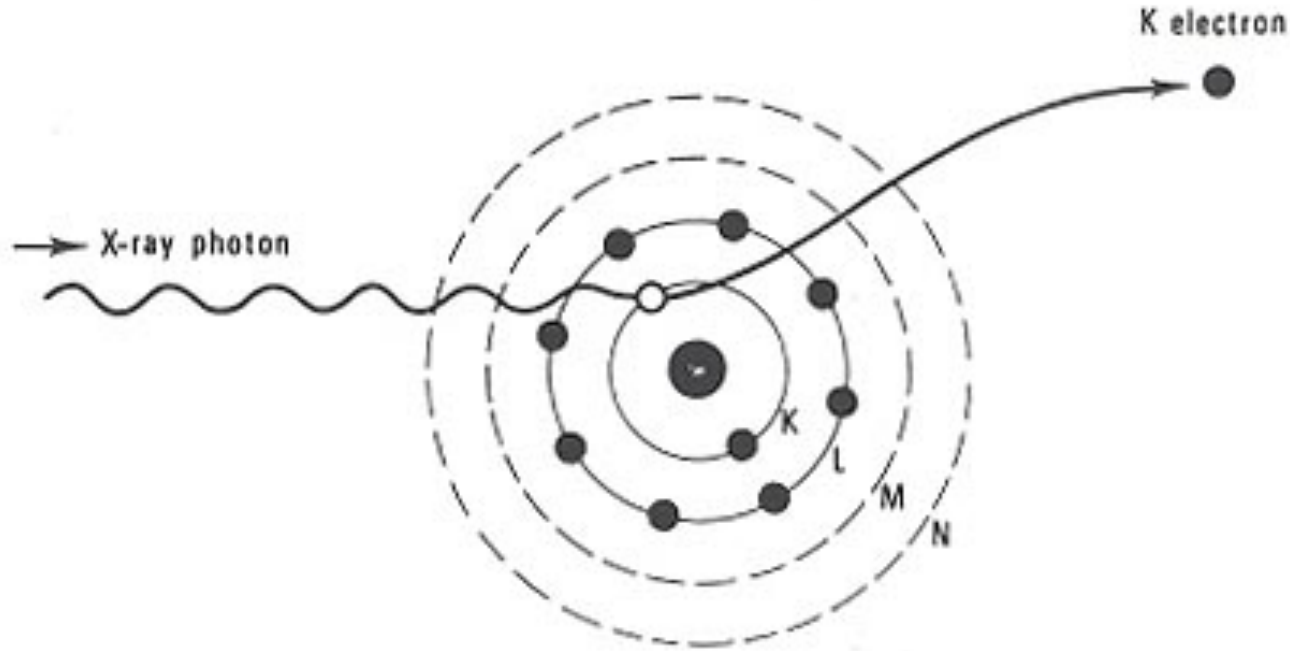


Figure 1.1. Ionization of the K shell by an incident x-ray photon.

Emmision of characteristic x-ray spectra

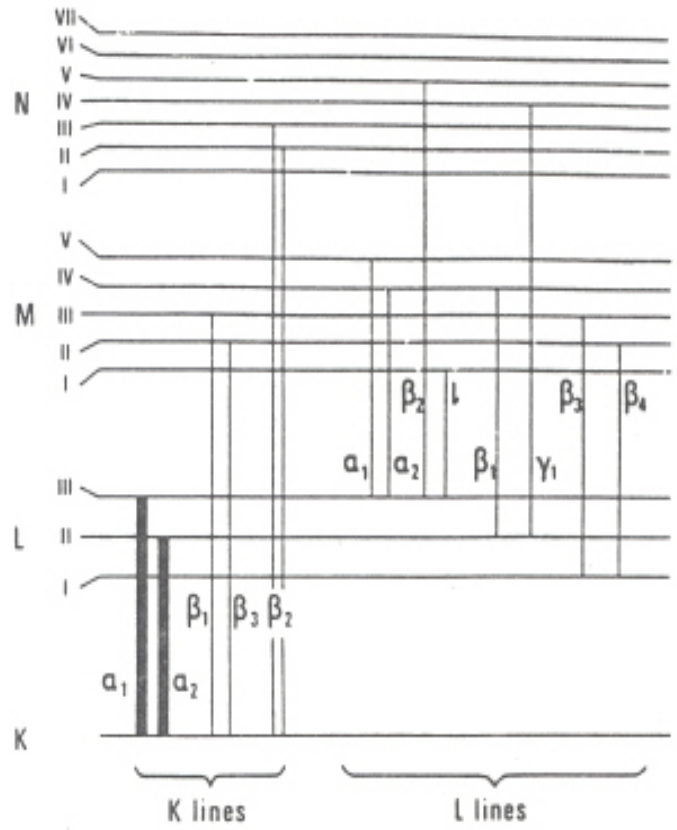
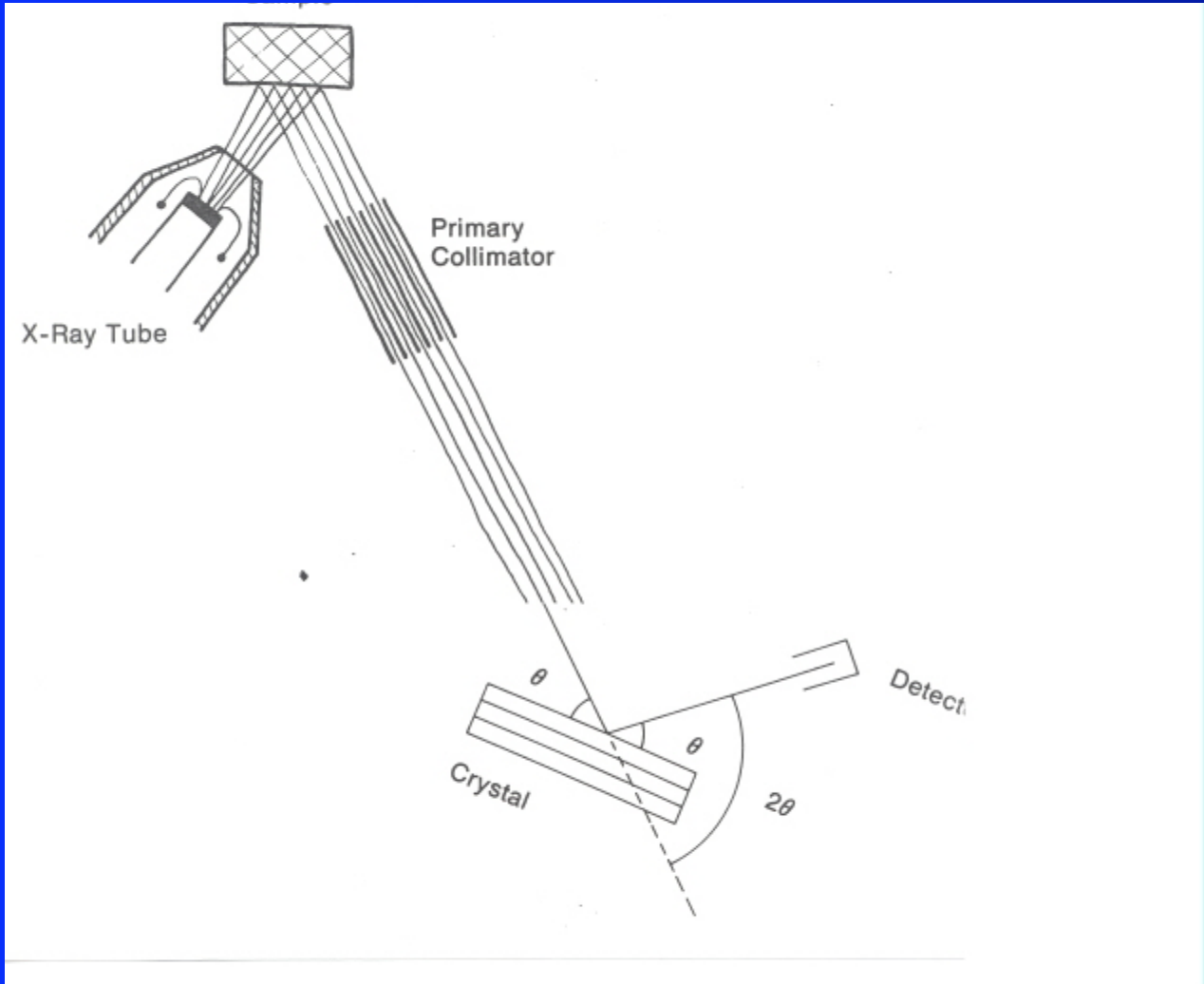


Figure 1.2. Partial energy level diagram showing the origin of the main lines in the K and L spectra.

Spectrometer Configuration



Infinite Thickness

"Infinite Thickness" for NaK$_\alpha$ in Portland Cement

Assume: 45% Ca, 9% Si, 2.6% Al, 2% Fe, 1.6% Mg, 1.4% S, 0.75% K, 0.2% Na, 36% O

$$\ln\left(I - I_t/I_\infty\right) = -\overline{(\mu/\rho)}\,\rho t$$

or,
$$t = \frac{\ln(0.001)}{-\overline{(\mu/\rho)}} \qquad \{\mu/\rho = \text{mass absorption coeff.}\}$$

where $\overline{(\mu/\rho)} = (\mu/\rho)\lambda_{,pri} \csc \emptyset + (\mu/\rho)\lambda_L \csc \Psi$

$\emptyset$ = incident angle of 1° beam on sample
Ψ = take off angle of 2° x-rays from sample
$\lambda_{,pri} \cong 2/3 \bullet$ analyte absorption edge
$(\mu/\rho)\lambda_L = \Sigma$ (wt. fraction i) $\bullet$ $(\mu/\rho)_i$

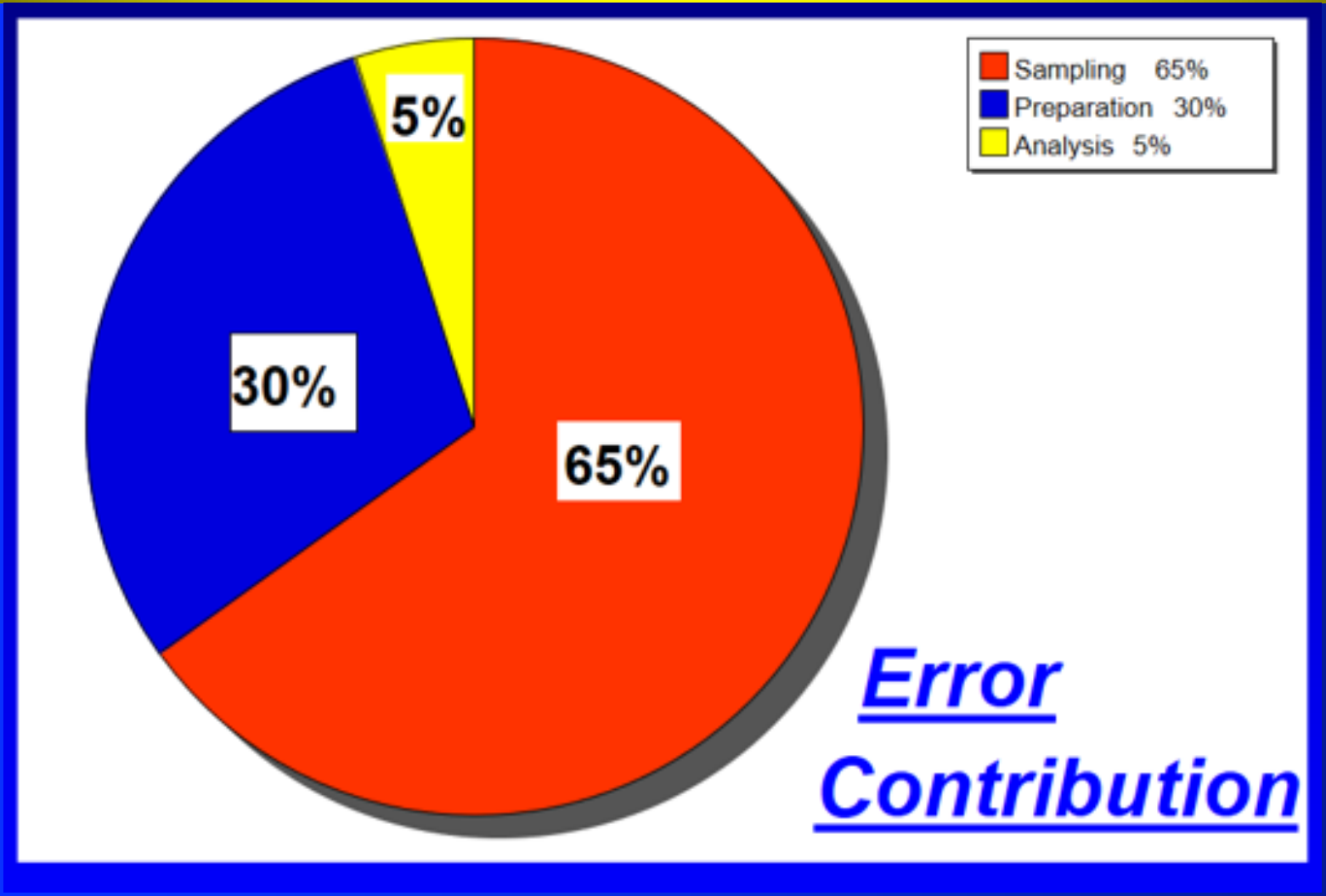
- In a typical portland cement briquette (35.5% porosity) the mass of the specimen actually analyzed is about 2.5 mg for sodium, 50mg for calcium!

Why Consider Sampling?

- Analytical chemists use samples; *they* are in charge of QC and usually blamed when analytical results, which depend heavily on sampling errors, reveal discrepancies.

Pierre M. Guy, "The analaytical and economic correctness in sampling" Anal Chim Acta 190, 13-23, 1986

Errors associated with..



Different Shapes & Sizes

What is different about this sample?

Sources of Contamination

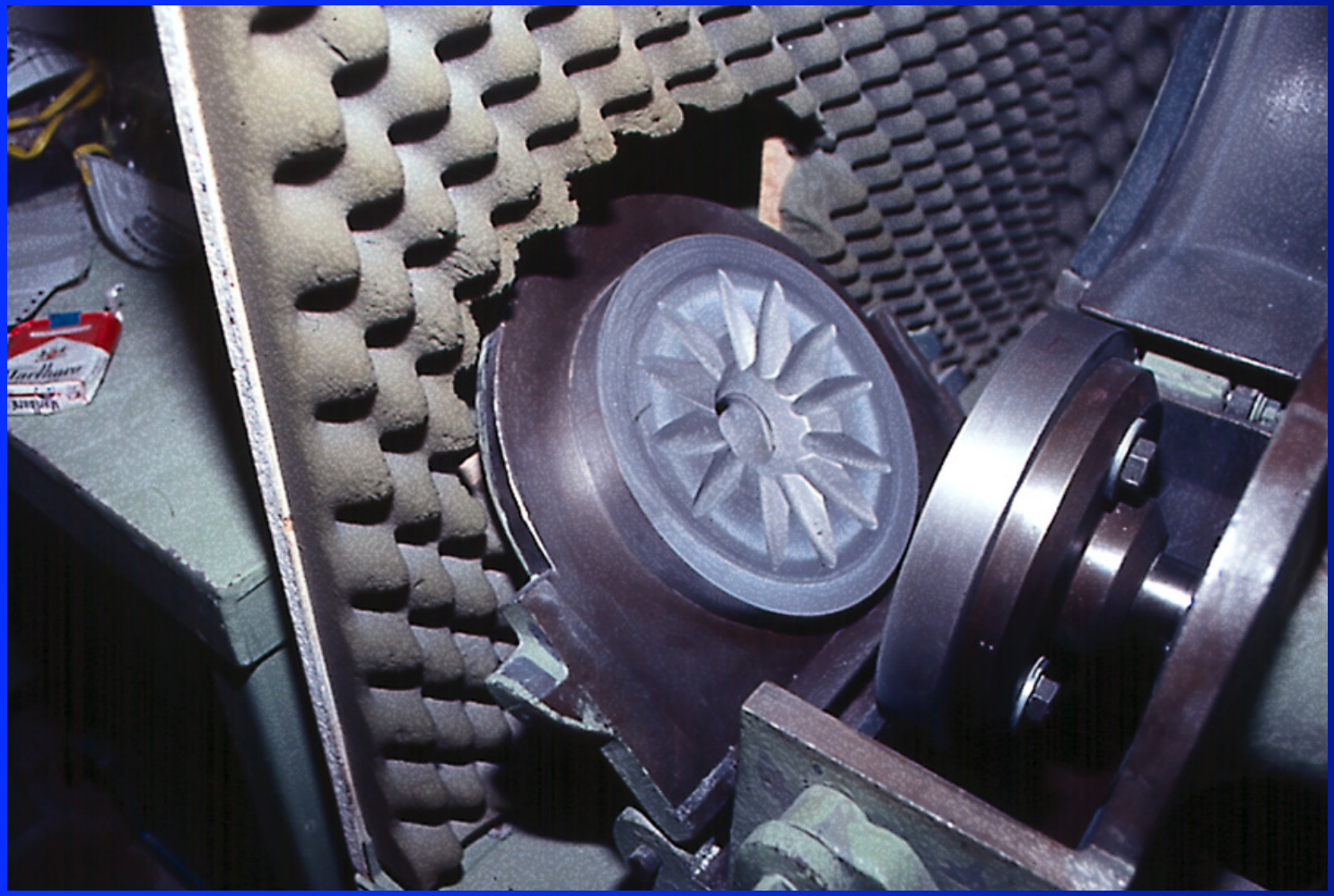
- Sampling Equipment
- Handling
- Storage Containers
- Processing / Crushing / Grinding Equipment

Crushing / Grinding

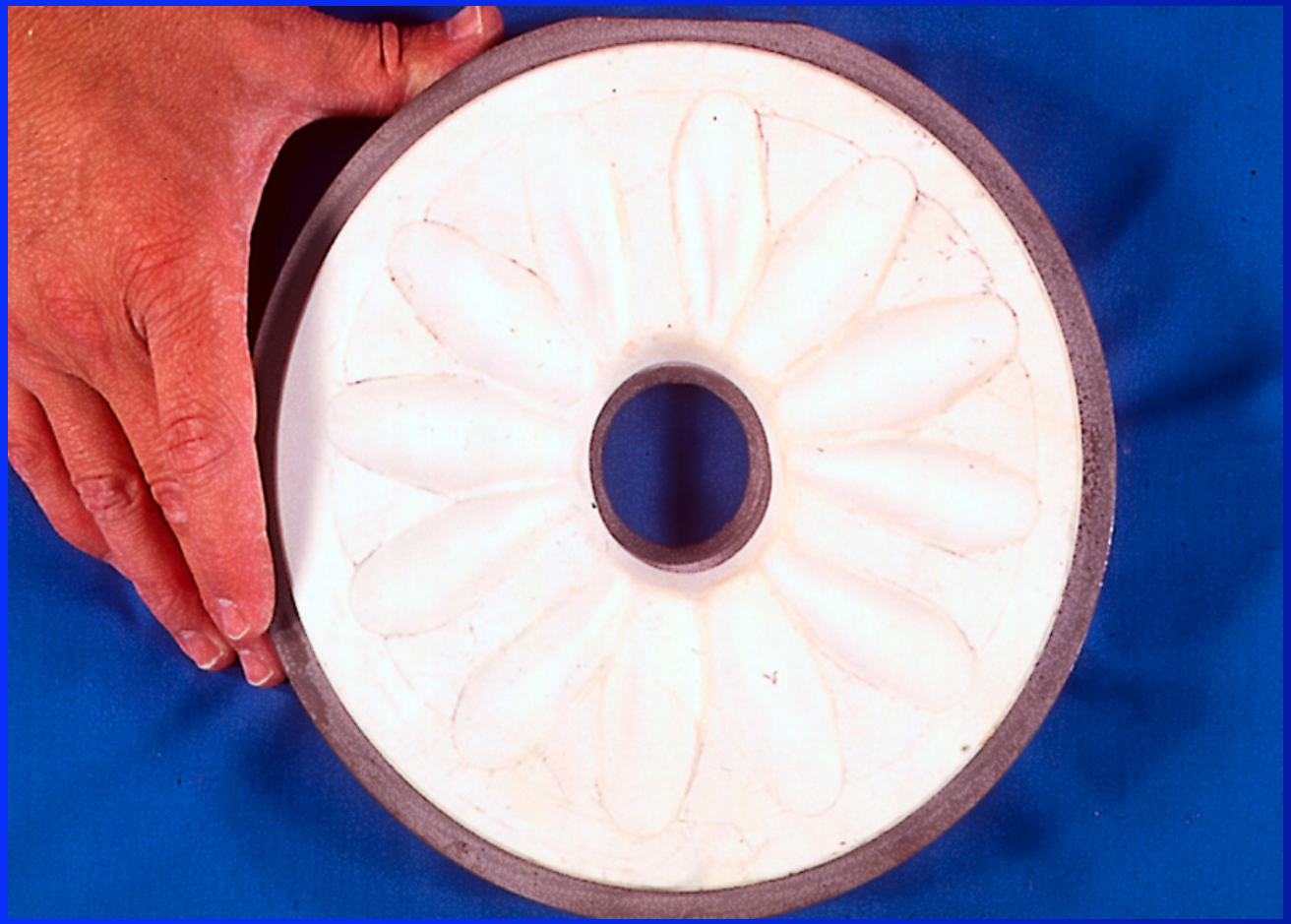
- Jaw Crusher
- Disc Pulverizer
- Blueler Mill

Jaw Crusher

Disc Pulverizer



Disc Pulverizer

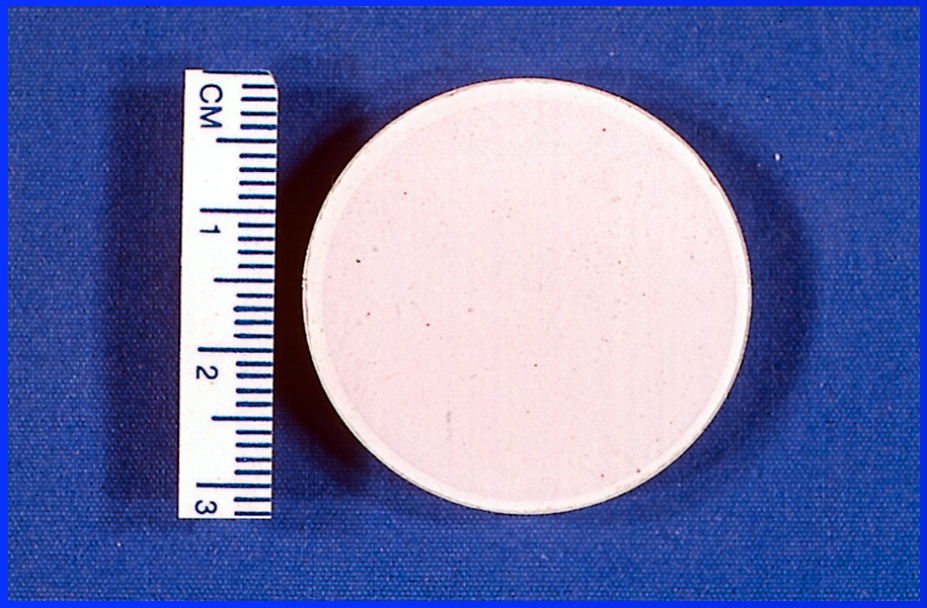


Contamination ?

Ring & Puck Mill
(or any process equipment)
What is it made of/elements of interest?

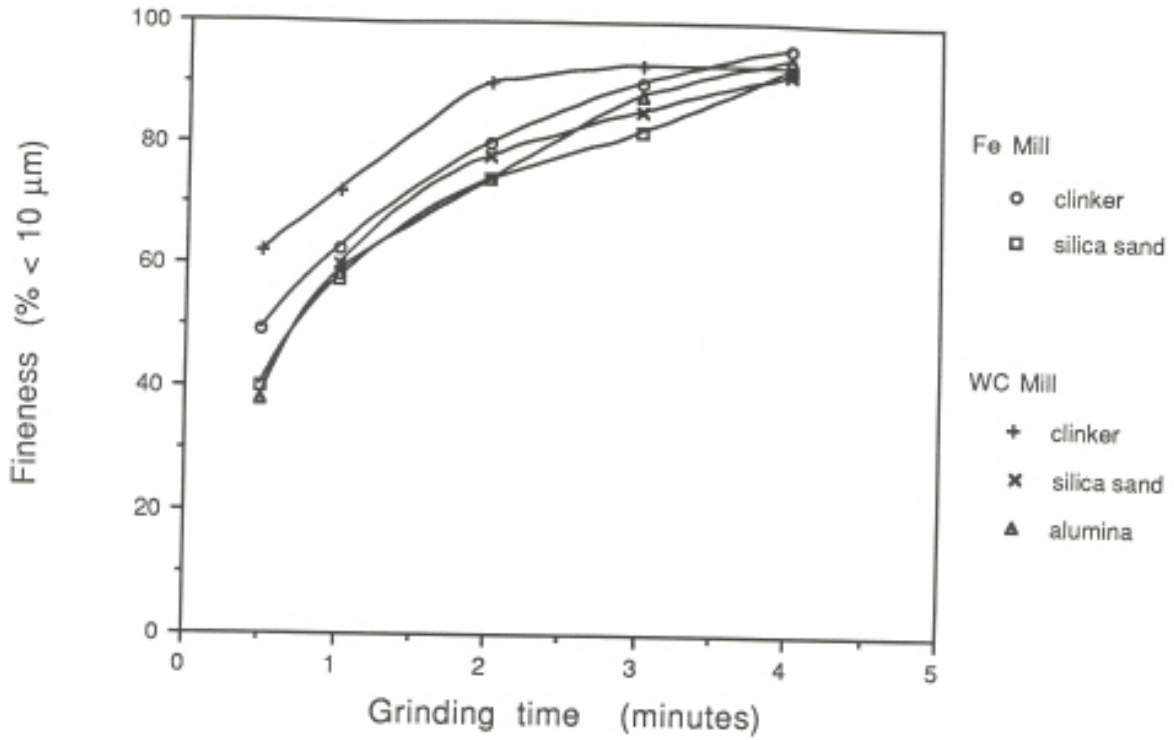
Ring & Puck Mill

Contamination



Sampling from a Bottle

Grinding Time vs Fineness (with different mill types)

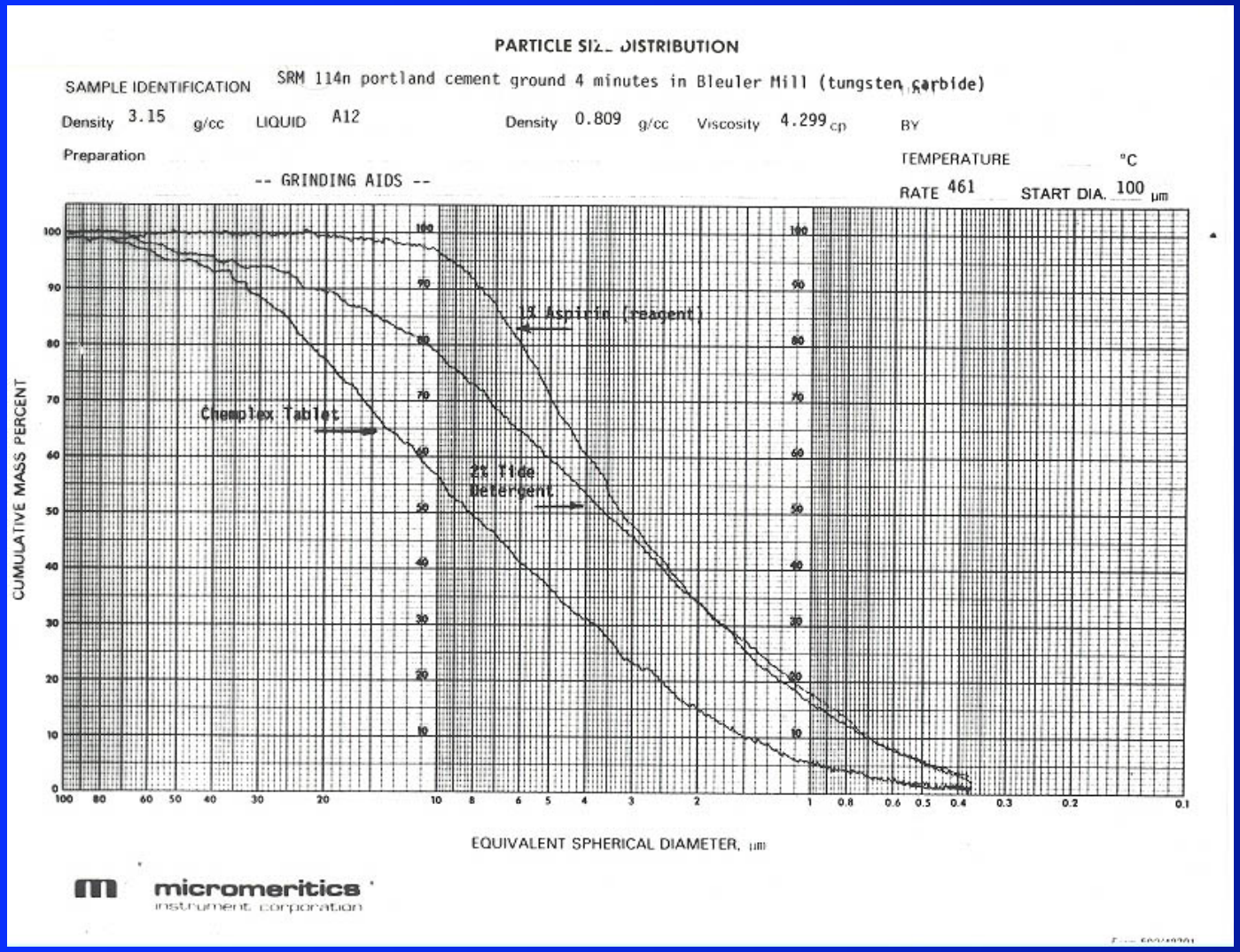


Swing-mill grinding with ring and puck. Starting materials were 0.3-0.15 mm (No. 50/100 sieve fraction). 10 g samples ground with 2 drops ethylene glycol as grinding aid. Mill speed approximately 1000 rpm.

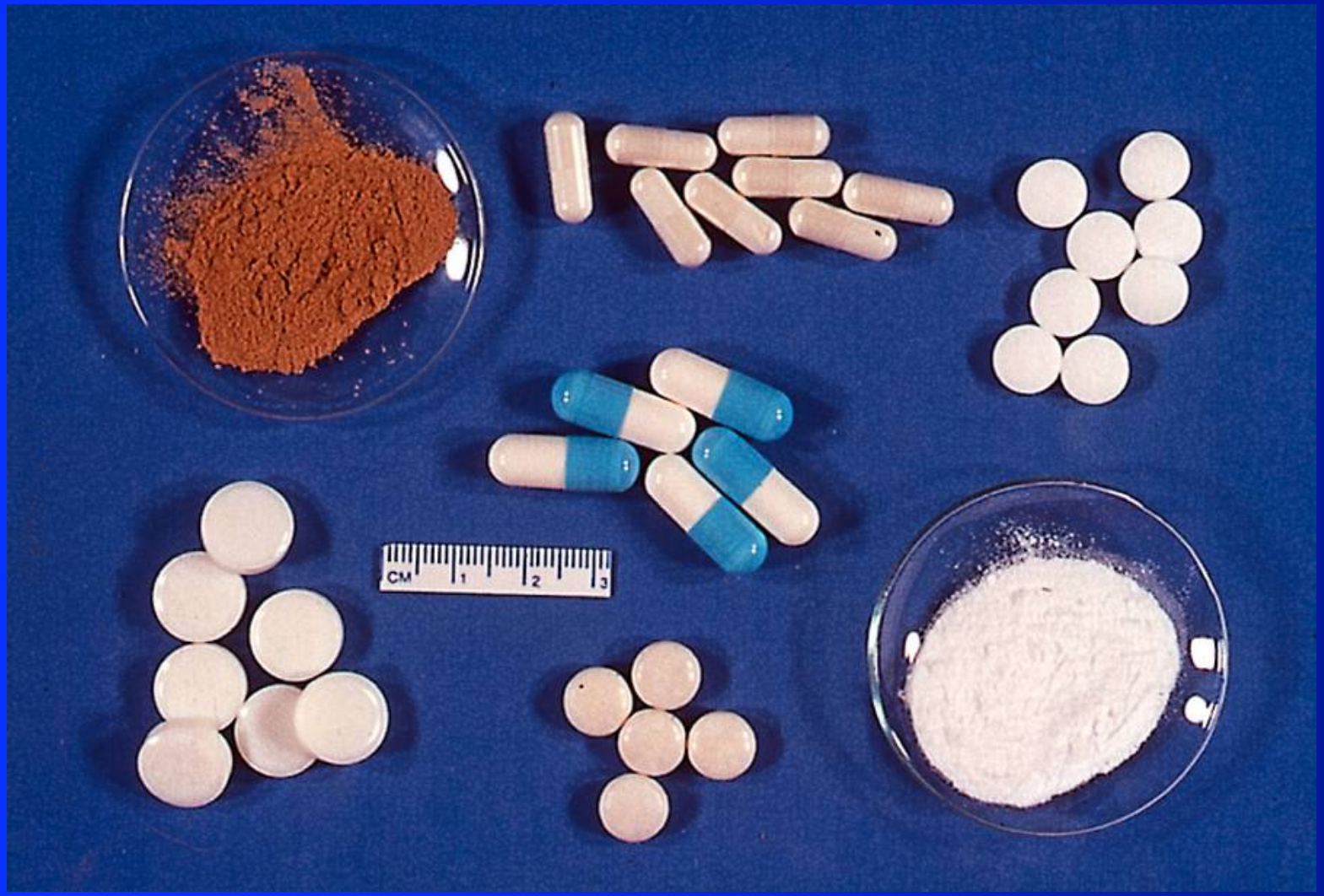
Chemical Grinding Aids

- Propylene glycol
- Aspirin
- Liquid freon
- Soaps
- Detergents
- Water
- Commercial Tablets-Grinder/Binder?

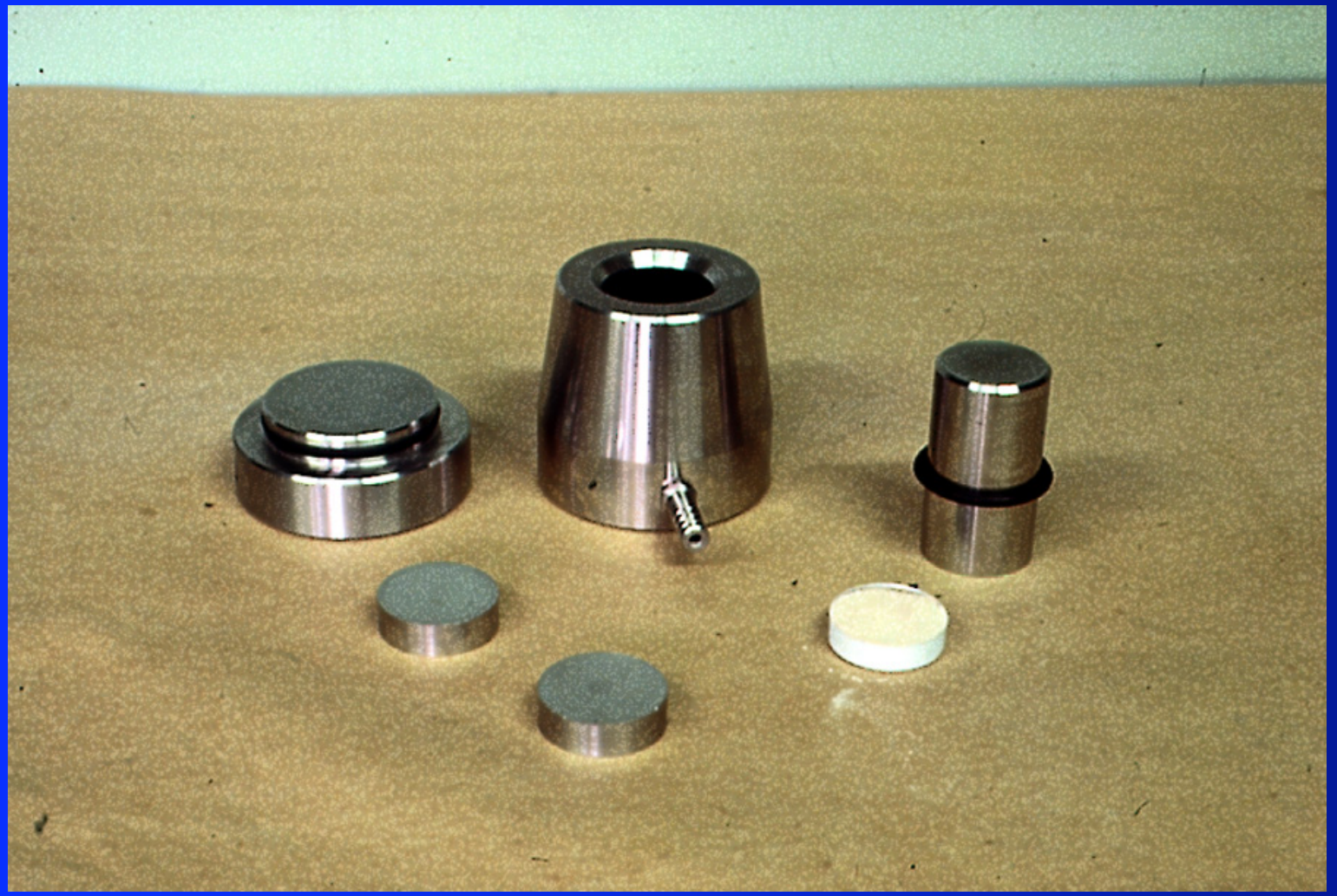
Particle Size Distribution



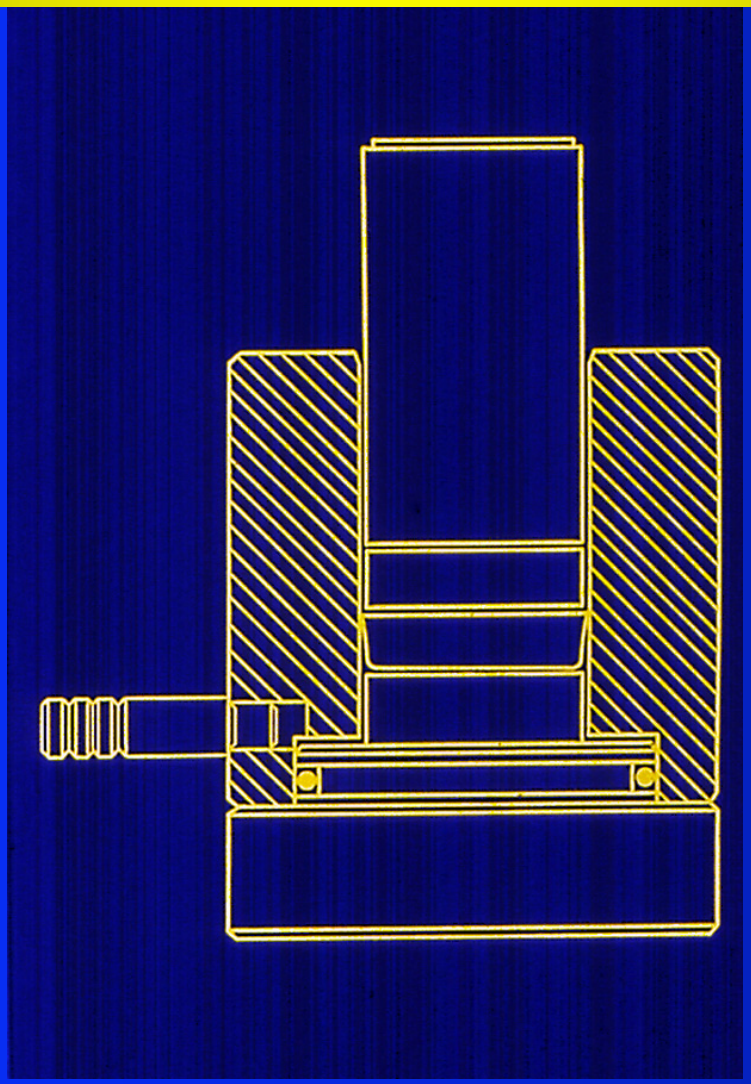
Commercial Binders



Die Assembly

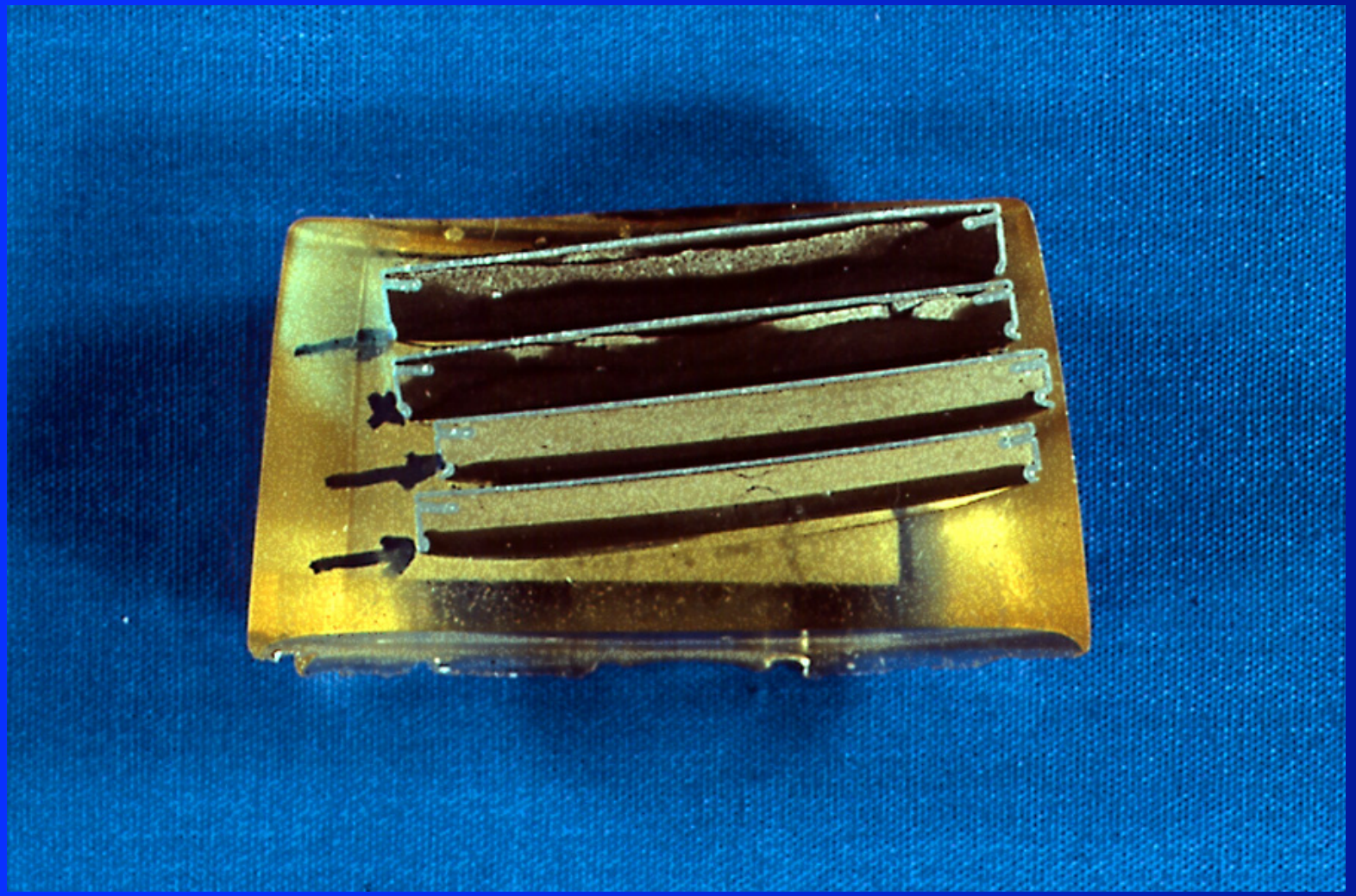


Die (Assembled)

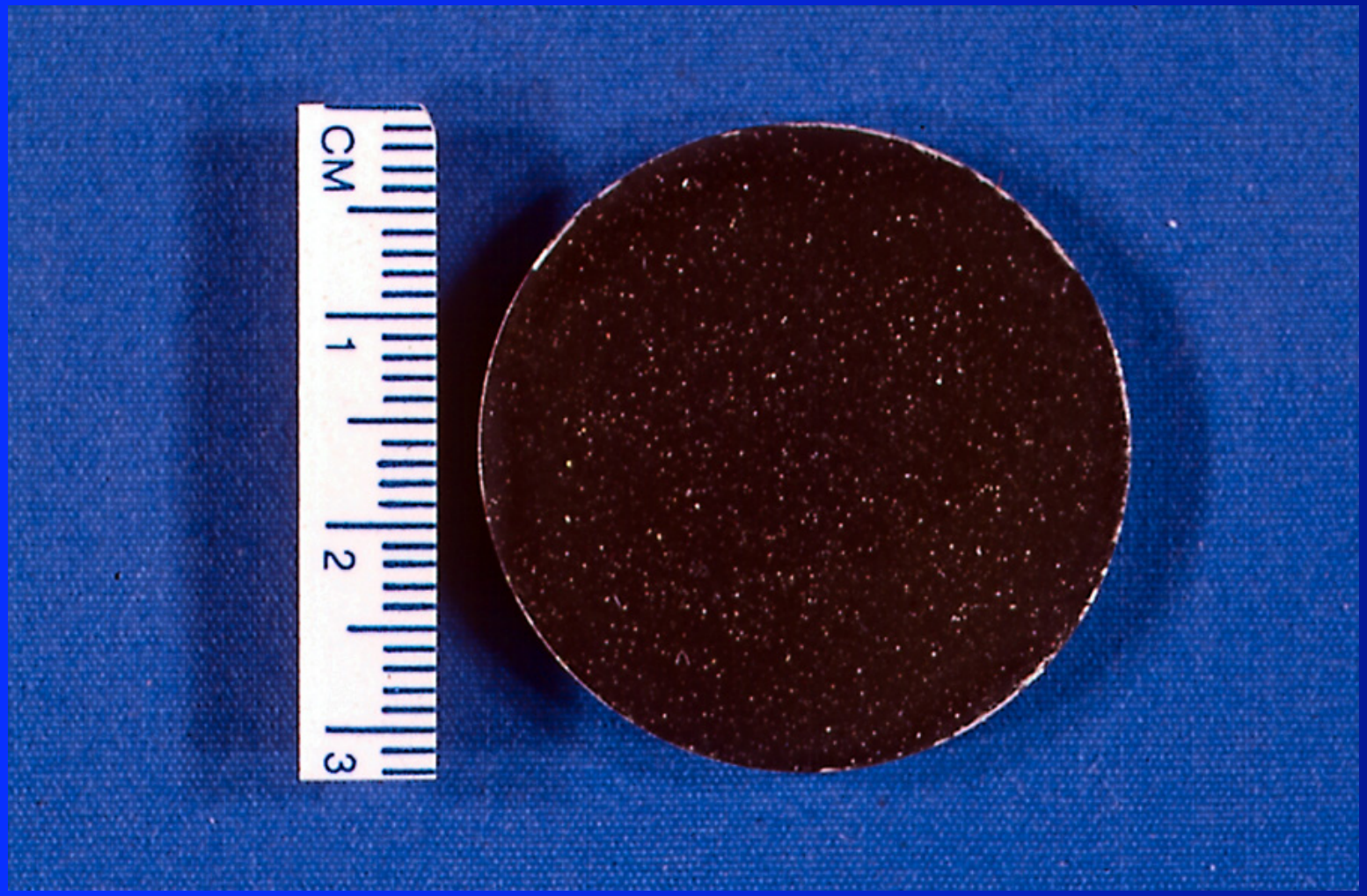


Spex X-Press

Longer Grinding Times



Appearance of Pellet



Compare Colors

Pressed Powder Technique

- Obtain representative sample (<100 US Standard Sieve)
- Weigh 7 grams & place in ring & puck mill
- add 1-2 drops propylene glycol
- Grind 3-4 minutes
- add binder, grind additional 30 seconds
- press into briquett @ 50,000 (25 tons)
- Place in dessicator until analyzed

Borate Fusions

Why Fuse?

- Calibrations look GREAT!
- No particle size effects!
- No Mineralogical effects!
- Use pure compounds to calibrate
- Measure “real” inter-element effects
- Less contamination from intense grinding needed for pressed powders
- No powder deposition on x-ray tube

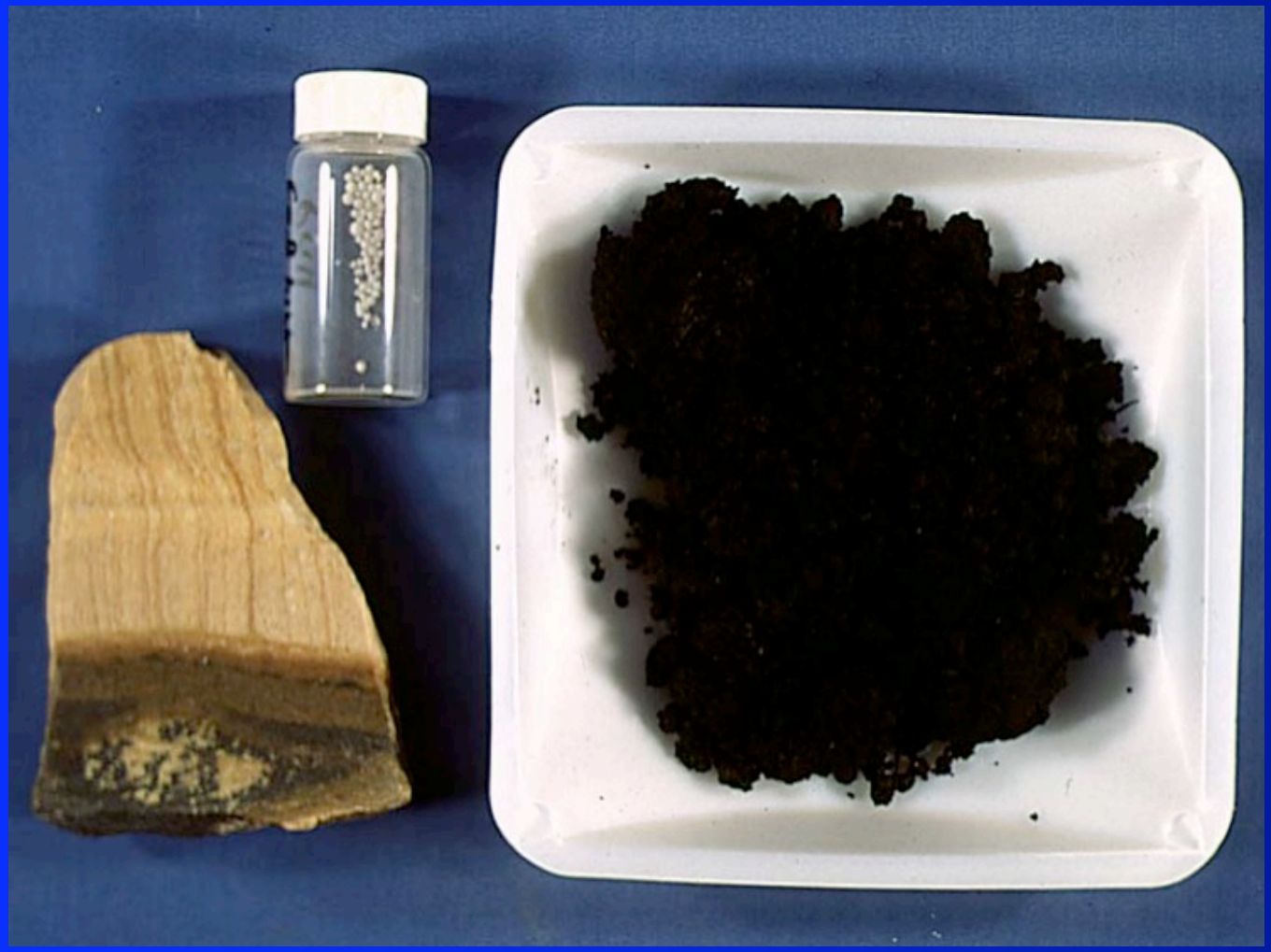
Why Not?

- Volatiles evaporated (time and temp dependent)
- dilution means higher detection limits
- somewhat more complicated
- costly- machine, platinum, & flux

Typical Materials Analyzed

- Limestone
- Clay
- Iron ore
- Fly ash
- Cement
- Gypsum
- Shale
- sludge
- silica fume
- slag

Geologicals and Industrial by-Products



Powder Deposition on Tube? None!

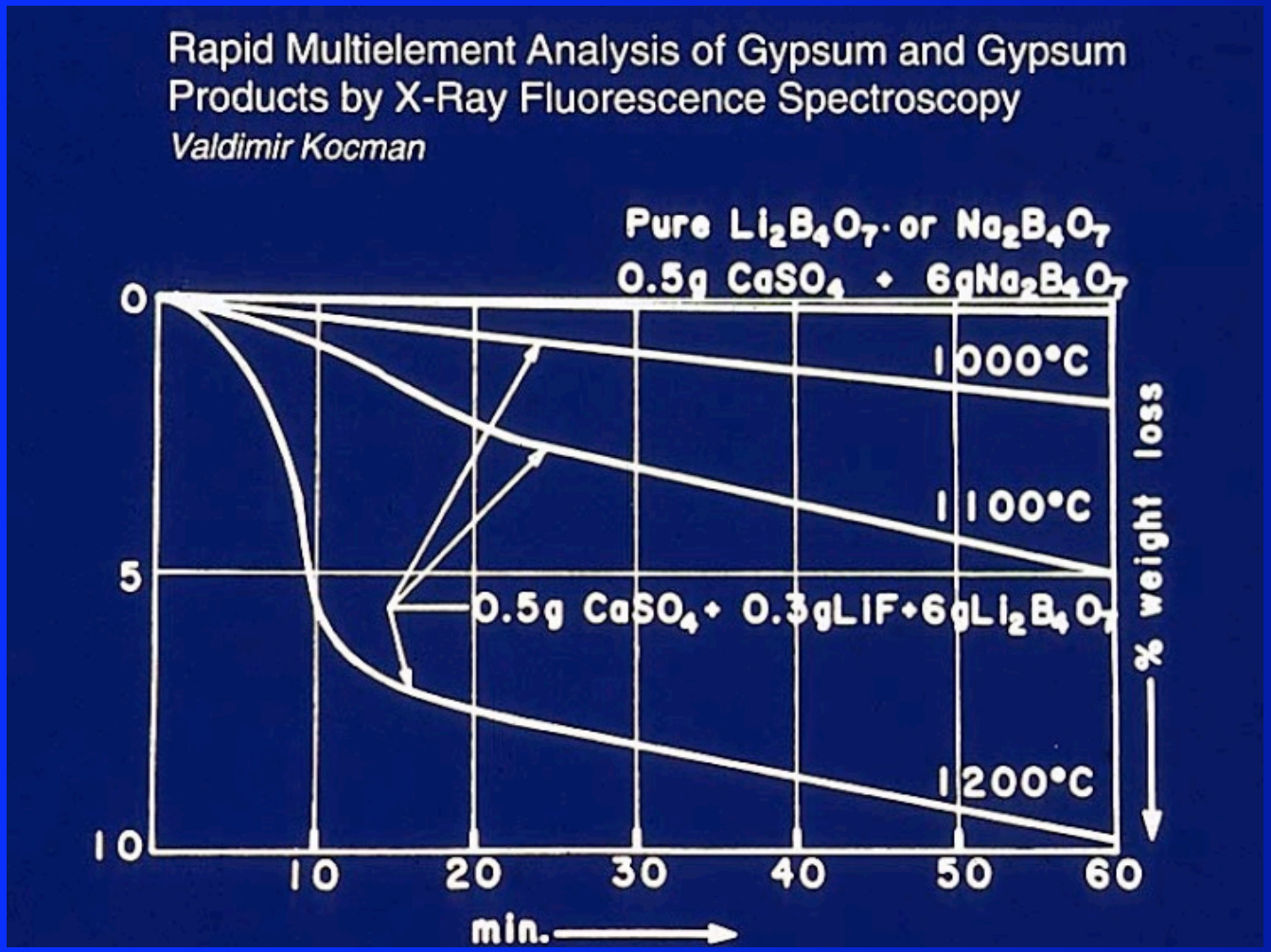
Releasing Agents

- NaBr
- LiBr
- KI
- NH4I
- Need to evaluate line overlaps (Br-Al)
- Measure I^{o} of releasing agent
- Optimize amount necessary!

Flux Choices

- Sodium tetraborate(very hygroscopic)
- Lithium tetraborate
- Lithium tetraborate/metaborate mixtures
- Lithium metaborate-(prep solns)
- In all cases measure Loss on ignition
- In all cases fuse “blank” run and check for contaminants/purity

Flux Choices



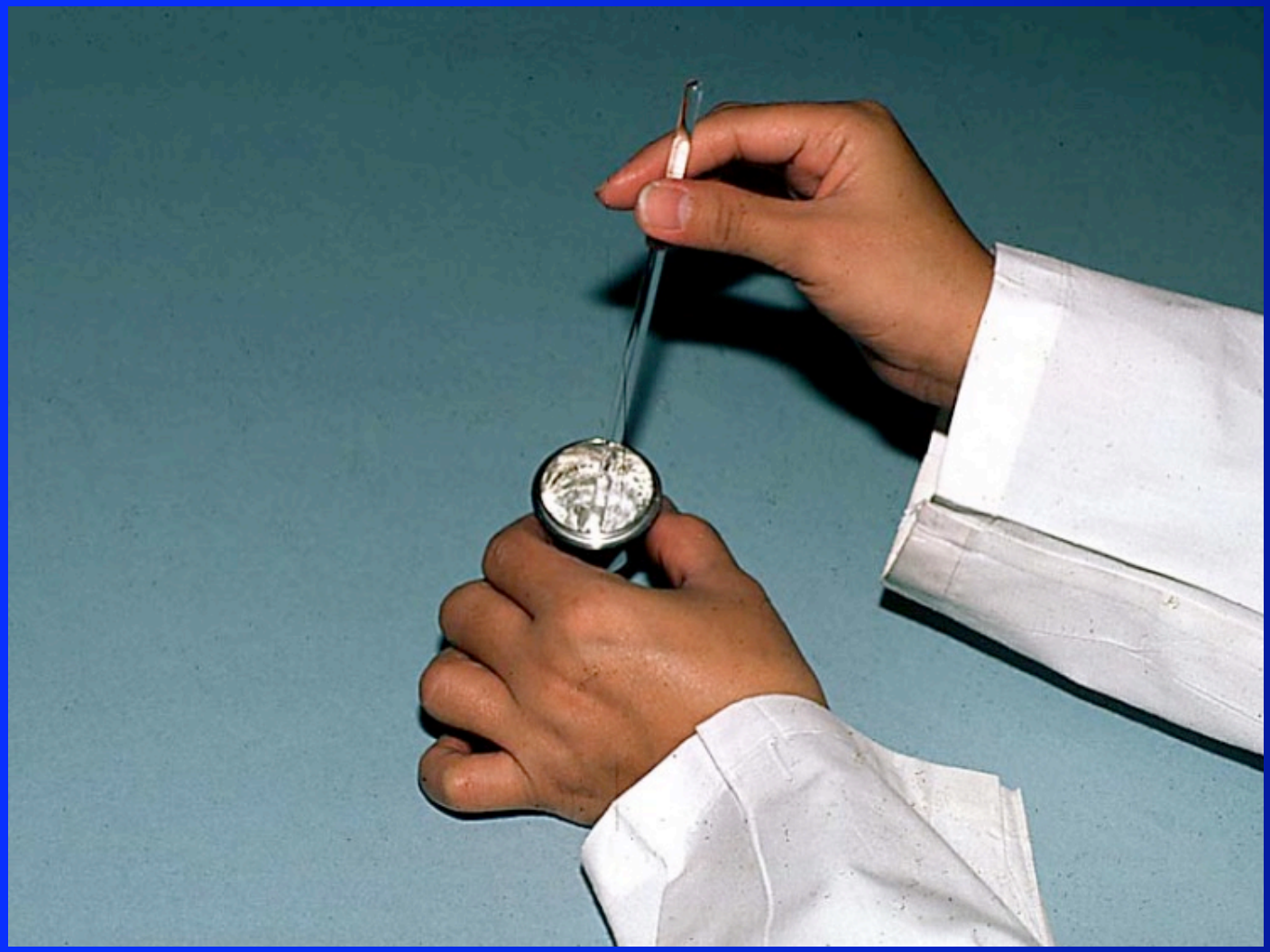
Optimize Conditions of Fusion

- Measure temperature of molten flux
- Type S thermocouple inside of flux- also measure crucible wall temperature
- Measure Loss on Fusion of material to analyze. Sulfur loss good indicator.
- Minimum Time/Minimum Temp

Procedure

- Determine L.O.I.
- Use Freshly Calcined Material or Balance for L.O.I.
- Weigh 1gram Sample + 5 Grams L.O.I. Corrected Flux
- Add Anti-wetting Agent (LiBr?)
- Fuse,Cast & Cool
- Check for Disc Integrity

Mixing Sample-Right/Wrong?



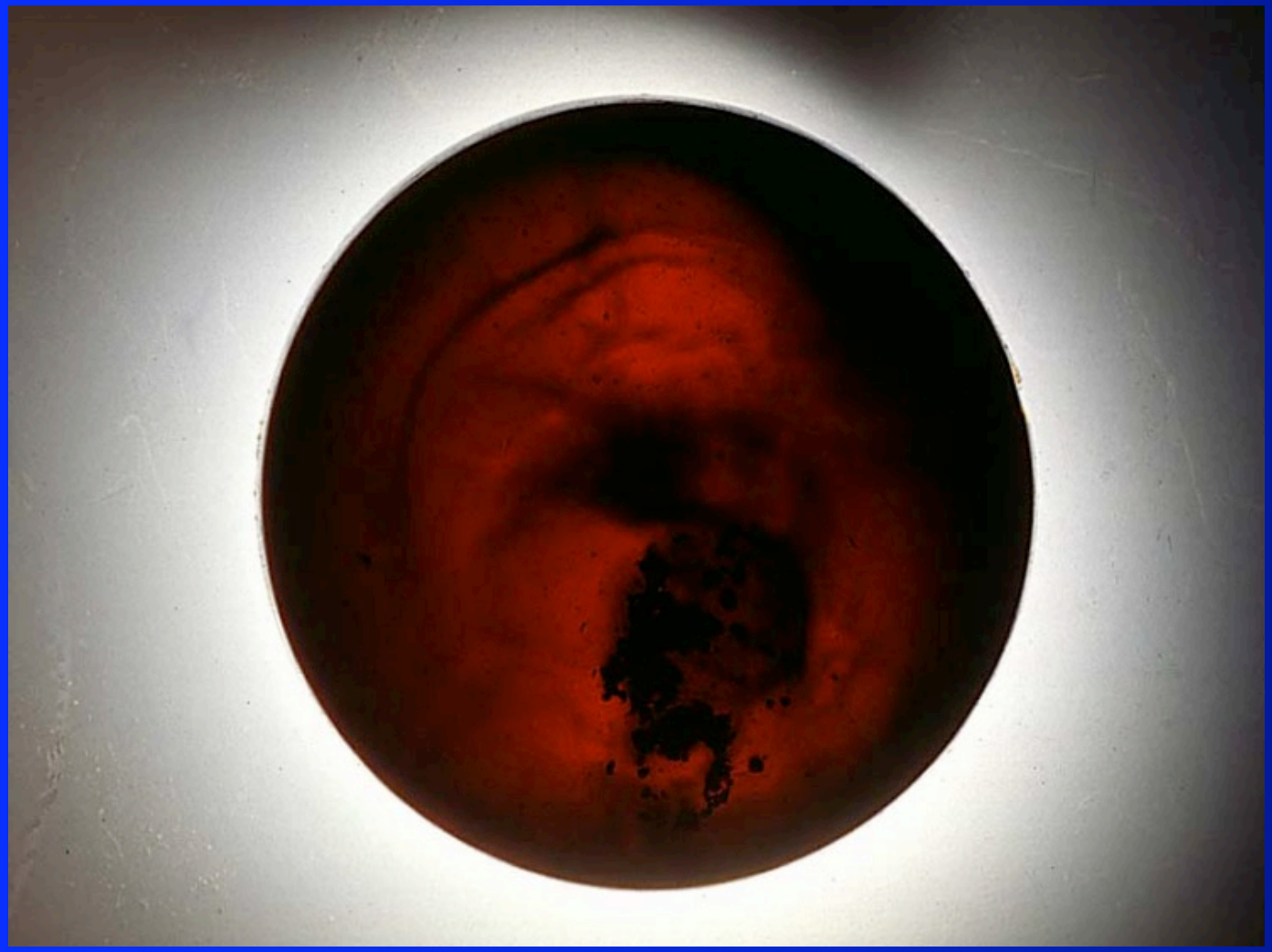
Quick Check

Scintering-post Ignition requires grinding

Fluxer Operation

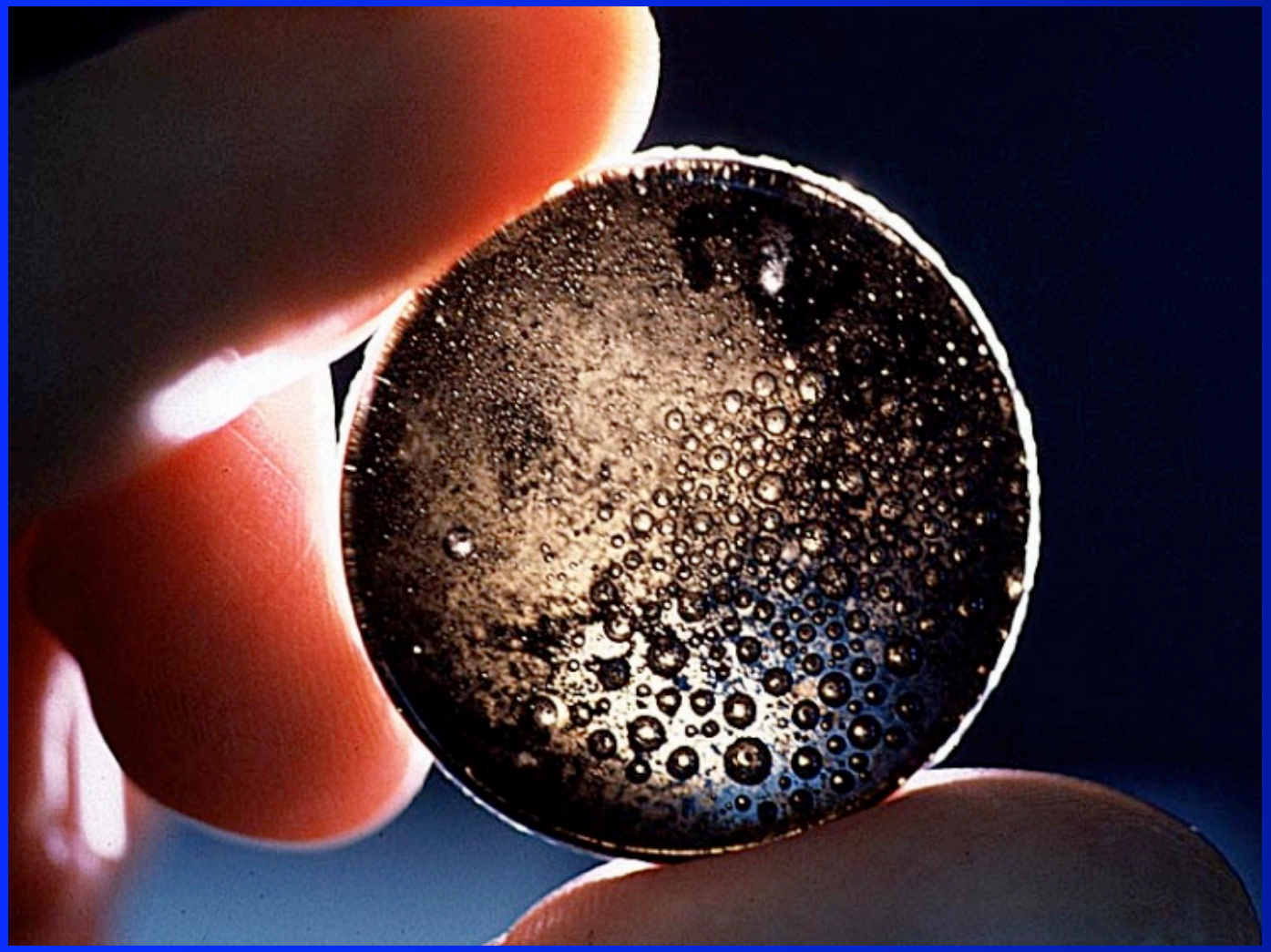
Dark Blue Disc
Good/no Good? Why?

Dark Disk-Illuminate it!

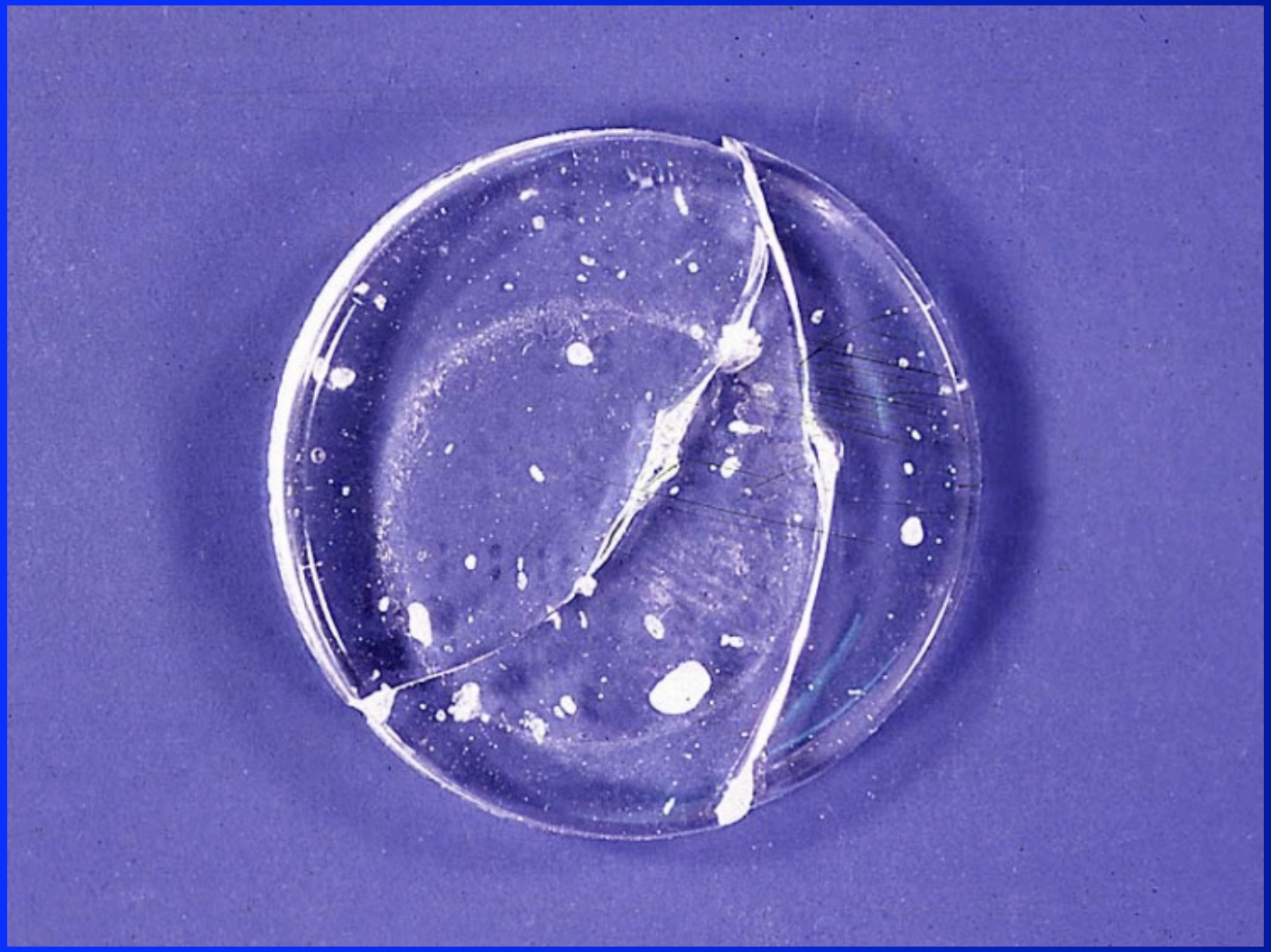


Recrystallization

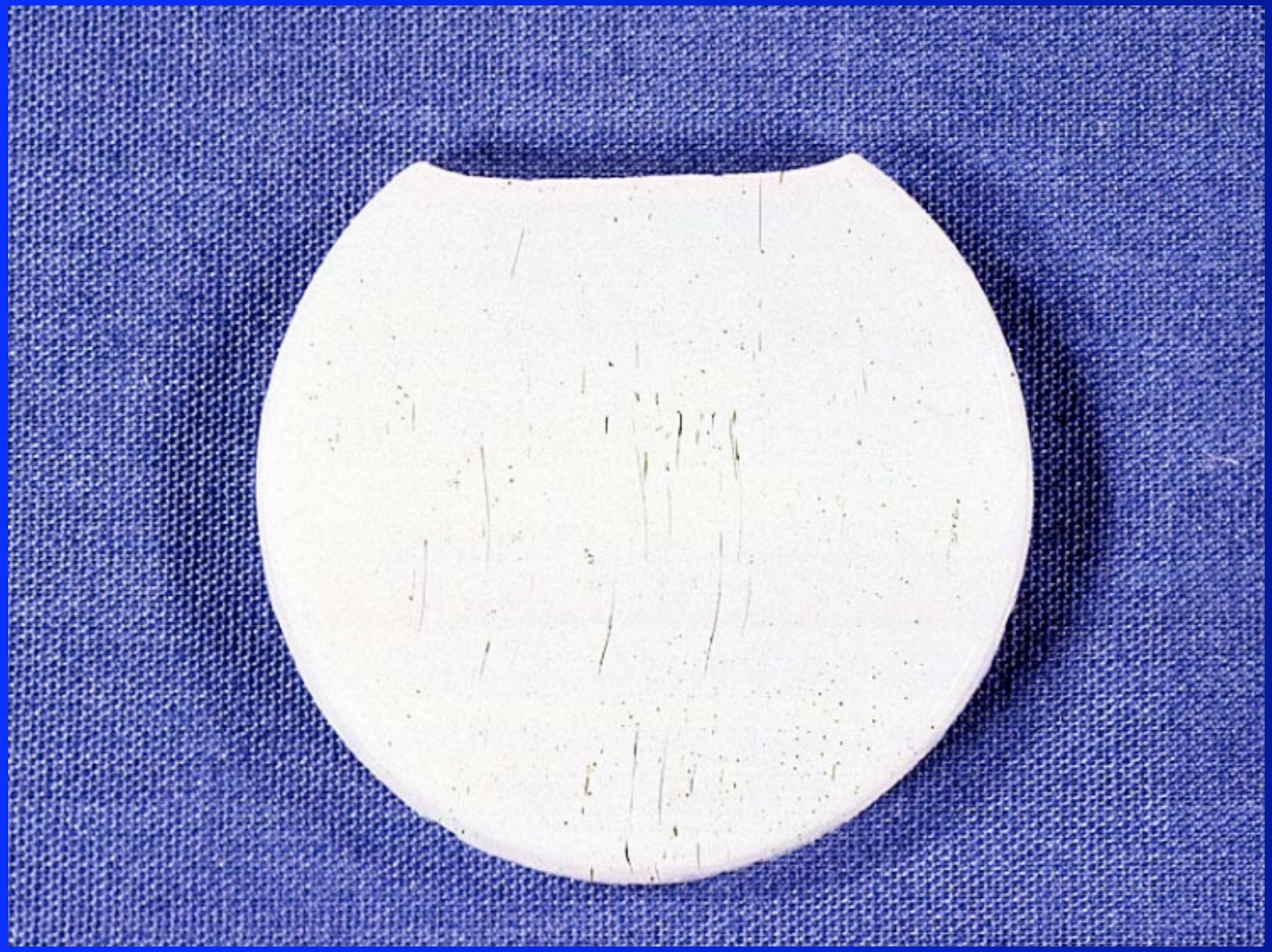
Bubbles in Analytical Surface-incomplete ignition?



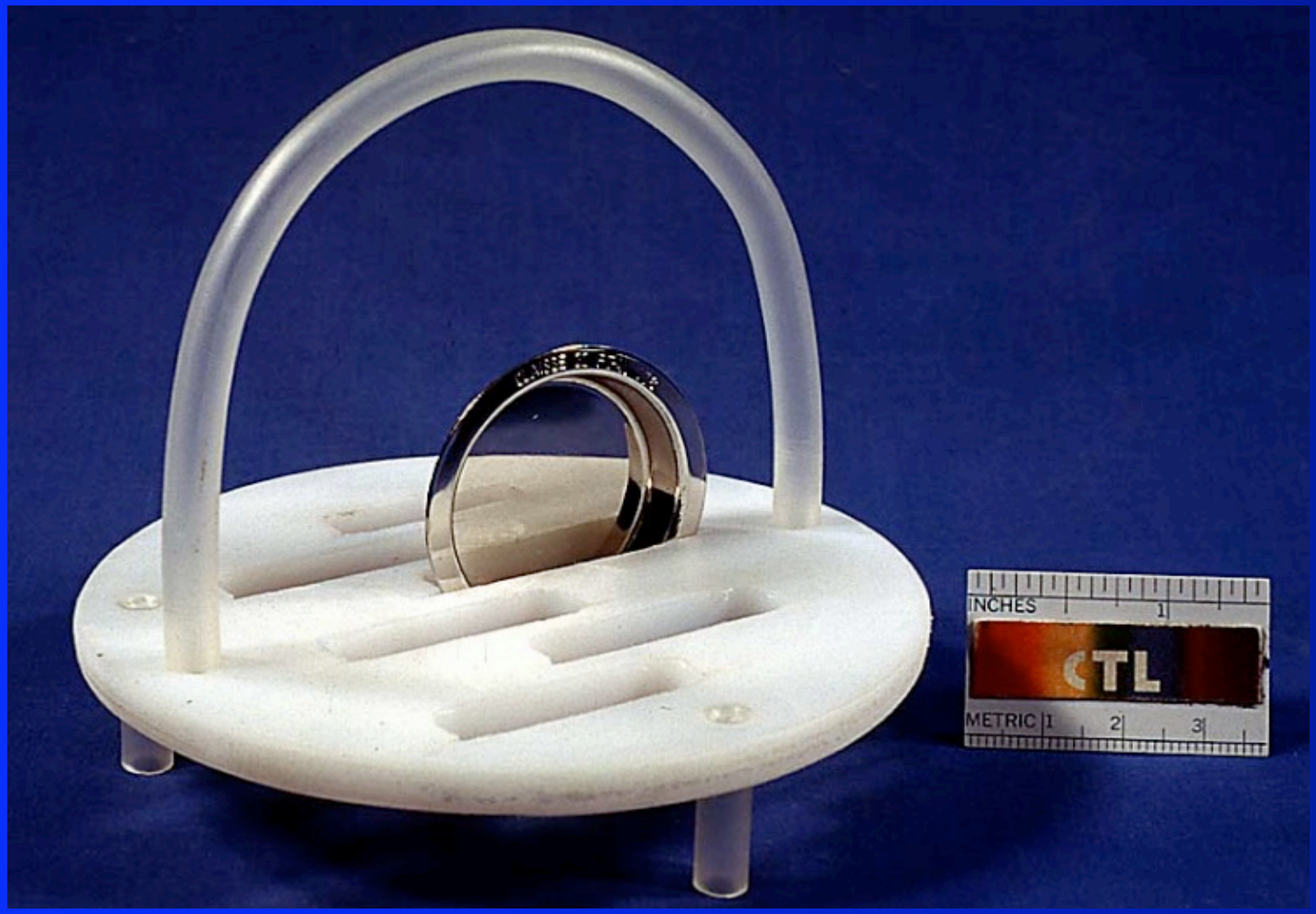
Incomplete fusion.
Not ground fine enough? / Wrong Flux?/Too cool when casting.



Incomplete Disc/recrystallized - too much anti-wetting agent/wrong flux



Care & Cleaning



Touch-ups

Liquids in XRF Analysis

Cup, film holder

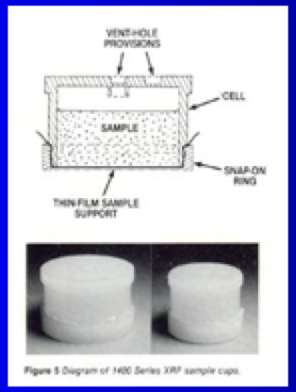


Figure 5 Diagram of 1400 Series XRF sample cups.

CTL

Questions

- How many people have run XRF liquid analysis in the past week?
- How many have the helium option?
- How many need to routinely analyze liquid samples using other instrumentation, ie AA, ICP, IC, or traditional gravimetric, colorimetric , titrimetric methods?

Thin film transmittance

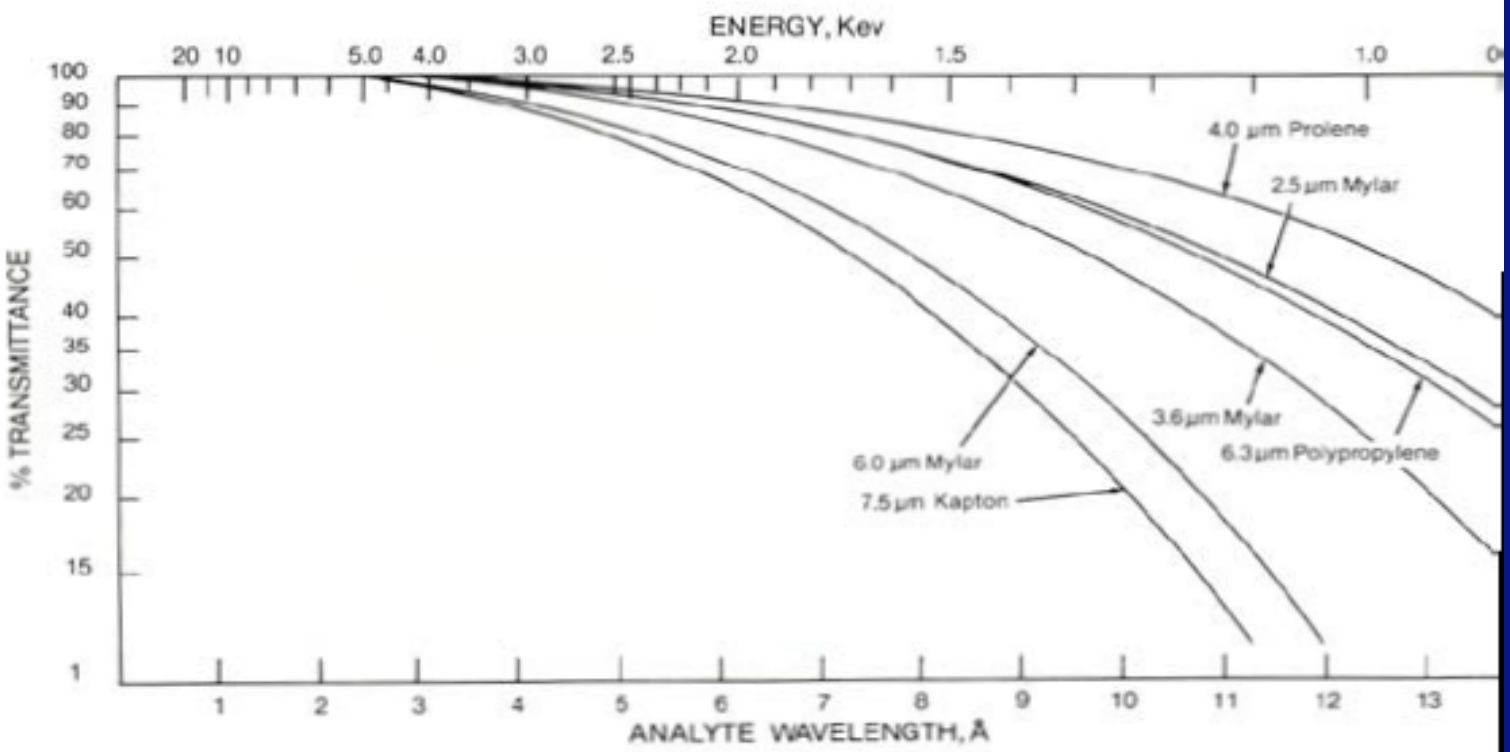


Figure 12 *Relative percent transmittance and gauge for thin-film sample support material*

Film Degradation Resistance

Table 1
Degradation Resistance of Thin-Film Substances

Chemical Classification	Mylar®	Polycarbonate	Etnom®	Polypropylene	Polyimide (Kapton®)	Prolene®	Ultra-Polyester®
Acids, dilute or weak	G	G	G	E	N	G	G
Acids, concentrated	G	G	G	E	N	E	G
Alcohols, aliphatic	N	G	G	E	G	E	N
Aldehydes	U	F	F	E	E	E	U
Alkalis, concentrated	N	N	G	E	E	E	N
Esters	N	N	F	G	G	G	N
Ethers	F	N	F	N	U	N	F
Hydrocarbons, aliphatic	G	N	E	G	E	G	G
Hydrocarbons, aromatic	N	N	E	N	E	N	N
Hydrocarbons, halogenated	F	N	F	N	F	N	F
Ketones	N	N	G	G	G	G	N
Oxidizing Agents	F	N	F	F	N	F	F

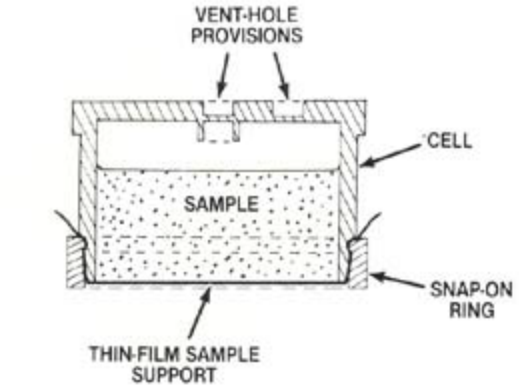
E = Excellent, **G** = Good, **F** = Fair, **N** = Not Recommended, **U** = Unknown

NOTE: The information contained in the above illustrations is provided as a matter of information only and it is not intended to preclude actual testing of the subject material for suitability of use and applications

Chemplex

CTL

Cup, film holder



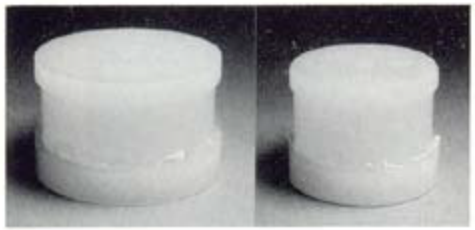
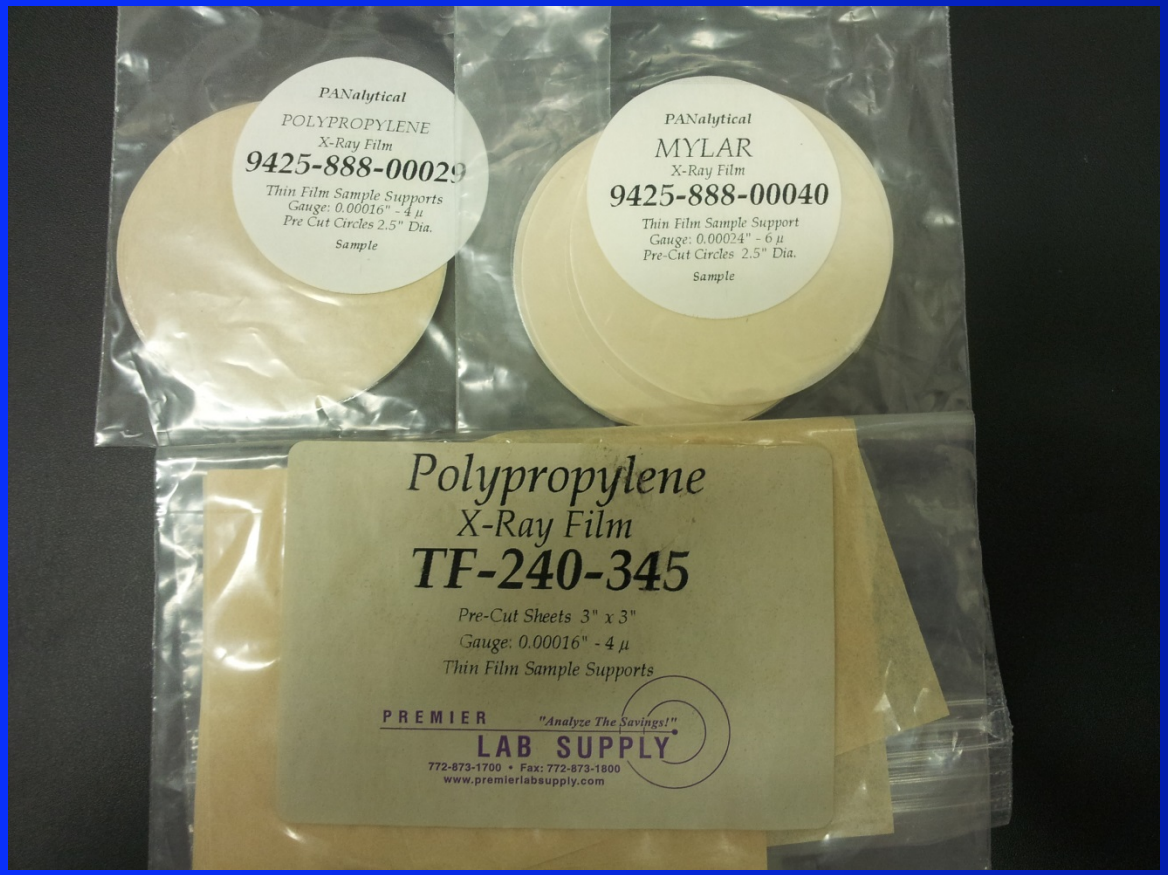


Figure 5 *Diagram of 1400 Series XRF sample cups.*

Variety of films



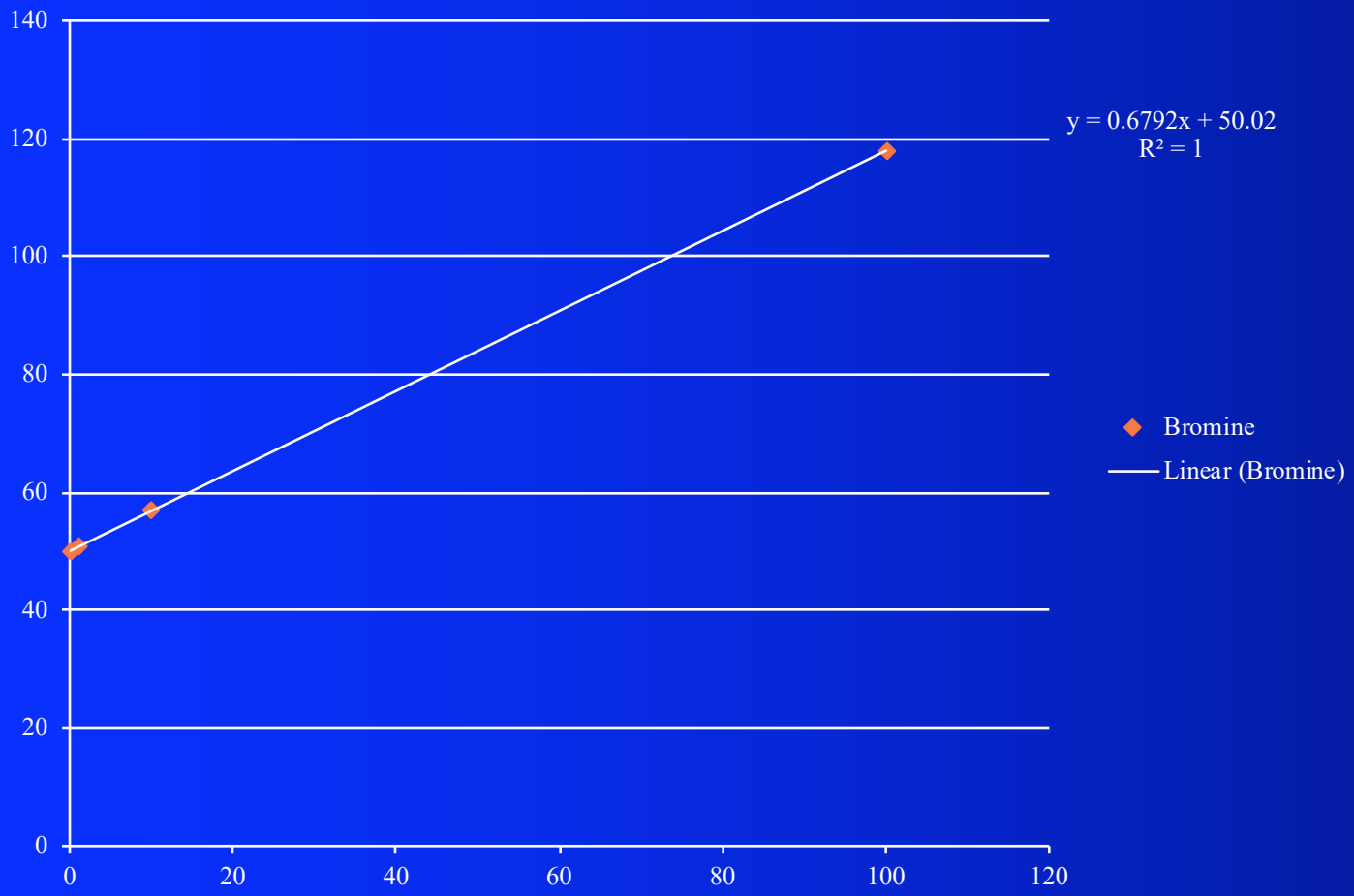
Film supports

Size matters

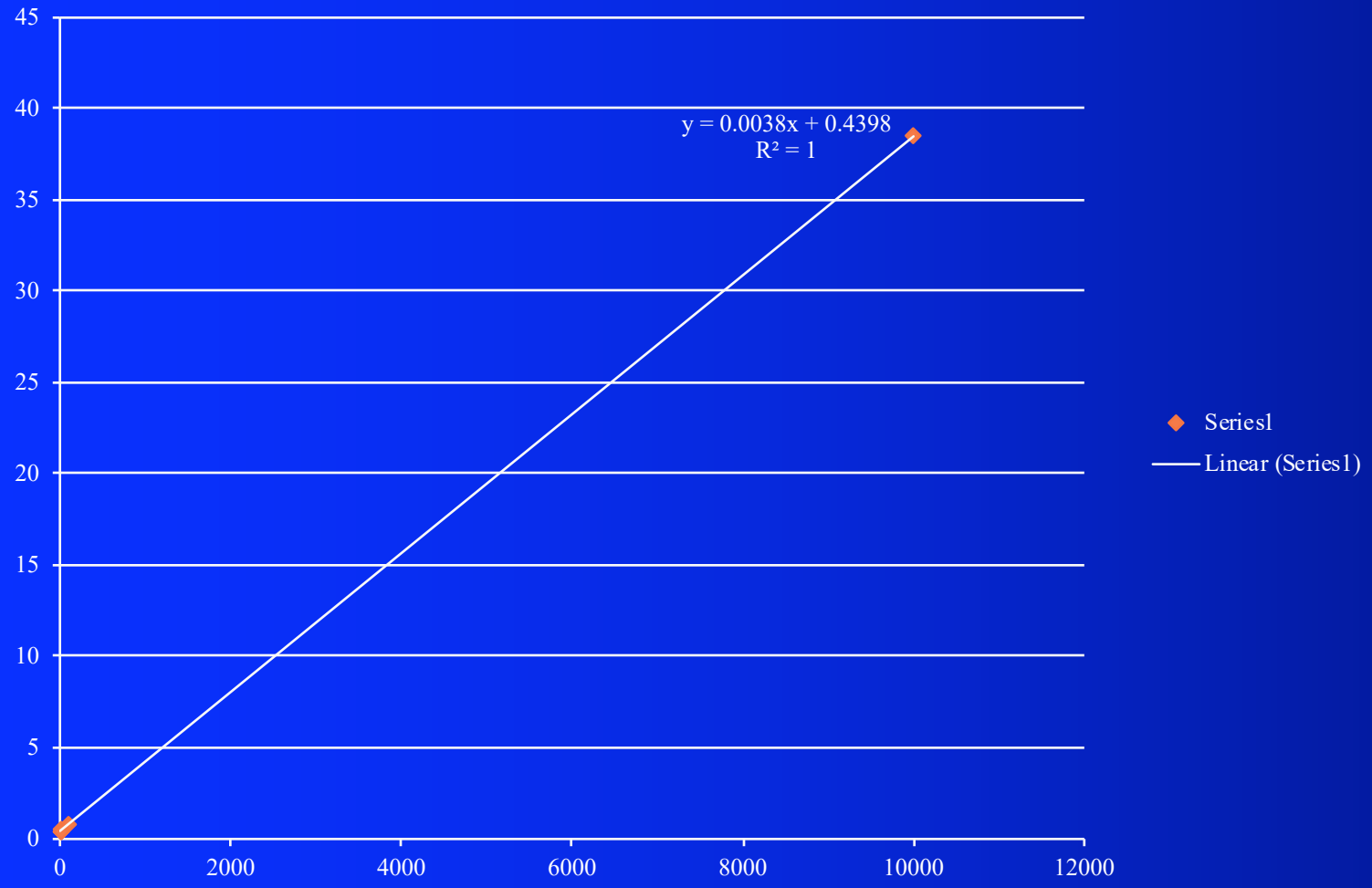
Cups, various sizes to fit XRF

Liquid safety

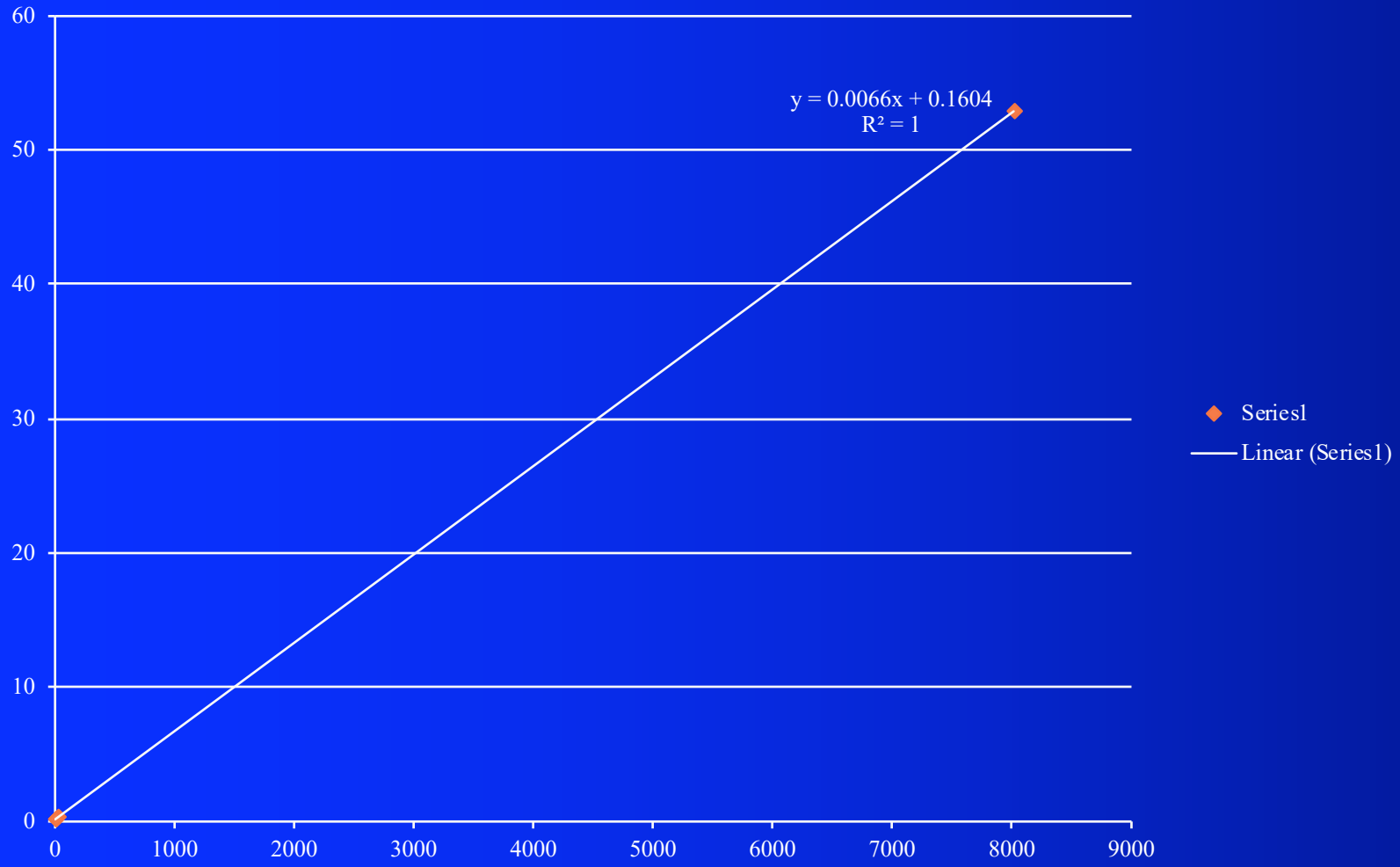
Bromine


140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
y = 0.6792x + 50.02
R² = 1
Bromine
Linear (Bromine)

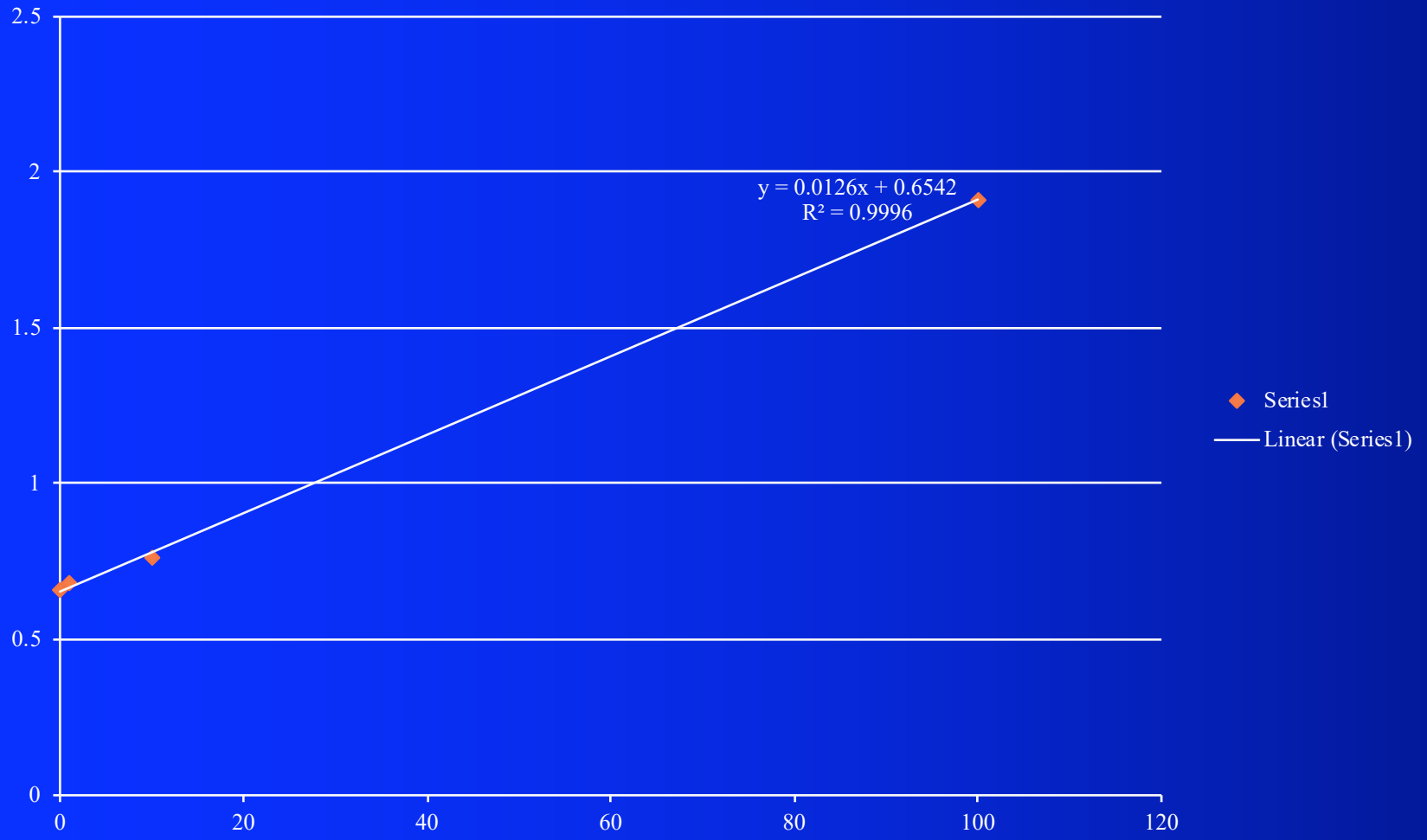
Chlorine


y = 0.0038x + 0.4398
R² = 1
45
40
35
30
25
20
15
10
5
0
0
2000
4000
6000
8000
10000
12000
Series1
Linear (Series1)

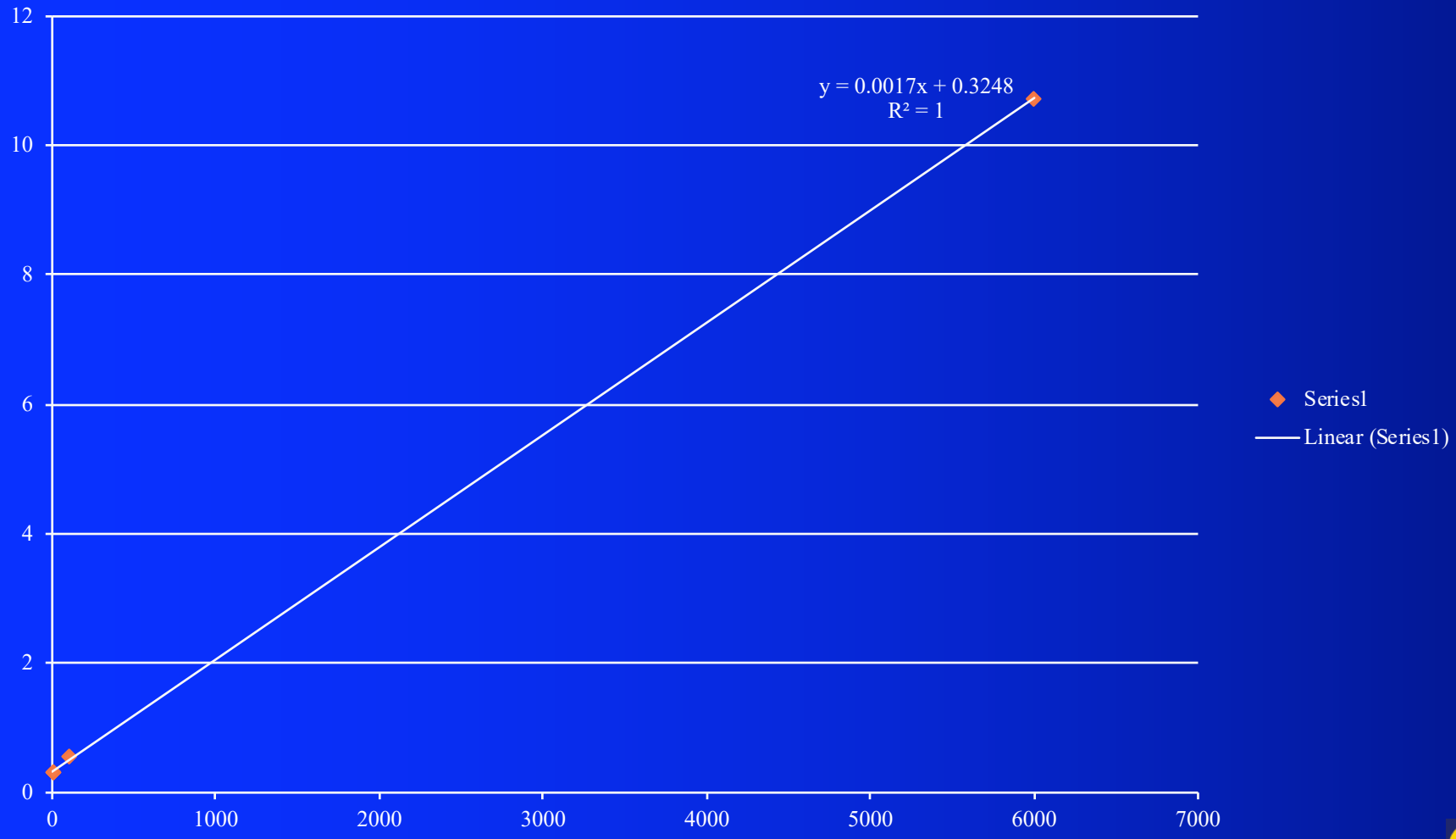
Sulfur


y = 0.0066x + 0.1604
R² = 1
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
Series1
Linear (Series1)

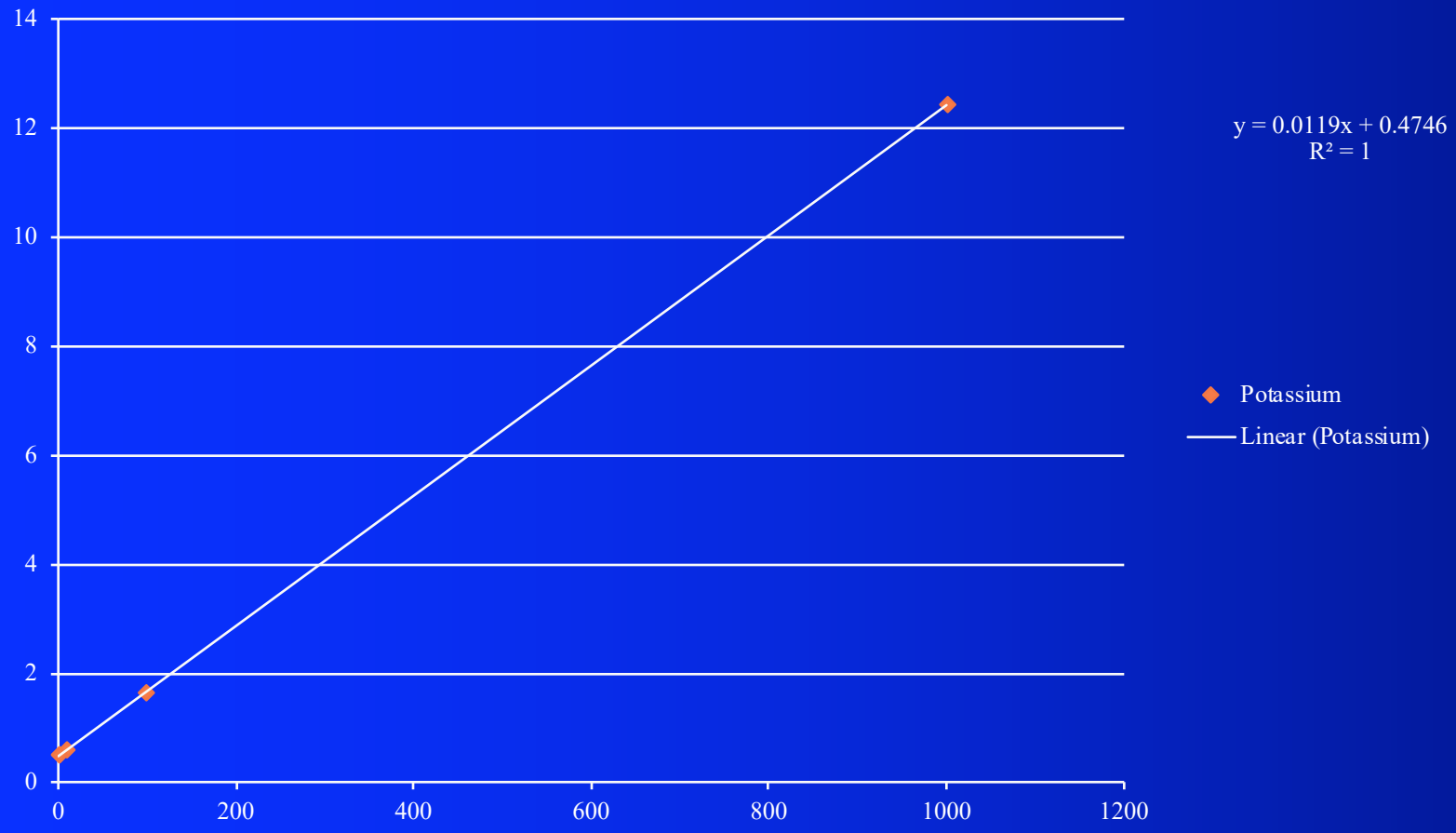
Calcium


2.5
2
1.5
1
0.5
0
0
20
40
60
80
100
120
y = 0.0126x + 0.6542
R² = 0.9996
Series1
Linear (Series1)

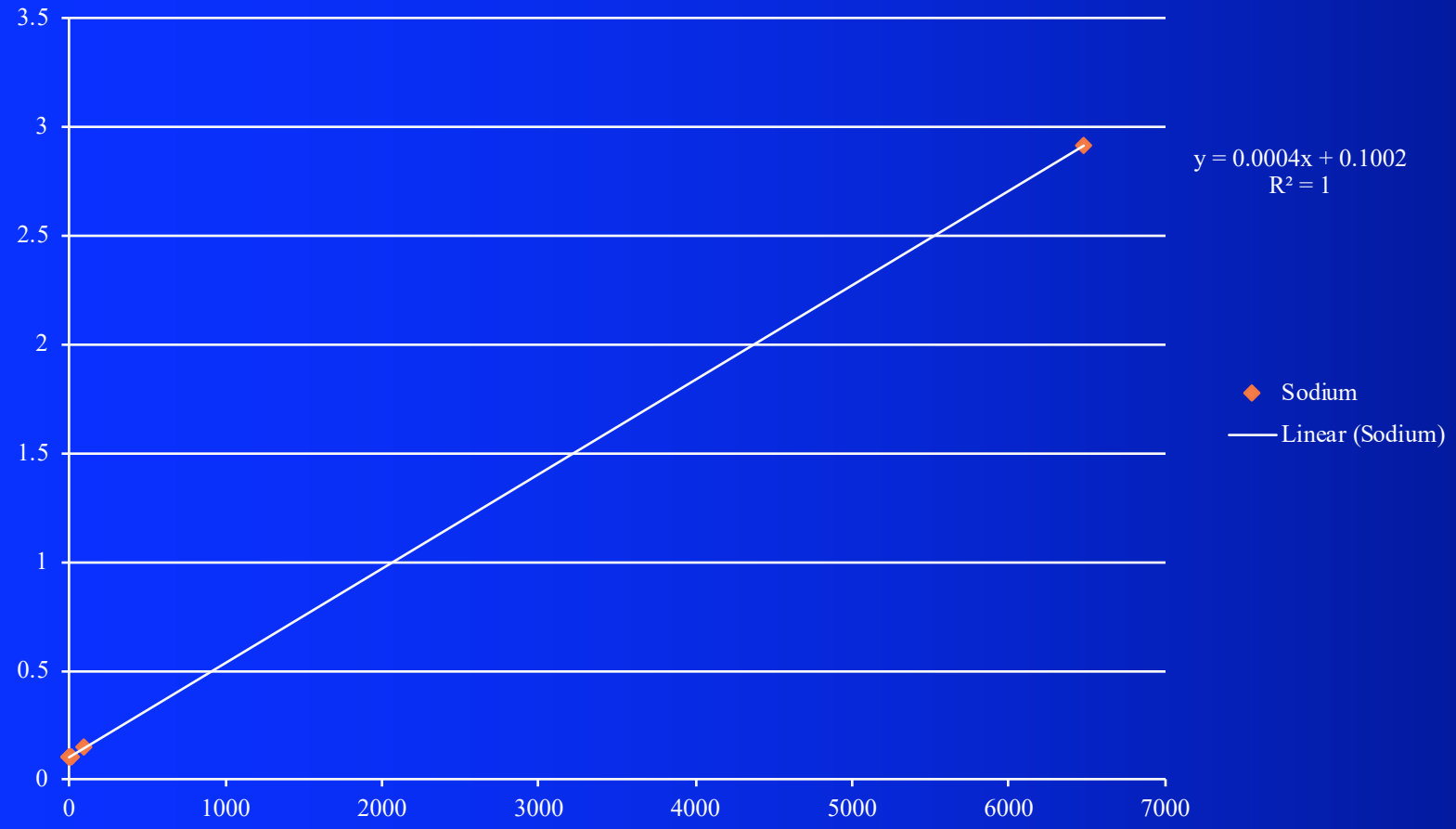
Magnesium


y = 0.0017x + 0.3248
R² = 1
12
10
8
6
4
2
0
0
1000
2000
3000
4000
5000
6000
7000
Series1
Linear (Series1)

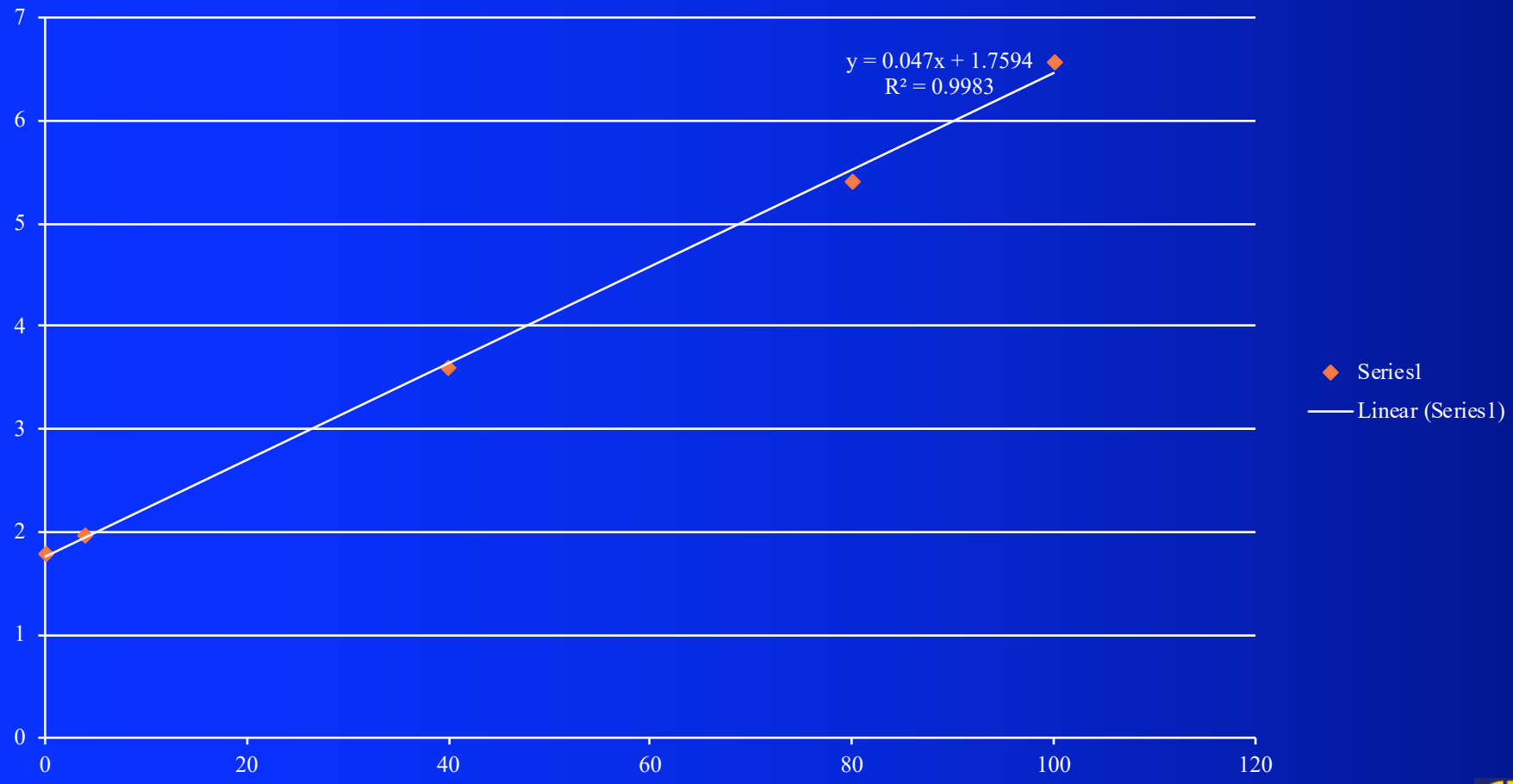
Potassium


14
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
y = 0.0119x + 0.4746
R² = 1
Potassium
Linear (Potassium)

Sodium


3.5
3
2.5
2
1.5
1
0.5
0
0
1000
2000
3000
4000
5000
6000
7000
y = 0.0004x + 0.1002
R² = 1
Sodium
Linear (Sodium)

Water –Soluble Cr



INTER-ELEMENT CORRECTIONS

And now the math!

Didn’t you always want to know what happens for calculations!

General form of influence correction is:

- C_i (corrected) = C_i (apparent)$(1+\{\Sigma\ \alpha_{ij} \times c_j\})$

  C_i = concentration of element of interest

  a_{ij} = influence coefficient of element j on element i

- j = refers to interfering element

  c_j = refers to concentration of interfering element

Iterative Calculations

		1st iteration		2nd iteration		3rd iteration	
j	αij	Cj	αijCj	Cj	αijCj	Cj	αijCj
Ca	-	62.47		62.967474			
Si	0.0003	17.14	0.005142				
Al	-0.0005	5.26	-0.00263				
Na	-0.0013	0.32	-0.00042				
Mg	-0.0014	2.59	-0.00363				
Si	0.002	3.38	0.00676				
K	0.0228	0.88	0.020064				
P	0.00016	0.29	4.64E-05				
Fe	-0.0028	2.88	-0.00806				
LOI	-0.0067	1.39	-0.00931				
Sum			0.007963				

Sources of errors

Item	Random/Systematic	Major or Minor Concern	What to do
Sampling	S	major	ASTM C702, D 75
Contamination	S	can be major	cleanliness
Instrument electronics	Random/Systematic	minor (hopefully!)	maintenance
Counting statistics	Random/Systematic	major	collect enough
Sample prep	S	major	establish method
Interelement correc'n	S	minor (hopefully!)	look at residual errors
analyst	S&R	major	training
environment	S	major	well controlled is ideal
x-ray tube	S	major	make drift corr'ns

Errors due to counting statistics

- There will be a random error associated with the measured value of N

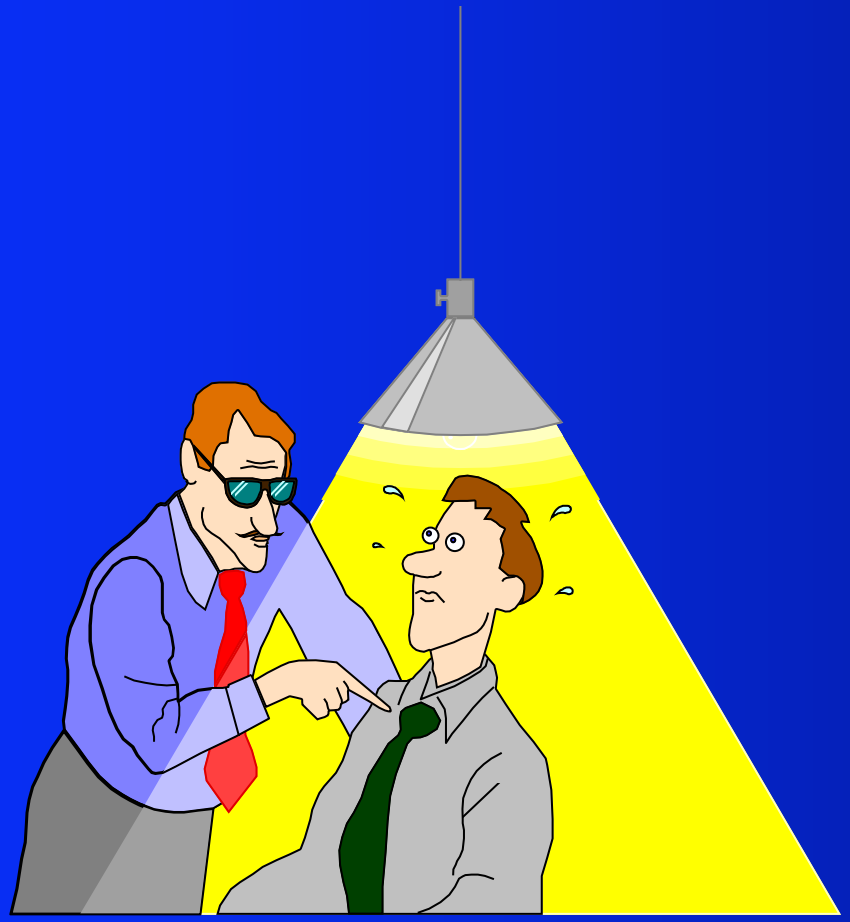
  Approximately 68% of all of the data lies within one standard deviation of the mean.
- Approximately 95% of all the data is within two standard deviations of the mean.
- Approximately 99.7% of the data is within three standard deviations of the mean.

- Do not associate errors of counting statistics with error in concentrations

Common errors associated with calibration

- Failure to adequately separate instrumental and matrix dependent effects.
- Poor judgement on the part of the analyst as to whether or not a correction should be made.
- Poor technique on the part of the analyst in the determination of influence corrections. i.e. $2n^2+1$=Number of stds needed to apply. (n= number of inter-element correction's)
- Poor quality and/or range of calibration standards.
- Inadequacy of the regression program.
- Application of the technique where the specimens are inadequately homogeneous.

Questions?



Thank You

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