



ROYAL CANADIAN MINT
MONNAIE ROYALE CANADIENNE



***The Application of XRF to
Gold Refining and Coin
Manufacturing at the Royal
Canadian Mint***

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The Business of the Mint



ROYAL CANADIAN MINT
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- **Circulation Coins (Canada & Other Countries)**
- **Numismatic Coins (Sterling Silver & 22 Karat Gold)**
- **Investor Coins (99.99% Gold and Silver)**
- **Gold Refining Services**

Ottawa



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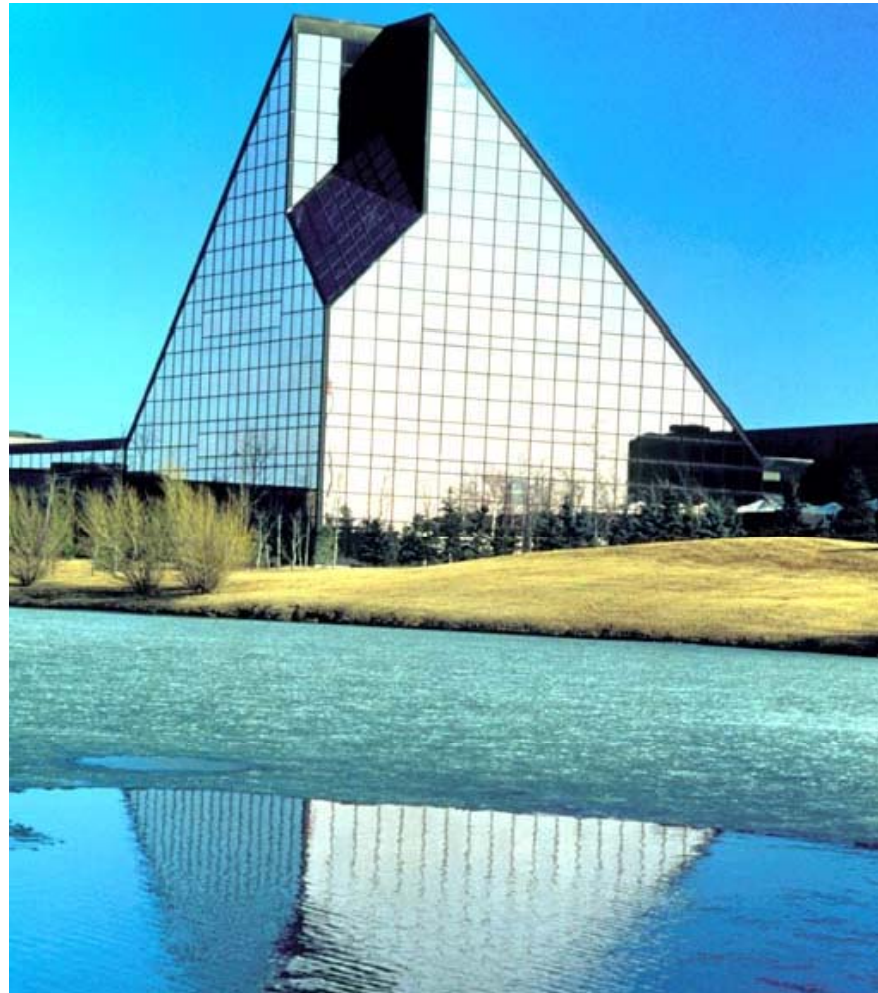


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Winnipeg



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Why XRF?



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- Fast turnaround
- Minimal sample preparation
- Minimal labour
- Simple to use (for operators)
- Some models have an auto-sampler
- Determination of major, minor, and trace elements in one analysis
- Can be used for unknown materials

Overview of Applications



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- **Ag and P in Sterling Silver**
- **Au, Ag, Cu & Other Elements in Impure Gold and Silver to assist Fire Assay**
- **Ag and Cu in Chlorinated Gold as an Endpoint Indicator**
- **As, Cd, Hg, Se, & Te in Impure Gold and Silver coming into the Refinery**
- **Plated Layer Thickness in Circulation Coin Blanks**



Wavelength Dispersive XRF

- Panalytical PW2404 (1999 – 2010)
- Panalytical Axios (2010)
- Energy Dispersive
 - Spectro 200
 - InnvoX Omega Xpress (portable)

Sterling Silver Alloy



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- Alloy: Ag 92.5%, P 700 ppm (max), Cu balance
- Used for Numismatic Coins
- Charges made from Ag, Cu, and P
- Alloy is continuously cast (point of sampling)
- Rolled, blanked, and stamped

Analysis Criteria



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- **Silver**
 - precision ± 0.03 % RSD (n = 3)
 - lower alloy limit 92.30%
- **Phosphorous**
 - precision ± 5 % RSD (n = 3)
 - 700 ppm max.
- **Copper**
 - Balance
- **Analysis time < 5 minutes**



Sample Handling

- Total sample analysis time < 5 minutes
 - 2 replicates & sample loading
- Minimal change to sample cutting (Concast)
- Minimal sample preparation (Assay)
- Autosampler to handle sample block (30mm)³

Continuous Casting Furnace



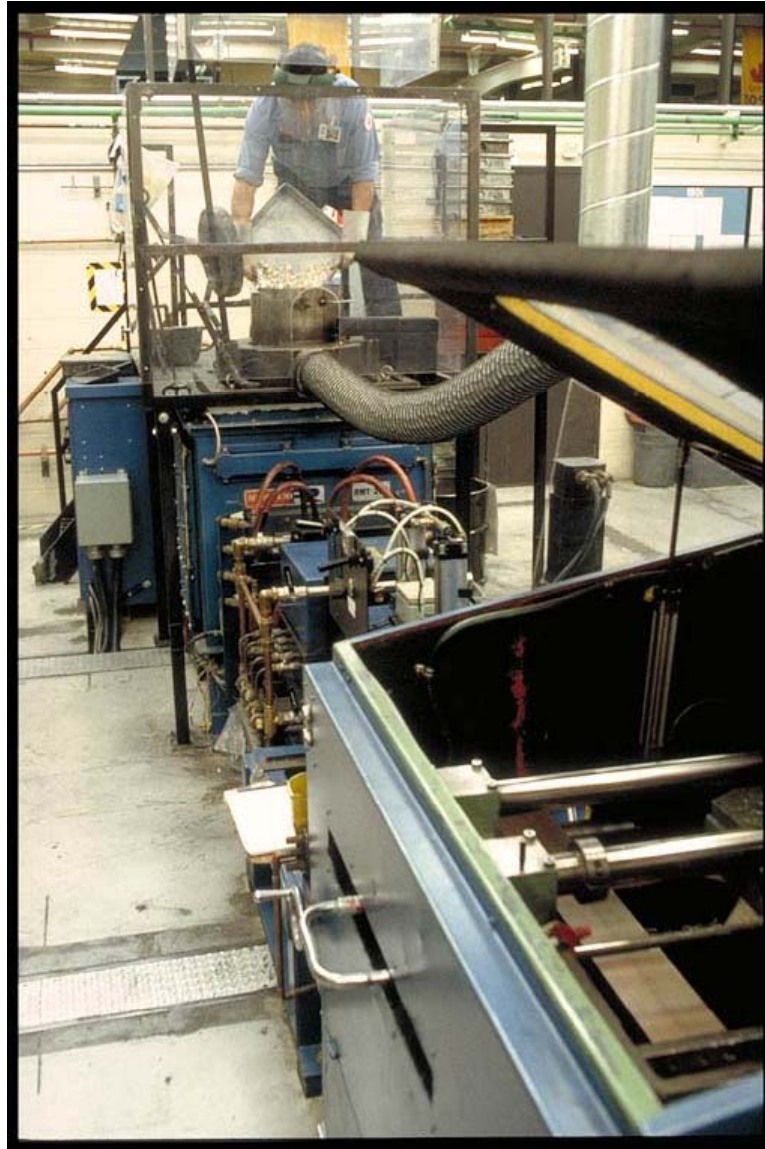
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Continuous Casting Furnace



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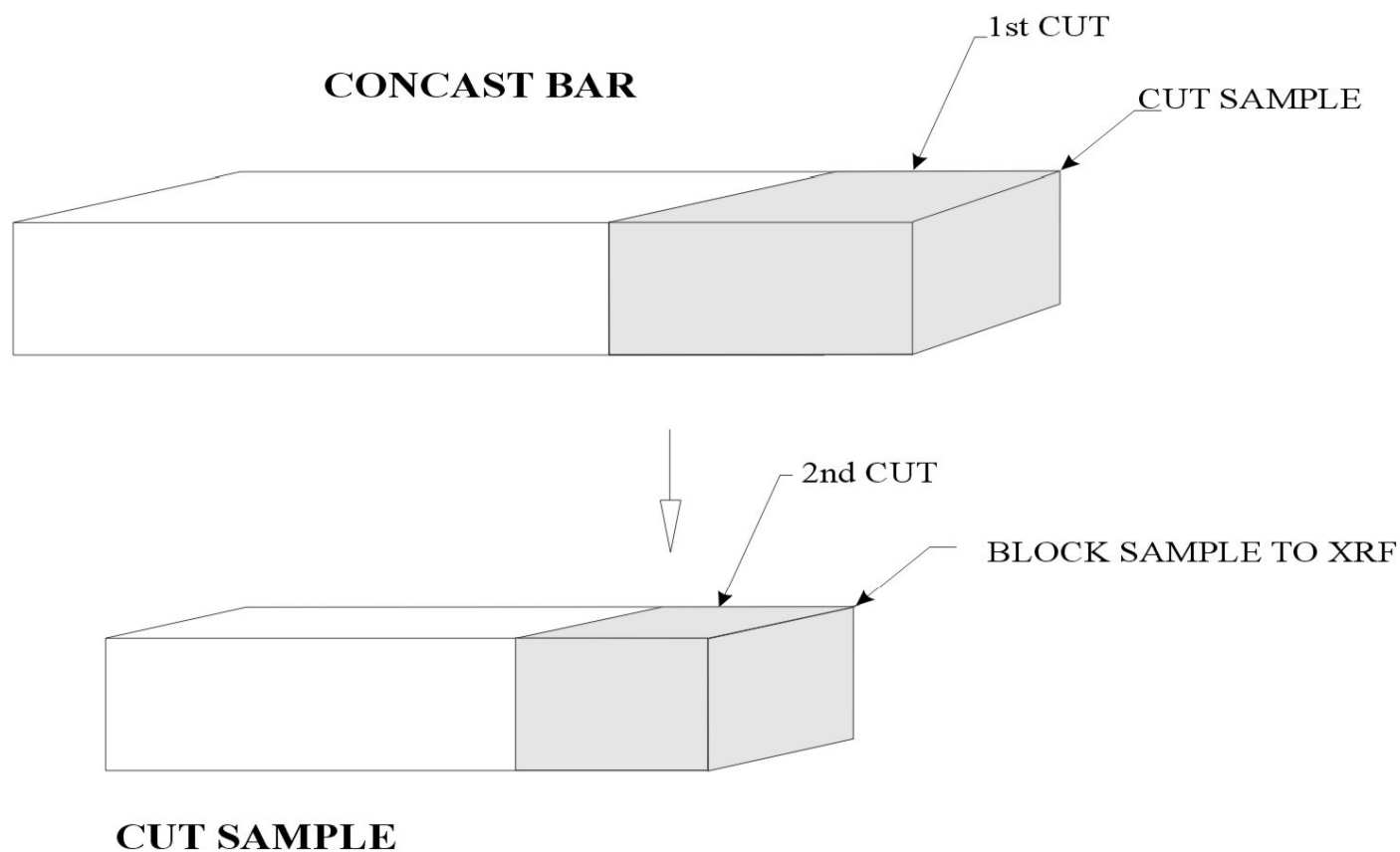


Cutting a Sample



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CONCAST SAMPLE



Sample Loading into XRF



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XRF Parameters – Sterling Ag



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Element	Line	X-tal	Detector	Time (s)
Ag	K _α	LiF 200	Duplex	80
Cu	K _α	LiF 200	Duplex	10
P	K _α	Ge111-C	Flow	20
<hr/>				
Total Time				110 s

X-ray tube settings

PW2404: 60 kV, 66 mA

Axios 60 kV, 50 mA

Achieving Exceptional Precision



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- Measure using the same cup
- Long Counting Time
- Keep X-ray tube at set power for 2 – 4 hr
- Sample Surface Preparation
- Control Environment
 - Inside wall
 - Air conditioning

Challenges for Ag 925 Samples



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- **Sample size to fill the aperture & fit the cup**
- **Constant sample size**
- **Sample labeling**
- **Smooth top - vacuum seal auto-sampler**
- **Sample flatness on analysed side**
- **Timely delivery of the samples**



Polishing (old):

- **Analysed Side**
 - Lathe the face (flatness) or press flat
 - 1st wet polish 400 mesh SiC paper (20 s)
 - 2nd wet polish 125 mesh SiC paper (20 s)
- **Opposite Side**
 - Wet polish 400 mesh SiC paper (20 s)
 - Auto-sampler pick-up

Milling Machine (new):

- Mill both surfaces
- Analysed side more carefully done

Ag 925 Standards



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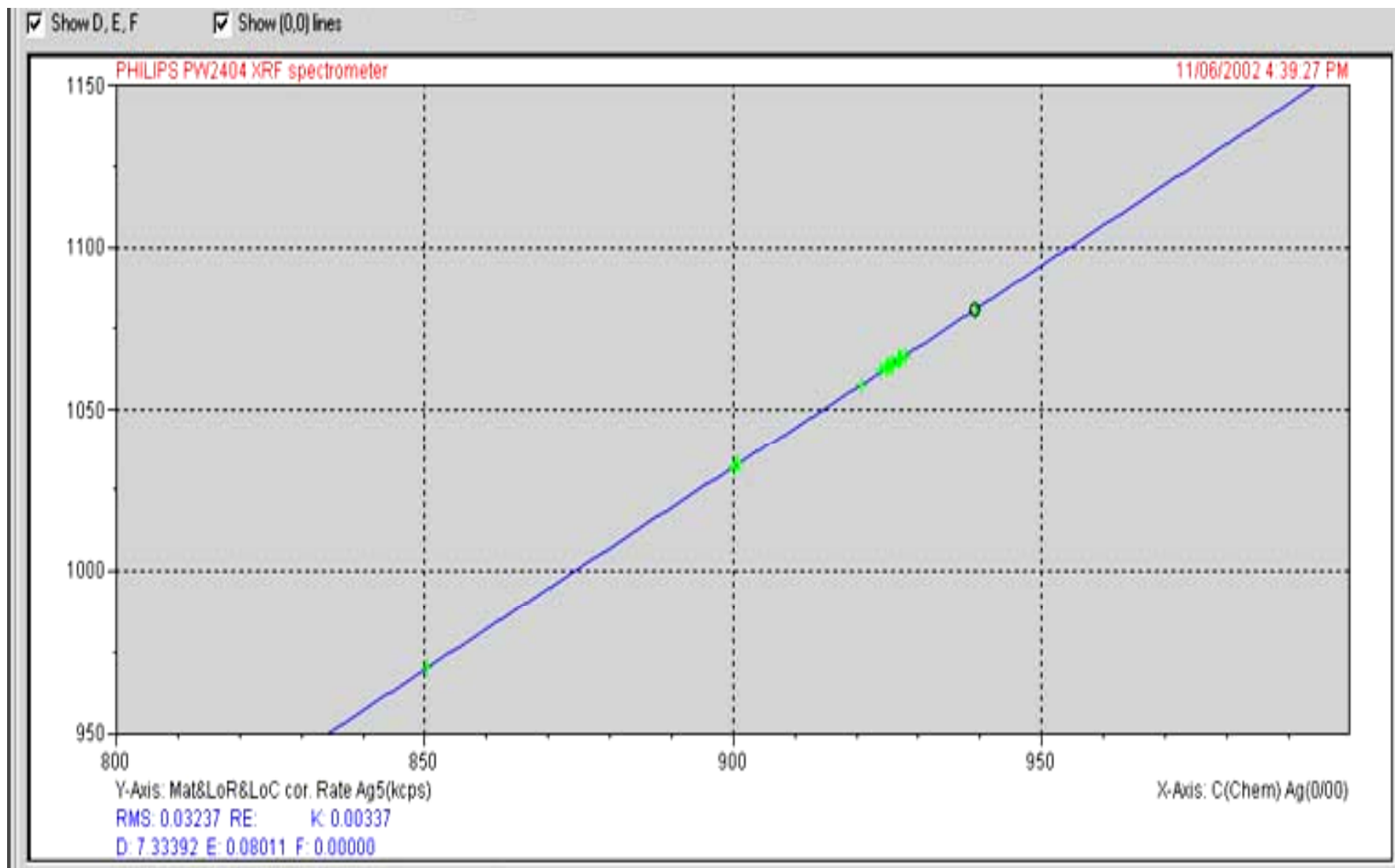
- Collected accepted and rejected samples
- Ag determined by Gay Lusac Method
 - back titration (AgCl formation from excess Cl)
- P determined by solution ICP-AES
 - 190.3 nm
 - matrix matched standards
- Cu by difference

Ag Calibration: 85 – 94%

Algorithm: De Jong (similar L-T)



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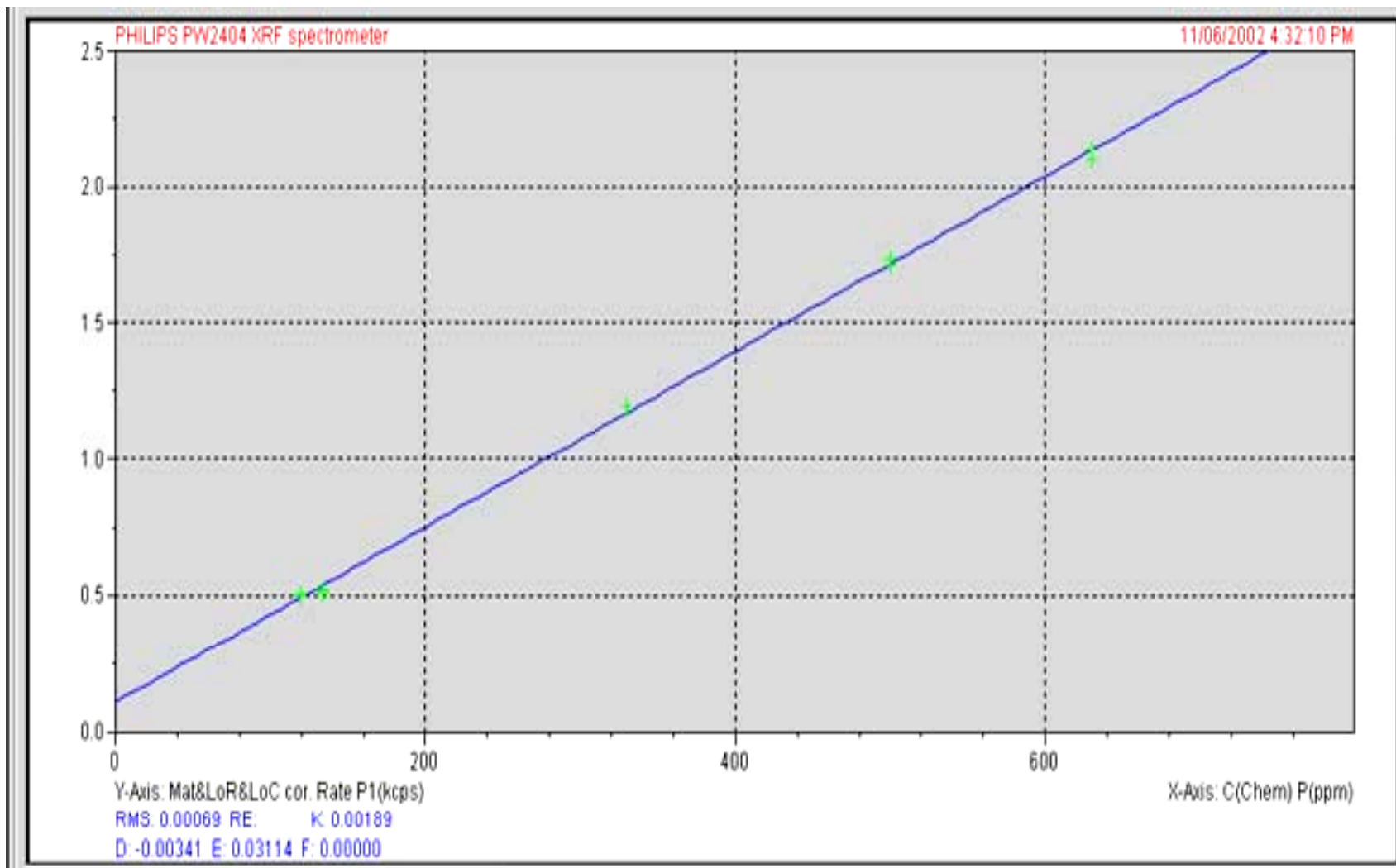


P Calibration: 0 – 700 ppm

Algorithm: De Jong (similar L-T)



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Ag Precision: QC 32-96 (4000W)



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Time Period	Precision RSD	Number of Replicates
1 hour	0.02 %	10
8 hour	0.02 %	20
7 days	0.03 %	98

Cu Precision: QC 32-96 (4000W)



ROYAL CANADIAN MINT
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Time Period	Precision RSD	Number of Replicates
1 hour	0.06%	10
8 hour	0.06%	20
5 days	0.06%	98

P Precision: QC 32-96 (330 ppm)



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Time Period	Precision RSD	Number of Replicates
1 hour	1.4%	10
8 hour	1.2%	20
5 days	2.6%	98

Accuracy: Ag (n=5 replicates)



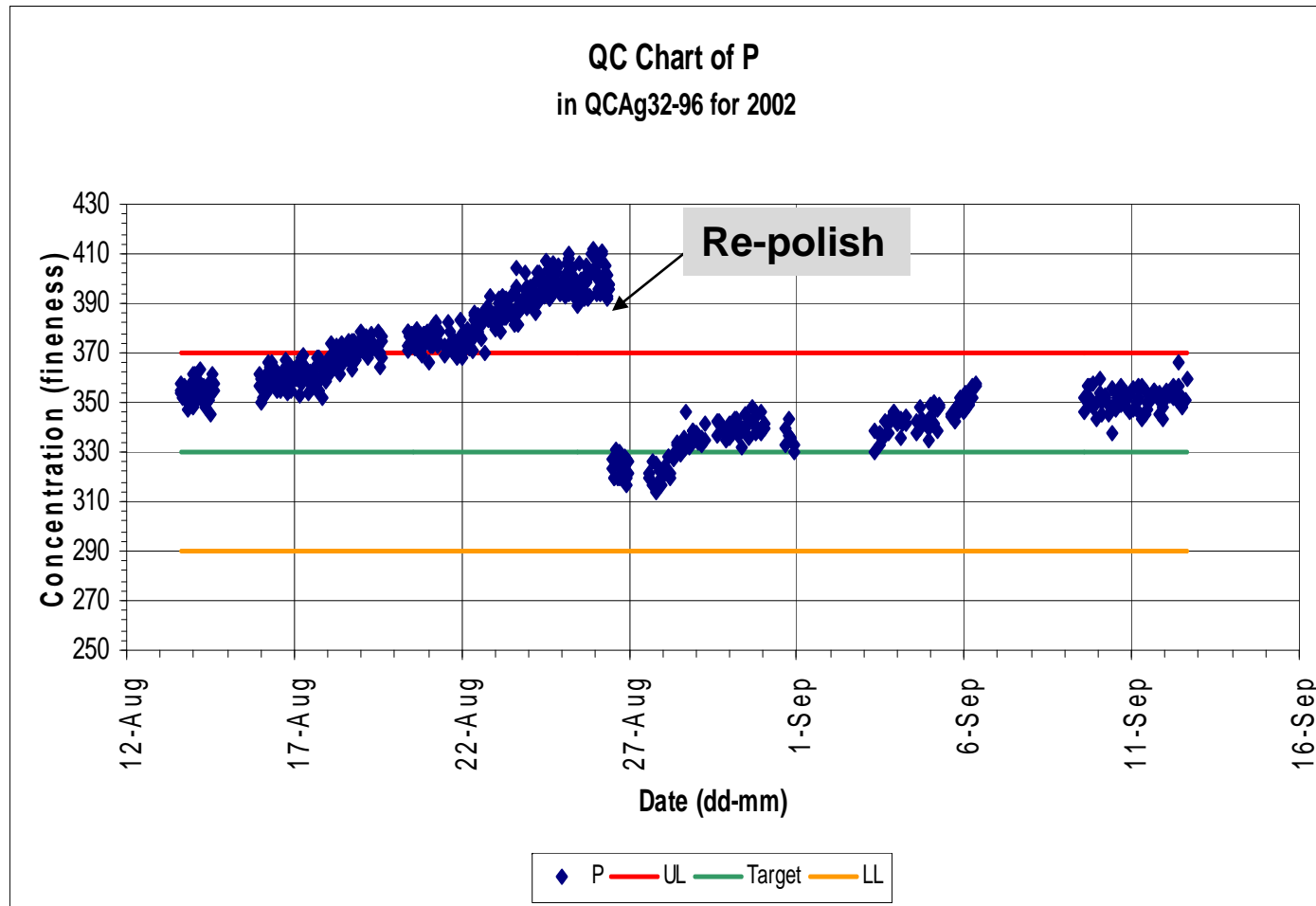
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Sample	XRF	Gay Lusac	Sig. Diff.
277	925.6 ± 0.21	925.5 ± 0.4	No
282	923.4 ± 0.15	924.2 ± 0.5	No
287	925.7 ± 0.14	926.2 ± 0.34	No
2A	921.3 ± 0.23	920.8 ± 0.35	No
4B	938.7 ± 0.15	939.2 ± 0.25	No

P contamination – vacuum oil



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Measuring Ag Alloy Coin Blanks



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- One contract had blanks with diameter less than 27 mm
- Must use 12 mm sample aperture
- Lower counts from lower surface area
- Must increase counting time

Blank compared to sample cups



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27 vs 12 mm Comparison



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Parameter	27 mm	12 mm
Ag counts, kcps	800	120
Effective Diameter, mm	25	10
Effective Area, mm²	491	78.5
<hr/>		
Ratios 27 vs 12 mm	Area 6.25	Count 6.67

Precision: 12 vs 27 mm cups

Ag 90% alloy; n = 10



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Parameter	12 mm	27 mm
Ag Counting Time, s	120 (20 bkgd)	80
Precision, %RSD	0.03 - 0.04	0.02 - 0.03
P Counting Time, s	30 (10 bkgd)	20 (10 bkgd)
Precision, % RSD	2	2

Analysis of Impure Gold



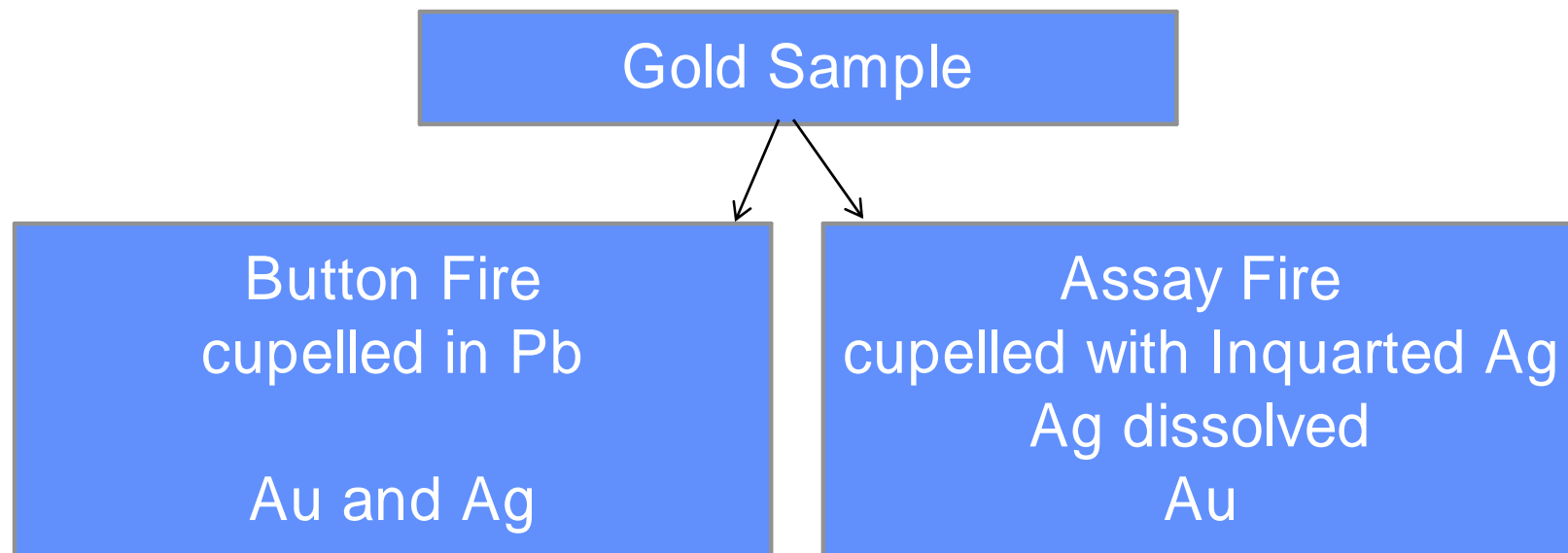
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- **Settlement of Gold Deposit**
 - After melt mass
 - Determine Au and Ag by Fire Assay
- **Fire Assay:**
 - Gravimetric
 - High precision and accuracy
 - Industry standard
- **XRF used to streamline Fire Assay**

Overview of Fire Assay



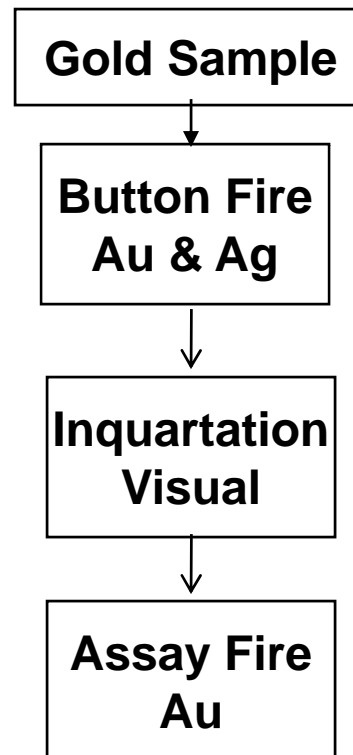
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Traditional Fire Assay



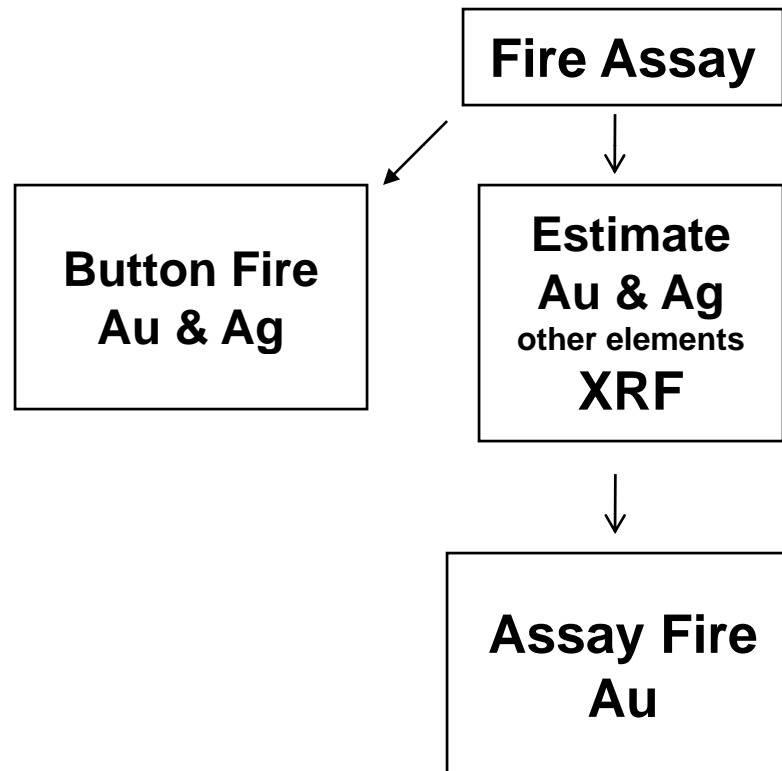
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Fire Assay with XRF



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XRF for Ag Inquartation (FA)



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- Measurement of Au and Ag used to add Inquartation Ag for the Assay Fire
 - $Ag\ Inq = ((2.5 * Au) - Ag) / 2$
- Ag Inq must be within ± 50 mg Ag
- Minimal sample and sample prep
 - Press small dip sample
 - Polish
- 3 minute analysis time
- Elements: Au, Ag, Cd, Cu, Fe, Ni, Pb, Pt, Pd, Te, Zn

XRF for FA: Limitations



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- **Small sample size 12 mm aperture**
- **Automation required: large number cups**
- **Fast response**
- **Personnel with minimal training**
- **4000 W power (60 kV and 66mA)**
- **Must also have a 6 mm aperture program**
 - **Some samples break apart**



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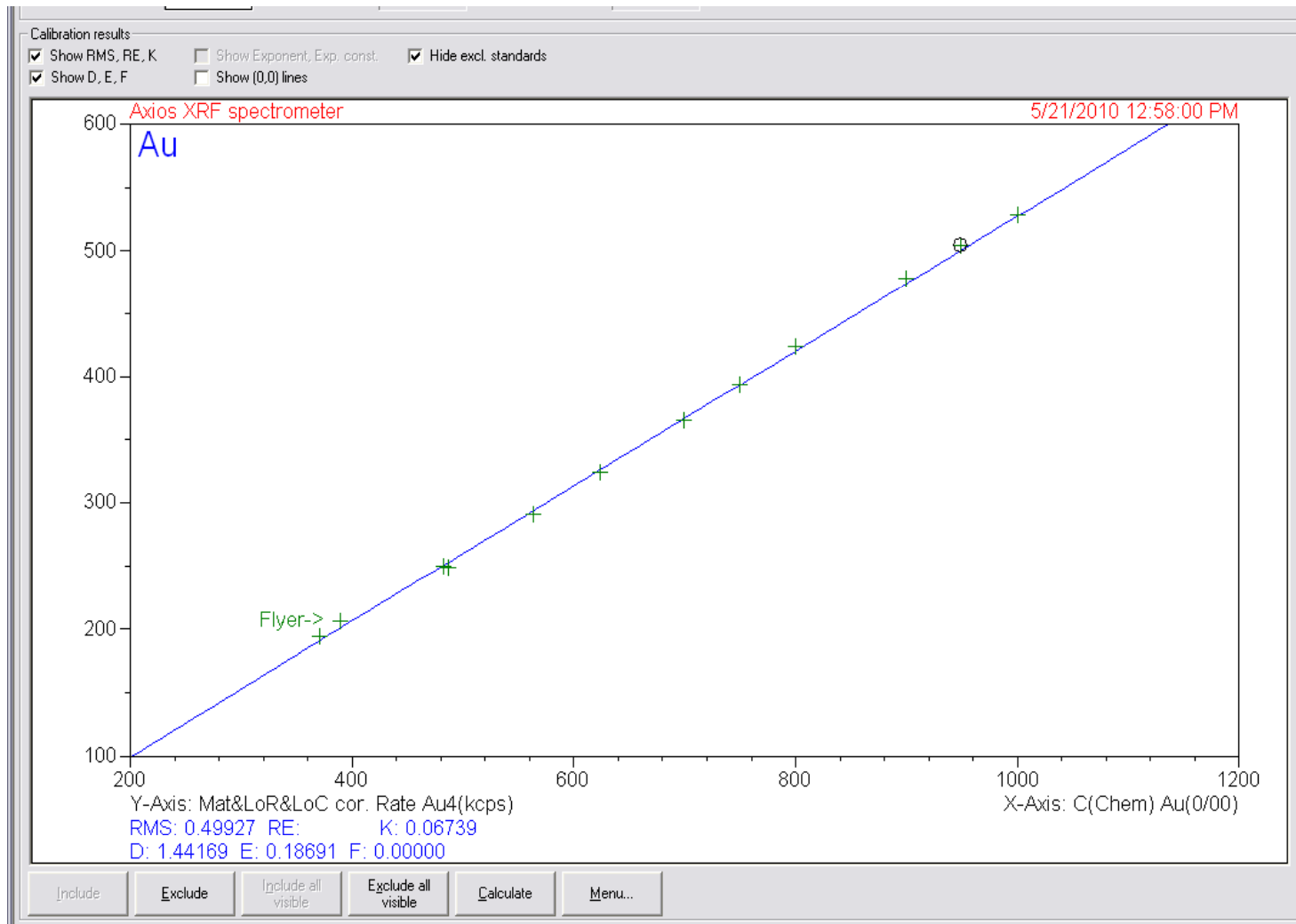
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INQ12 Au Calibration (40–100%)



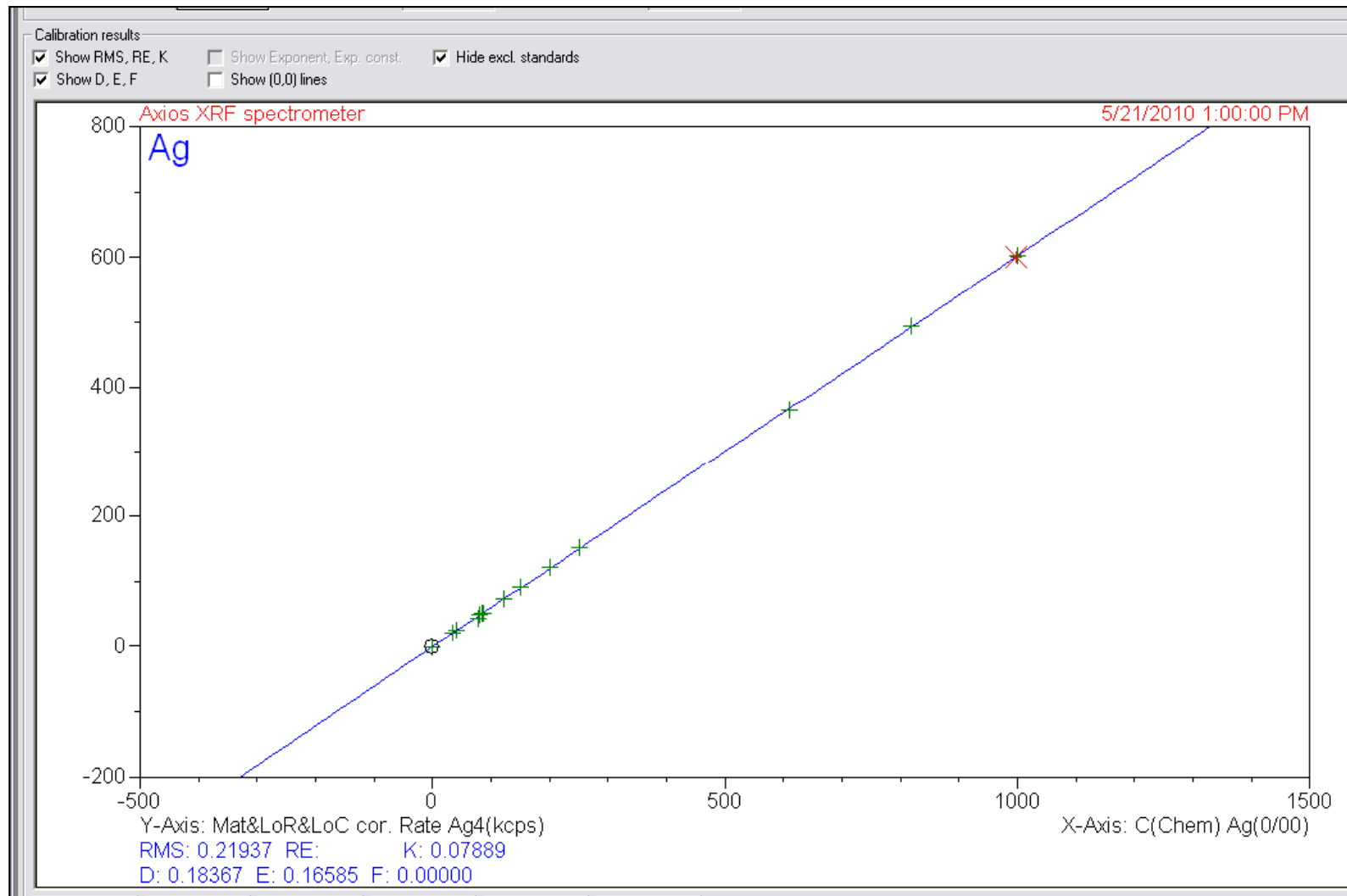
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INQ12 Ag Calibration (0-100%)



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Au & Ag Analytical Results



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Standard: INQ12QC2, n= 38 determinations over 3 weeks

Units: parts per thousand or fineness

	Au	Ag
Average	624.3	85.6
Std Dev	0.7	1.7
RSD	0.1%	2%
Certified Values	623.8	84.7
Difference	0.5	0.9
% Error	0.1%	1%

Au & Ag Analytical Results



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Standard: QC60847, n= 5 determinations

Units: parts per thousand or fineness

	Au	Ag
Average	644.5	73.5
Std Dev	0.8	0.1
RSD	0.1%	0.1%
Certified Values	646.0	75.5
Difference	-1.5	-2.0
% Error	-0.2%	-3%



Good analytical results from XRF due to:

- **Sampling molten metal (induction melt)**
- **XRF application**
 - Background, overlap corrections
- **Calibration Standards**
 - Produced in-house
 - Specially cast or use normal samples
 - Rigorously analysed
 - Fire Assay
 - Fire Assay ICP-AES – Ag, Pd, & Pt (Cu & Pb)
 - ICP-AES
 - FAAS



XRF very useful to refining and coin operations:

- **Timely results**
- **Analytical performance**
 - **Accuracy (standards)**
 - **Precision**
- **Ease of use**
- **Minimal sample preparation**

XRF requires investment in:

- **Standard manufacturing & analysis**
- **Method development**

Acknowledgements



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