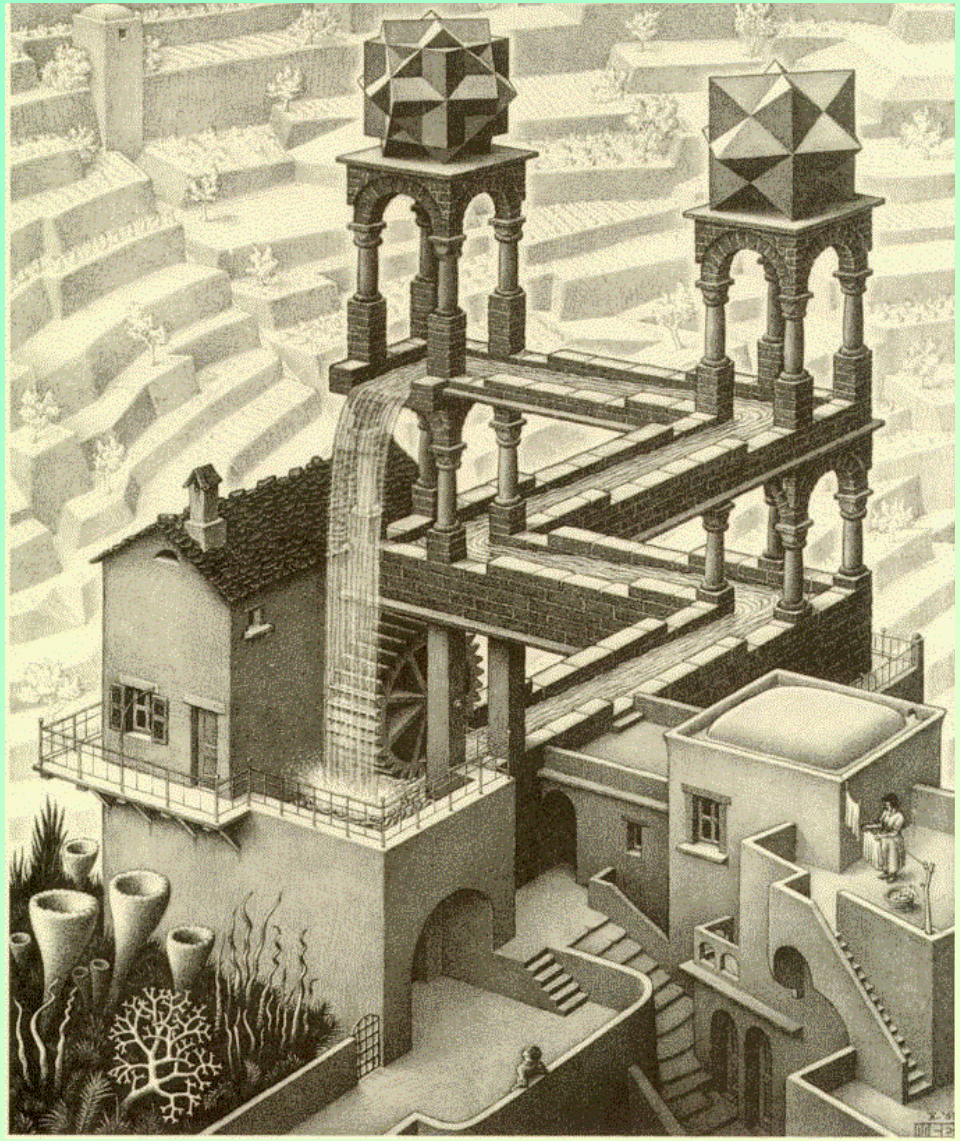
# The Power of Iteration



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# CAMCOR

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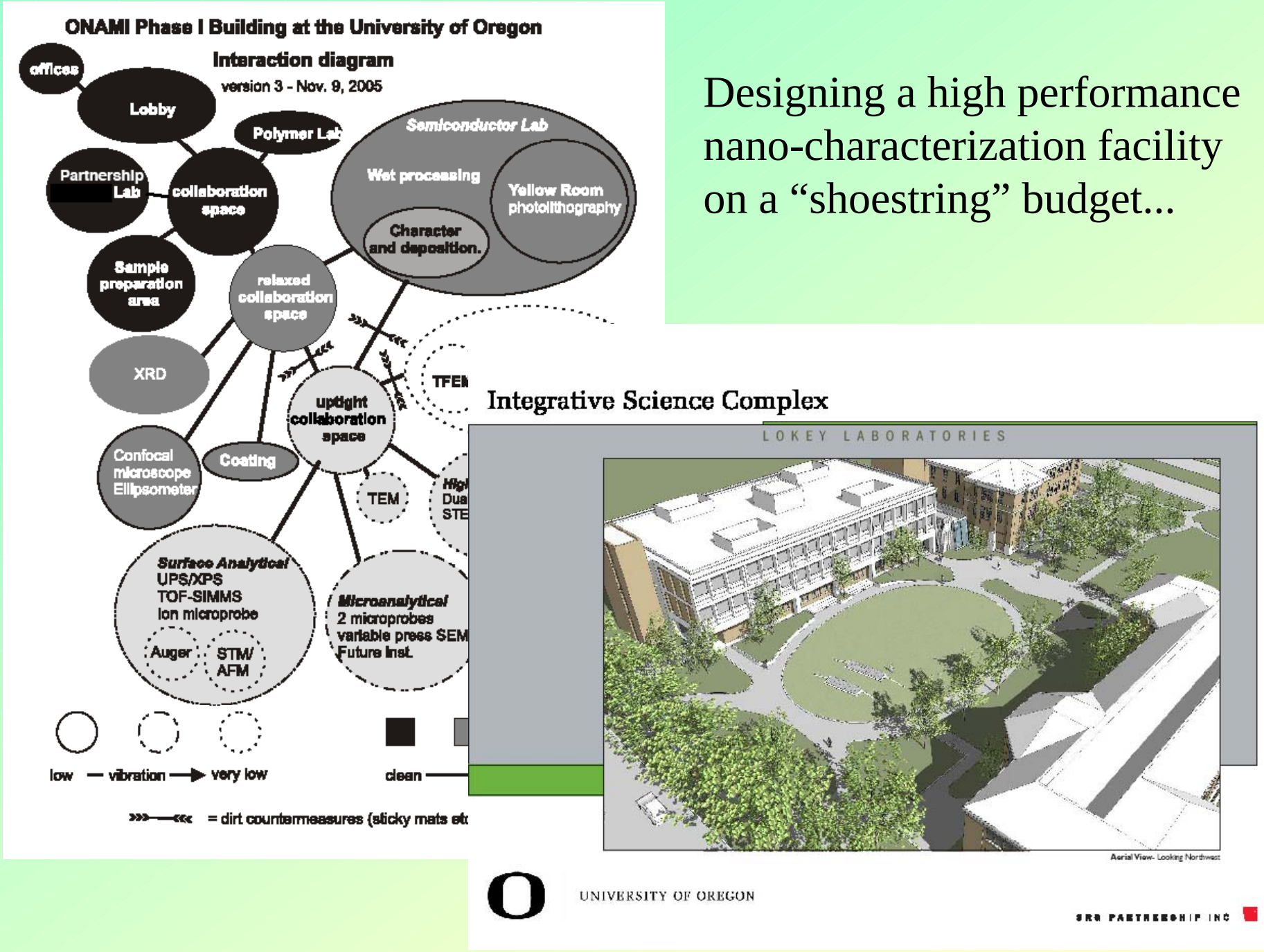
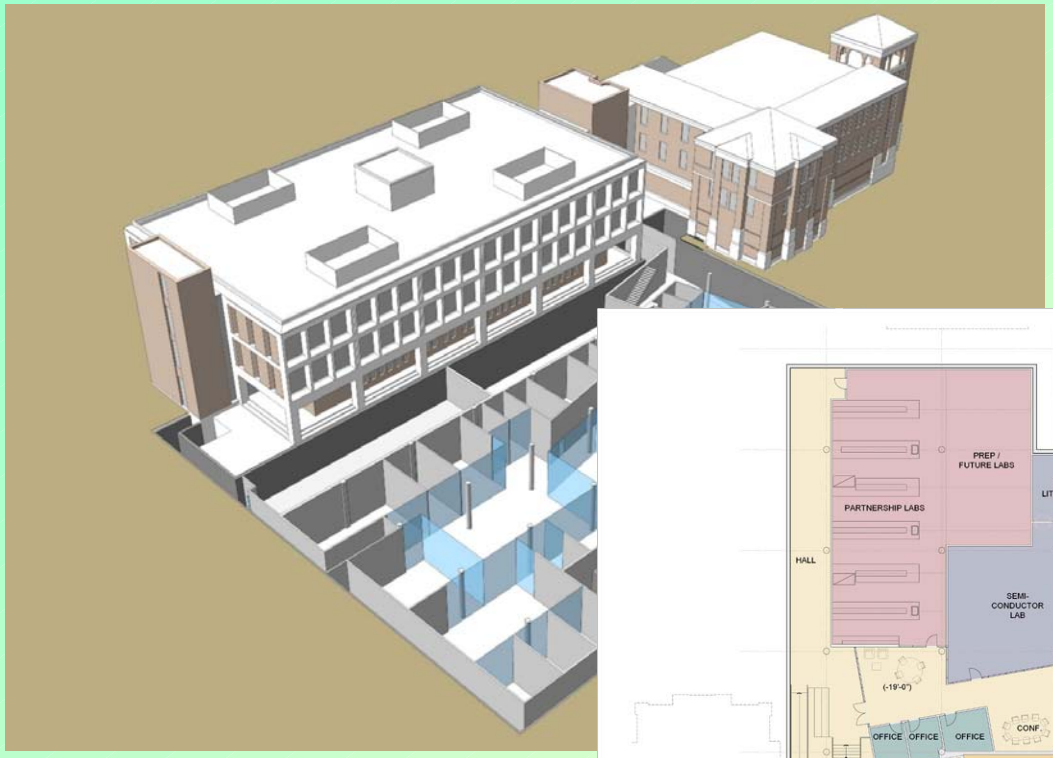
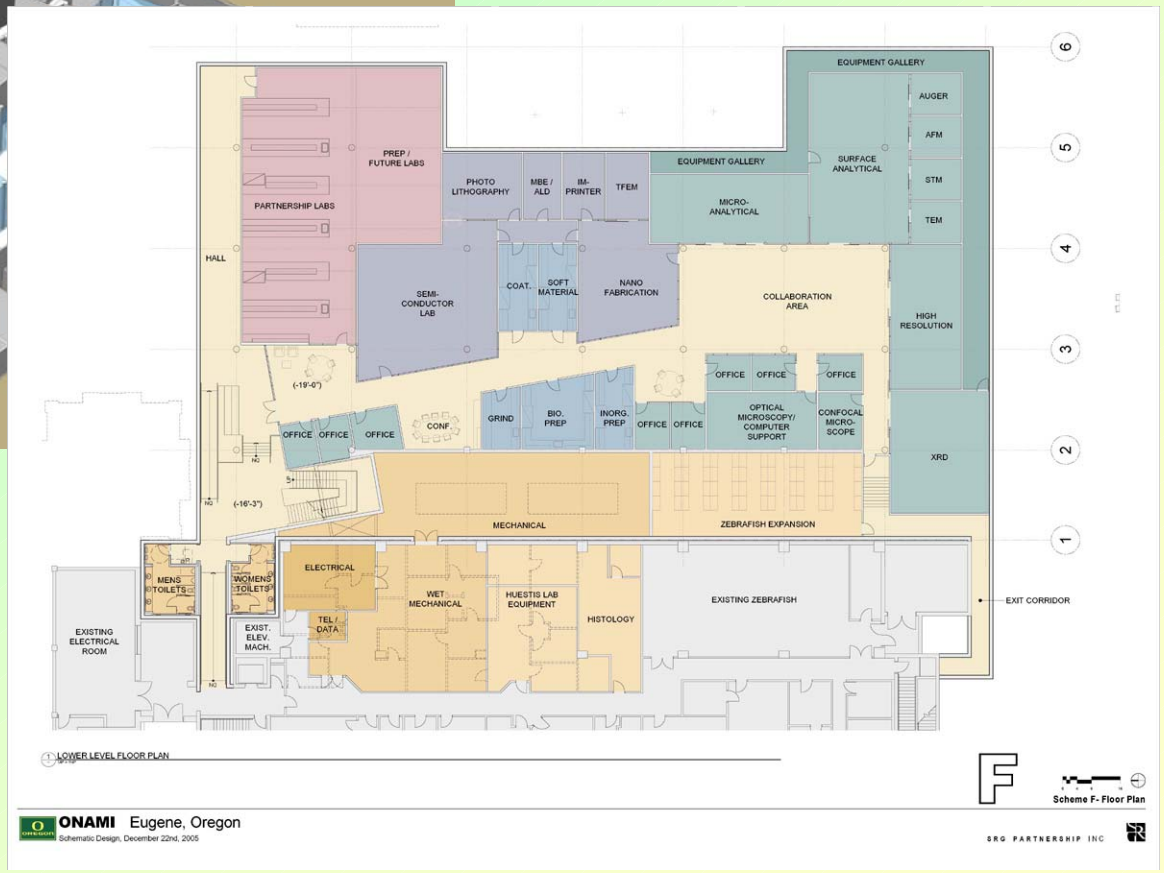



Designing a high performance nano-characterization facility on a “shoestring” budget...

# Integrated Science Complex (Phase I)



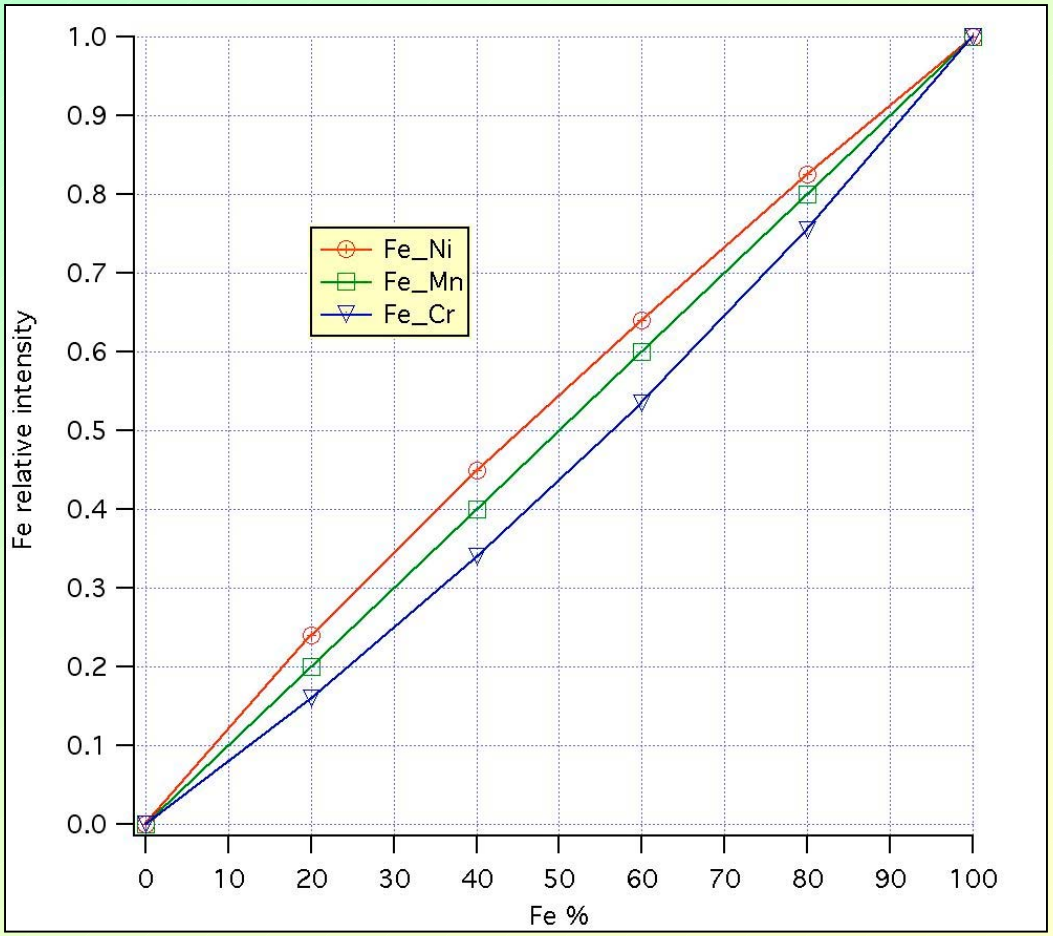


# Lorry I. Lokey Laboratory

# Matrix Correction

$$C_i^{unk} \approx \frac{I_i^{unk}}{I_i^{std}} C_i^{std}$$

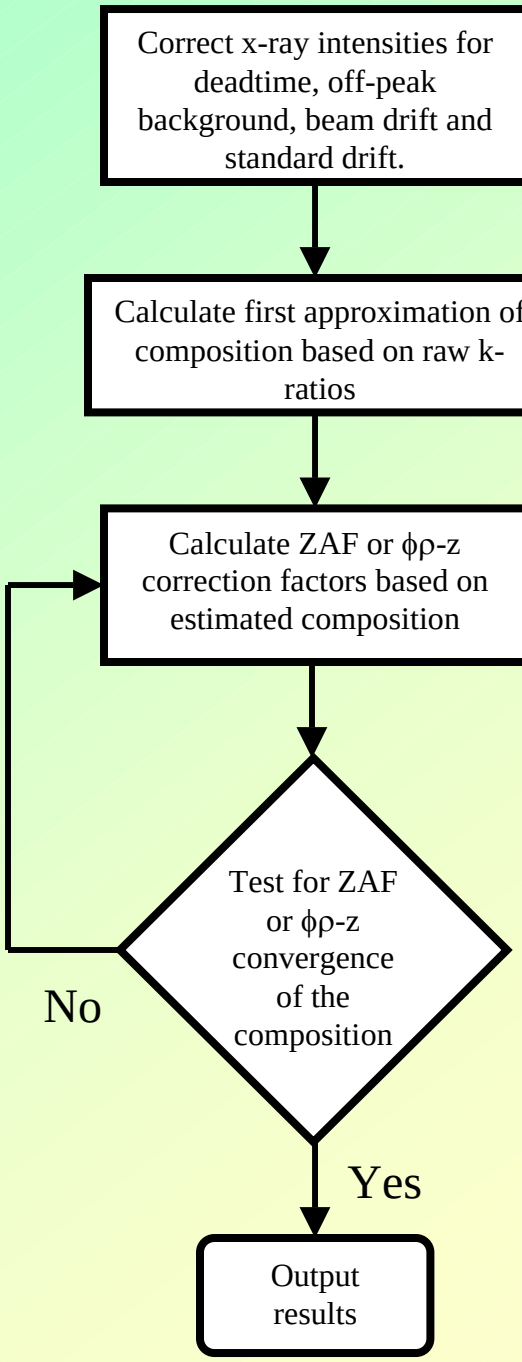
$$C_i^{unk} = \frac{I_i^{unk}}{I_i^{std}} \frac{ZAF_i^{unk}}{ZAF_i^{std}} C_i^{std}$$



# Matrix Iteration...

```
Sub TestMatrixCalculateMatrix(mLastElmts As Long, mLastChan As Long, mElement() As Long, mXrayn() As Long, mCations() As Double, mOxygen() As Double, mAtomicWt() As Double, mAlpha1() As Double, mAlpha2() As Double, mAlpha3() As Double, mUnkIter() As Doubl
e, mUnkPercent() As Double, mStdIter() As Double, mStdIterI() As Double, mCalculateFlag() As Long, mCalculatePercent() As Double, mUnkIterI() As Double, mUnkPercentI() As Double, mStdPercent() As Double, mTotal As Double)
'Calculate matrix correction using a Bence-Albee iteration
'mLastElmts = number of elements (not counting cations)
'mLastChanIn = number of absorbing elements (not measured, only specified or calculated weight percents)
'mElement#() = element atomic numbers (1 to mLastChanIn)
'mXrayn#() = xray lines (1=Ka, 2=Kb, 3=La, 4=Lb, 5=Ma, 6=Mb, 7=absorber only) (1 to mLastChanIn)
'mCations#() = number of stoichiometric cations (1 to mLastChanIn)
'mOxygen#() = number of stoichiometric oxygens (1 to mLastChanIn)
'mAtomicWt#() = atomic weights (1 to mLastChanIn)
'mAlpha1#(), mAlpha2#(), mAlpha3#() = matrix of alpha factor parameters
'mUnkIter#() = measured unknown intensities (1 to mLastElmts)
'mStdIter#() = standard intensities (from calcStdMatrixCalcMatrix, SETUP.MDB database) (1 to mLastElmts)
'mStdPercent#() = standard percents (from call to MatrixCorrMatrix, SETUP.MDB database) (1 to mLastElmts)
'mCalculateFlag%() = absorbing element calculation flags (0 = specified concentration, 1 = by difference, 2 = by stoichiometry)
'mCalculatePercent#() = absorbing element specified weight percents (1 to mLastChanIn)
'
'Returned parameters and arrays
'mUnkBeta#() = returned unknown beta factors (1 to mLastElmts) (must be initialized to 1.0)
'mUnkPercent#() = corrected weight percents (matrix corrected) (1 to mLastChanIn)
'mUnkPercentI#() = original weight percents (1 to mLastChanIn)
' mTotal# = weight percent total

iserr = False
On Error GoTo TestMatrixCalculateMatrixErr:

Const MAXMATRIXITER% = 20
Const MATRIXMINTOLE# = 0.05! ' in weight percent
Const MATRIXMINTOTAL# = 0.001 ' in weight percent

Dim bDifferenceElement As Boolean, bStoichiometricElement As Boolean
Dim iDifferenceElement As Long, iStoichiometricElement As Long
Dim chan As Long
Dim MatrixIter As Long

Dim maxDiff As Double, diff As Double
Dim stoichiometricoxygen As Double

ReDim pj(1 To mLastChanIn) As Double ' stoichiometric ratio variable

' Determine if there is an element by difference and/or an element by stoichiometry
For chanIn = mLastElmts + 1 To mLastChanIn
If mCalculateFlag%(chanIn) = 1 Then ' element by difference
bDifferenceElement = True
iDifferenceElement% = chanIn
End If

If mCalculateFlag%(chanIn) = 2 Then ' element by stoichiometry
bStoichiometricElement = True
iStoichiometricElement% = chanIn
End If
Next chanIn

' Bence-Albee iteration begins here
MatrixIter% = 0
Do Until MatrixIter% >= MAXMATRIXITER%

' Calculate weight percents for analyzed elements
For chanIn = 1 To mLastElmts
If mUnkIter#(chanIn) <= 0# Then GoTo TestMatrixCalculateMatrixBadUnkIter:
If mStdPercent#(chanIn) <= 0# Then GoTo TestMatrixCalculateMatrixBadStdPercent:
If mStdIter#(chanIn) <= 0# Then GoTo TestMatrixCalculateMatrixBadStdCounts:
If mStdIterI#(chanIn) <= 0# Then GoTo TestMatrixCalculateMatrixBadStdIter:

mUnkPercent#(chanIn) = (mUnkIter#(chanIn) * mStdPercent#(chanIn)) * mUnkBeta#(chanIn) / (mStdIter#(chanIn) * mStdBeta#(chanIn))
Next chanIn

' Load specified concentrations (could be zero so%'s by default)
For chanIn = mLastElmts + 1 To mLastChanIn
mUnkPercent#(chanIn) = 0#
If mCalculateFlag%(chanIn) = 0 Then
mUnkPercent#(chanIn) = mCalculatePercent#(chanIn)
End If
Next chanIn

' Sum stoichiometric oxygen (do not include oxygen from element by difference)
If bStoichiometricElement Then
stoichiometricoxygen# = 0#
For chanIn = 1 To mLastChanIn
If chanIn <> stoichiometricElement% Then
pj#(chanIn) = mOxygen#(chanIn) * mCations#(chanIn) * mAtomicWt#(stoichiometricElement%) / mAtomicWt#(chanIn)
stoichiometricoxygen# = stoichiometricoxygen# + mUnkPercent#(chanIn) * pj#(chanIn)
End If
Next chanIn
mUnkPercent#(stoichiometricElement%) = stoichiometricoxygen#
End If

' Total all weight percents for difference element calculation
mTotal# = 0#
For chanIn = 1 To mLastChanIn
mTotal# = mTotal# + mUnkPercent#(chanIn)
Next chanIn

' Calculate element by difference based on current weight percents
If bDifferenceElement Then
If mTotal# < 100# Then
mUnkPercent#(iDifferenceElement%) = 100# - mTotal#
If bStoichiometricElement Then
pj#(iDifferenceElement%) = mOxygen#(iDifferenceElement%) * mCations#(iDifferenceElement%) * mAtomicWt#(stoichiometricElement%) / mAtomicWt#(iDifferenceElement%)
mUnkPercent#(iDifferenceElement%) = mUnkPercent#(iDifferenceElement%) / pj#(iDifferenceElement%)
stoichiometricoxygen# = stoichiometricoxygen# + mUnkPercent#(iDifferenceElement%) * pj#(iDifferenceElement%)
mUnkPercent#(stoichiometricElement%) = stoichiometricoxygen#
End If
End If
mTotal# = 100#
End If

' Check for decent total
If mTotal# >= MATRIXMINTOTAL# Then GoTo TestMatrixCalculateMatrixBadTotal

' Compare change in weight percents since last iteration
maxDiff# = 0#
For chanIn = 1 To mLastChanIn
diff# = Abs(mUnkPercent#(chanIn) - mOldPercent#(chanIn))
If diff# > maxDiff# Then maxDiff# = diff#
mOldPercent#(chanIn) = mUnkPercent#(chanIn)
Next chanIn

' Check for convergence
If maxDiff# <= MATRIXMINTOLE# Then GoTo 6000

' Compare sum of alpha factors for each element (beta factors)
Call TestMatrixCalculateBetaFactors(mLastElmts, mLastChanIn, mAlpha1#(), mAlpha2#(), mAlpha3#(), mUnkPercent#(), mUnkBeta#(), mTotal#)
If iserr Then Exit Sub

' Not converged, try again
MatrixIter% = MatrixIter% + 1
Loop

' If we get here, convergence failed
MsgBox "WARNING in TestMatrixCalculateMatrix- Convergence failed", vbOKOnly + vbExclamation, "TestMatrixCalculateMatrix"

' Converged, calculate total
6000:
mTotal# = 0#
For chanIn = 1 To mLastChanIn
mTotal# = mTotal# + mUnkPercent#(chanIn)
Next chanIn

Exit Sub

TestMatrixCalculateMatrixErr:
MsgBox Error$, vbOKOnly + vbCritical, "TestMatrixCalculateMatrix"
iserr = True
Exit Sub

TestMatrixCalculateMatrixBadUnkIter:
msg$ = "WARNING in TestMatrixCalculateMatrix- Bad unknown beta factor for element" & Str$(mElement%(chanIn)) & " " & Str$(mXrayn%(chanIn))
MsgBox msg$, vbOKOnly + vbExclamation, "TestMatrixCalculateMatrix"
iserr = True
Exit Sub

TestMatrixCalculateMatrixBadTotal:
msg$ = "WARNING in TestMatrixCalculateMatrix- InsufficientTotal"
MsgBox msg$, vbOKOnly + vbExclamation, "TestMatrixCalculateMatrix"
iserr = True
Exit Sub

TestMatrixCalculateMatrixBadStdPercent:
msg$ = "InsuffLow standard percents for element" & Str$(mElement%(chanIn)) & " " & Str$(mXrayn%(chanIn))
MsgBox msg$, vbOKOnly + vbExclamation, "TestMatrixCalculateMatrix"
iserr = True
Exit Sub

TestMatrixCalculateMatrixBadStdCounts:
msg$ = "InsuffLow standard counts for element" & Str$(mElement%(chanIn)) & " " & Str$(mXrayn%(chanIn))
MsgBox msg$, vbOKOnly + vbExclamation, "TestMatrixCalculateMatrix"
iserr = True
Exit Sub

TestMatrixCalculateMatrixBadStdIterac:
msg$ = "Bad standard beta factor for element" & Str$(mElement%(chanIn)) & " " & Str$(mXrayn%(chanIn))
MsgBox msg$, vbOKOnly + vbExclamation, "TestMatrixCalculateMatrix"
iserr = True
Exit Sub

End Sub
```

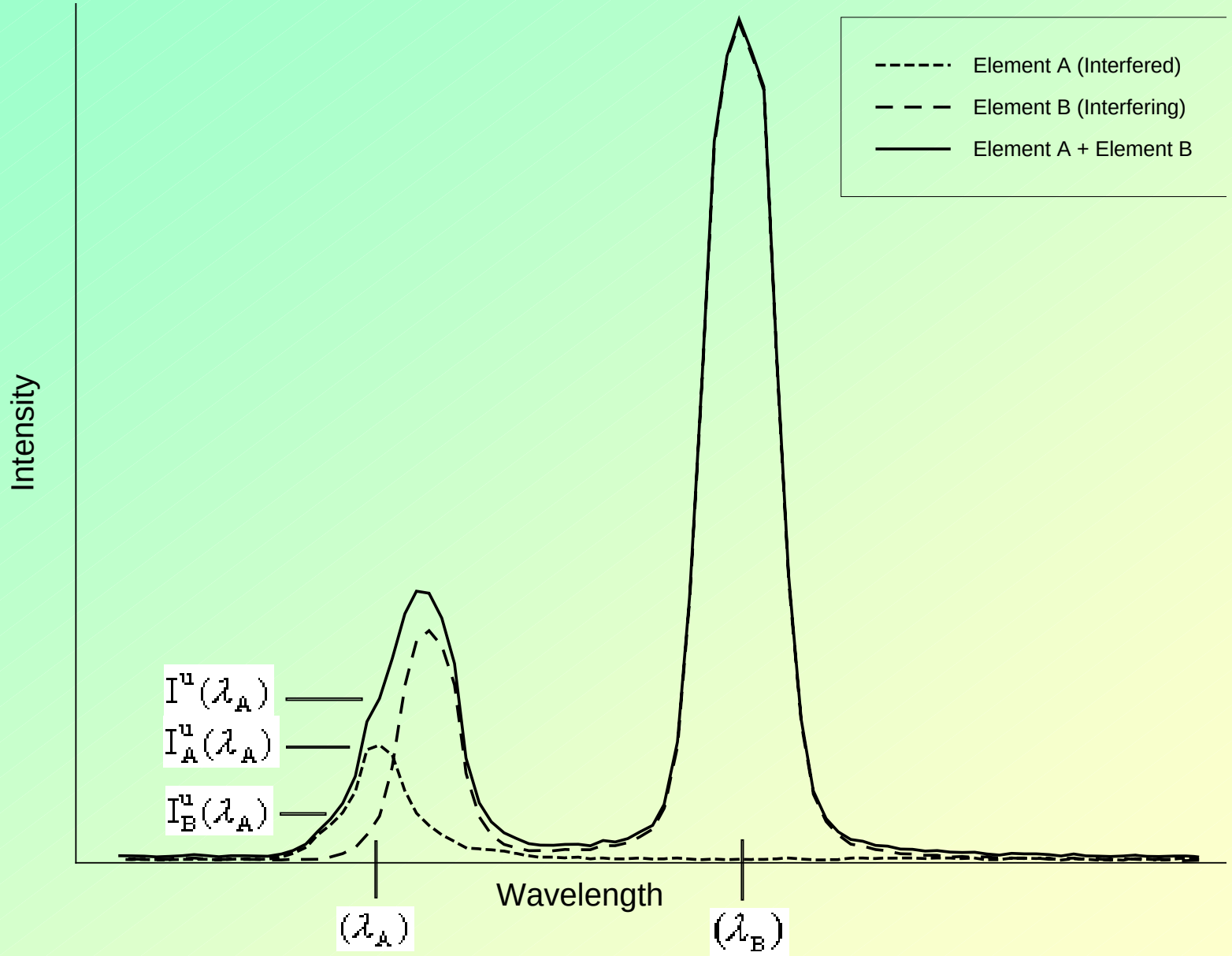
```
Sub TestMatrixCalculateBetaFactors(mLastElmts As Long, mLastChan As Long, mAlpha1() As Double, mAlpha2() As Double, mAlpha3() As Double, mUnkPercent() As Double, mUnkBeta() As Double, mTotal As Double)
' This routine accepts an array of weight percents and alpha factors and returns an array of beta factors

iserr = False
On Error GoTo TestMatrixCalculateBetaFactorsErr:

Dim i As Long
Dim emitter As Long, absorber As Long
Dim betaReaction As Double

ReDim wtfractions(1 To mLastChan&) As Double

' Convert to weight fractions
If mTotal# = 0# Then GoTo TestMatrixCalculateBetaFactorsBadTotal
For ilk = 1 To mLastChan&
wtfractions#(ilk) = mUnkPercent#(ilk) / mTotal#
Next ilk

' Calculate beta factors for "mLastElmt" emitters and "mLastChan" absorbers
For emitterIk = 1 To mLastElmts
mUnkBeta#(emitterIk) = 0#

For absorberIk = 1 To mLastChan&
betaFraction# = (mAlpha1#(emitterIk, absorberIk) + wtfractions#(absorberIk) * mAlpha2#(emitterIk, absorberIk) + wtfractions#(absorberIk) ^ 2 * mAlpha3#(emitterIk, absorberIk)) * wtfractions#(absorberIk)

' Sum beta factors fractions
mUnkBeta#(emitterIk) = mUnkBeta#(emitterIk) + betaFraction#

Next absorberIk
Next emitterIk

Exit Sub

' Errors
TestMatrixCalculateBetaFactorsErr:
MsgBox Error$, vbOKOnly + vbCritical, "TestMatrixCalculateBetaFactors"
iserr = True
Exit Sub

TestMatrixCalculateBetaFactorsBadTotal:
msg$ = "Total percent equals zero, cannot calculate beta factors"
MsgBox msg$, vbOKOnly + vbExclamation, "TestMatrixCalculateBetaFactors"
iserr = True
Exit Sub

End Sub
```



# Other Compositionally Dependent Corrections

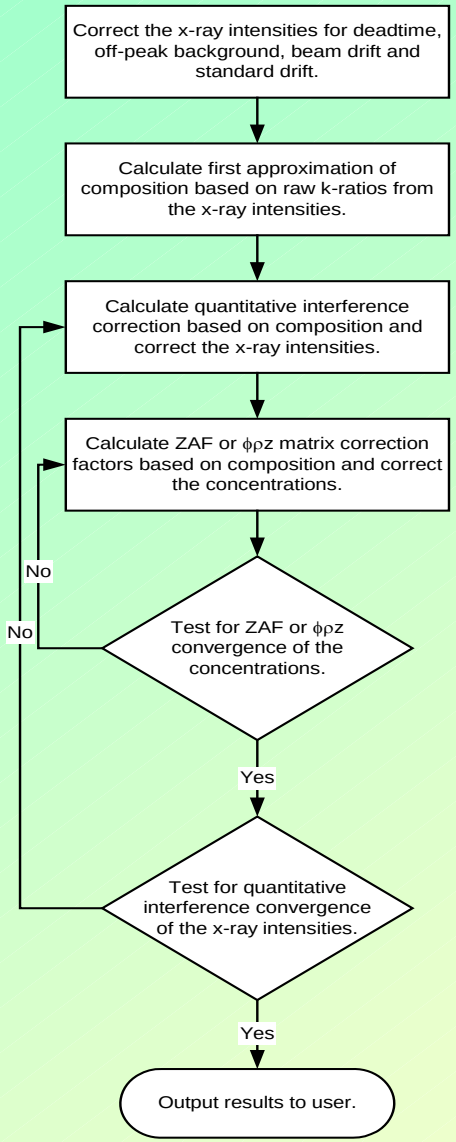
- Mean Atomic Number (MAN) Based Backgrounds
- Quantitative Spectral Interference Calculations
- Volatile Intensity Corrections
- Water by Difference (specified element effects)
- Compound Area-Peak Factor (APF) Calculations
- Blank (Zero) Value Corrections for Trace Elements

# Spectral Interferences



# Matrix Iteration

Flow Diagram of the Quantitative Iterated Interference Correction




Eq. 1

$$I_B^u(\lambda_A) \approx \frac{I_B^{\bar{s}}(\lambda_A)}{C_B^{\bar{s}}} \frac{I_B^u(\lambda_B)}{I_B^s(\lambda_B)} C_B^s$$

Gilfrich, *et al*., 1978

Eq. 2

$$I_B^U(\lambda_A) = \frac{[ZAF]_{\lambda_A}^{\bar{s}}}{C_B^{\bar{s}}} \frac{C_B^u}{[ZAF]_{\lambda_A}^u} I_B^{\bar{s}}(\lambda_A)$$

Donovan, Rivers and Snyder, 1993

$$C_A^u = \frac{C_A^s}{[ZAF]_{\lambda_A}^s} [ZAF]_{\lambda_A}^u \frac{I^u(\lambda_A) - \frac{[ZAF]_{\lambda_A}^{\bar{s}}}{C_B^{\bar{s}}} \frac{C_B^u}{[ZAF]_{\lambda_A}^u} I_B^{\bar{s}}(\lambda_A)}{I_A^s(\lambda_A)}$$

# Differences Between Eq. 1 and Eq. 2

## *Self-Interfering Analyses*

| | wt. % (nominal) | wt. % (uncorrected) | wt. % (Eq. 1) | wt. % (Eq. 2) |
|---|---|---|---|---|
| Ba Lα ↔ Ti Kα (PET) | Ba 33.15 [3]<br>Ti 11.69 | 33.26 ± 0.18<br>11.71 ± 0.08 | 33.08<br>11.59 | 33.08 ± 0.18<br>11.59 ± 0.08 |
| Pb Lα ↔ As Kα | Pb 59.69 [4]<br>As 21.58 | 106.20 ± 0.33<br>41.38 ± 0.27 | 19.64<br>6.60 | 61.25 ± 1.97<br>22.15 ± 1.04 |

[3] Benitoite ($BaTiSi_3O_9$) is assumed stoichiometric : Si 20.38, Ba 33.15, Ti 11.69, O 34.896

[4] Shultenite ($HAsPbO_4$) is assumed stoichiometric : Pb 59.69, As 21.58, O 18.44. The oxygen concentration was measured at 19.8 wt. % and included in the matrix correction calculations.

| | Pb Lα (cps) | As Kα (cps) | S Kα (cps) |
|---|---|---|---|
| PbS | 1473.3 ± 11.5 | 1213.0 ± 3.8 | 1453.3 ± 9.3 |
| GaAs | 1624.7 ± 29.9 | 1771.7 ± 8.2 | 2.5 ± 1.2 |
| FeS | 14.0 ± 3.3 | 13.9 ± 3.7 | 4986.9 ± 26.3 |

## *Cascade Interference Analyses*

| | wt. % (nominal) | wt. % (uncorrected) | wt. % (Eq. 1) | wt. % (Eq. 2) |
|---|---|---|---|---|
| Ni K → Fe Kα<br>Fe Kβ → Co Kα | Co 0.022 [1] | 0.089 ± 0.008 | 0.010 | 0.022 ± 0.008 |
| Ti Kβ → V Kα<br>V Kβ → Cr Kα | Cr 0.025 [2] | 0.268 ± 0.01 | -0.020 | 0.021 ± 0.010 |

[1] SRM 1159 includes : Ni 48.2, Fe 51.0, C 0.007, Mn 0.30, P 0.003, S 0.003, Si 0.32, Cu 0.038, Cr 0.06, Mo 0.01

[2] SRM 654b includes : Ti 88.974, Al 6.34, V 4.31, Fe 0.23, Si 0.045, Ni 0.028, Sn 0.023, Cu 0.004, Mo 0.013, Zr 0.008

# Pathological Interferences

**Re la  1.43298**
**Zn ka  1.43652**

“Self-Interferring”

```
Un   10 Zn-ReSCN gr2
TakeOff = 40  KiloVolts = 20  Beam Current = 20  Beam Size = 0

Results in Elemental Weight Percents
SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC

AVER:    1.900   5.000   4.200    .200
SDEV:     .000    .000    .000    .000

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
    53    .000    .000  19.463  74.142  17.309    .000 122.214
    55    .000    .007  20.459  74.986  16.357    .000 123.108
    56    .000    .019  19.578  75.195  17.997    .000 124.089

AVER:     .000    .009  19.833  74.774  17.221    .000 123.137
SDEV:     .000    .010    .545    .558    .824    .000
SERR:     .000    .006    .314    .322    .476    .000
%RSD:       .1  113.3     2.7      .7     4.8      .1
STDS:       834     730     660     575     730     660

Results Based on 6 Atoms of re
SPEC:        O       N       C       H
TYPE:     SPEC    SPEC    SPEC    SPEC

AVER:    1.774   5.334   5.225   2.965
SDEV:     .013    .040    .039    .022

ELEM:       Cs      Fe      Zn      Re       S      Se   SUM
    53    .000    .000   4.486   6.000   8.134    .000  34.048
    55    .000    .002   4.663   6.000   7.600    .000  33.518
    56    .000    .005   4.450   6.000   8.339    .000  34.005

AVER:     .000    .002   4.533   6.000   8.025    .000  33.857
SDEV:     .000    .003    .114    .000    .382    .000
SERR:     .000    .001    .066    .000    .220    .000
%RSD:       .8  113.2     2.5      .0     4.8      .8
```

# With Iterated Interference Correction

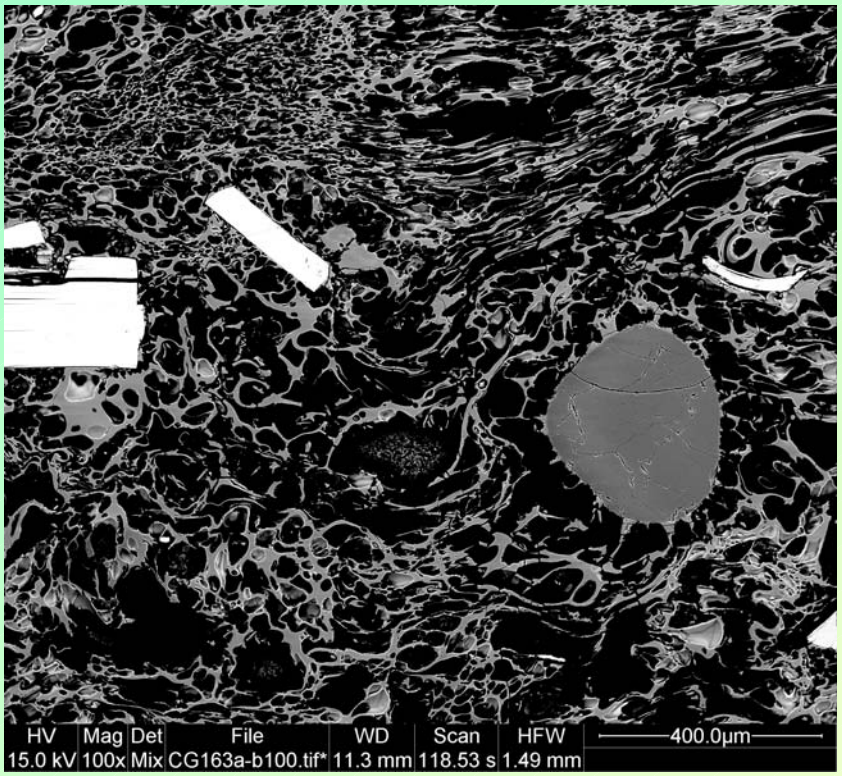
```
Un   10 Zn-ReSCN gr2
TakeOff = 40  KiloVolts = 20  Beam Current = 20  Beam Size = 0

Results in Elemental Weight Percents
SPEC:         O       N       C       H
TYPE:      SPEC    SPEC    SPEC    SPEC

AVER:     1.900   5.000   4.200    .200
SDEV:      .000    .000    .000    .000

ELEM:        Cs      Fe      Zn      Re       S      Se   SUM
    53     .000    .000   6.325  65.726  17.333    .000 100.683
    55     .000    .007   7.471  65.113  16.343    .000 100.233
    56     .000    .019   6.188  66.949  18.029    .000 102.486

AVER:      .000    .009   6.661  65.929  17.235    .000 101.134
SDEV:      .000    .010    .704    .935    .848    .000
SERR:      .000    .006    .407    .540    .489    .000
%RSD:        .1   113.3    10.6     1.4     4.9      .0
STDS:       834     730     660     575     730     660

Results Based on 6 Atoms of re
SPEC:         O       N       C       H
TYPE:      SPEC    SPEC    SPEC    SPEC

AVER:     2.013   6.050   5.926   3.363
SDEV:      .028    .085    .084    .047

ELEM:        Cs      Fe      Zn      Re       S      Se   SUM
    53     .000    .000   1.645   6.000   9.189    .000  34.236
    55     .000    .002   1.961   6.000   8.745    .000  34.274
    56     .000    .006   1.580   6.000   9.383    .000  34.053

AVER:      .000    .003   1.728   6.000   9.106    .000  34.188
SDEV:      .000    .003    .204    .000    .327    .000
SERR:      .000    .002    .118    .000    .189    .000
%RSD:       1.3   112.3    11.8      .0     3.6     1.4
```

6 rhenium to 9 sulfur

# Large magnitude “Self-Interferences”

| Interfering Pair | Wavelength Region (Å) | Approximate Overlap (% @ 50/50) |
|---|---|---|
| Ba Lα ↔ Ti Kα | 2.7 | 0.8 - 0.2 |
| Pb Lα ↔ As Kα | 1.17 | 150 - 65 |
| | | |
| Hg Lα ↔ Ge Kα | 1.25 | 120 - 15 |
| Ir Lα ↔ Ga Kα | 1.34 | 70 - 30 |
| Re Lα ↔ Zn Kα | 1.43 | 140 - 60 |
| Er Lα ↔ Co Kα | 1.78 | 110 - 50 |
| Eu Lα ↔ Mn Kα | 2.1 | 15 - 5 |
| In Lα ↔ K Kα | 3.74 | 50 - 20 |
| Th Mα ↔ Ag Lα | 4.13 | 30 - 60 |
| Bi Mα ↔ Tc Lα | 5.1 | 50 - 70 |
| Mo Lα ↔ S Kα | 5.4 | 30 - 15 |

# Volatile Element Corrections



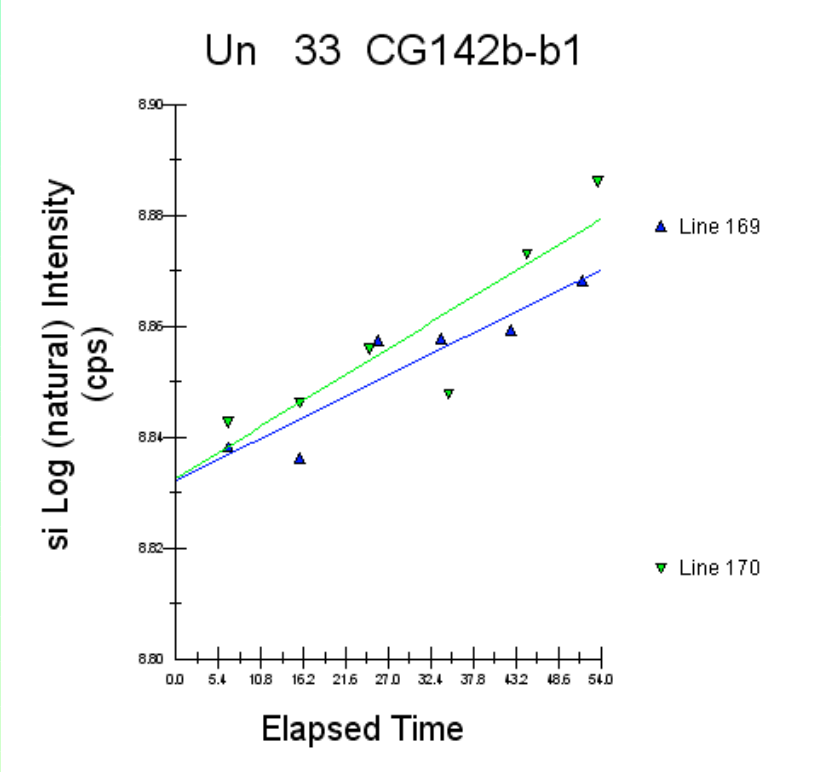

**Results in Oxide Weight Percents (12 keV, 20nA, focussed beam)**

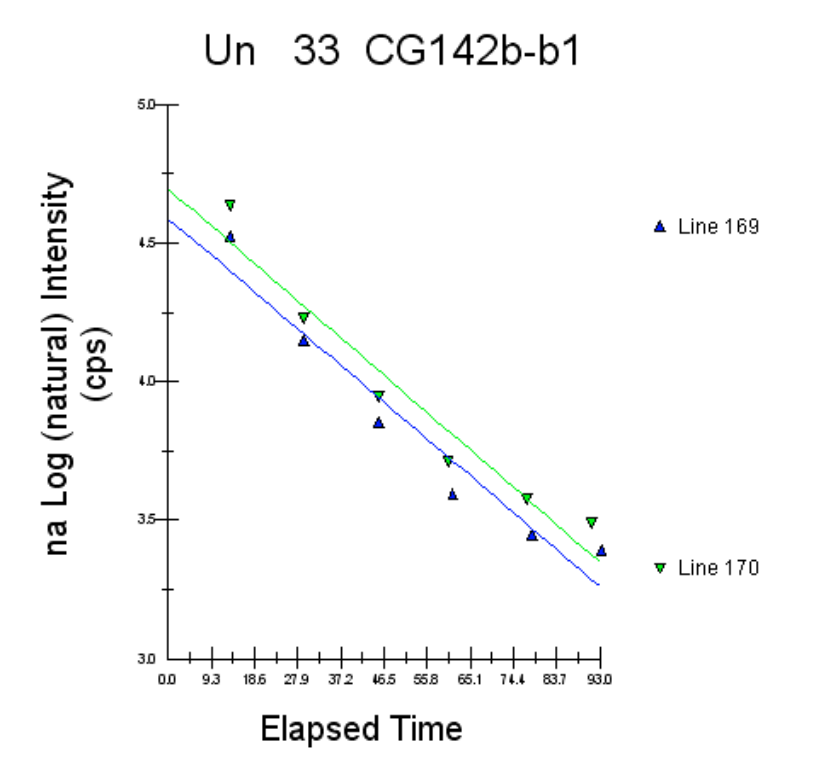
| ELEM: | Na2O | SiO2 | Al2O3 | MgO | TiO2 | MnO | P2O5 | Cl | FeO | K2O | CaO | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 169 | .541 | 74.315 | 12.294 | .065 | .080 | .052 | .007 | .174 | .492 | 2.708 | .824 | -.039 | 8.487 | 100.000 |
| 170 | .609 | 74.611 | 12.016 | .069 | .143 | .032 | -.009 | .173 | .512 | 2.834 | .869 | -.039 | 8.181 | 100.000 |
| AVER: | .575 | 74.463 | 12.155 | .067 | .112 | .042 | -.001 | .174 | .502 | 2.771 | .847 | -.039 | 8.334 | 100.000 |
| SDEV: | .048 | .209 | .197 | .003 | .045 | .014 | .011 | .001 | .014 | .089 | .032 | .000 | .216 | |
| SERR: | .034 | .148 | .139 | .002 | .032 | .010 | .008 | .001 | .010 | .063 | .023 | .000 | .153 | |
| %RSD: | 8.3 | .3 | 1.6 | 4.0 | 40.4 | 33.9 | -805.7 | .4 | 2.8 | 3.2 | 3.8 | -.4 | 2.6 | |

# Correcting for Intensity Loss (and Gain)

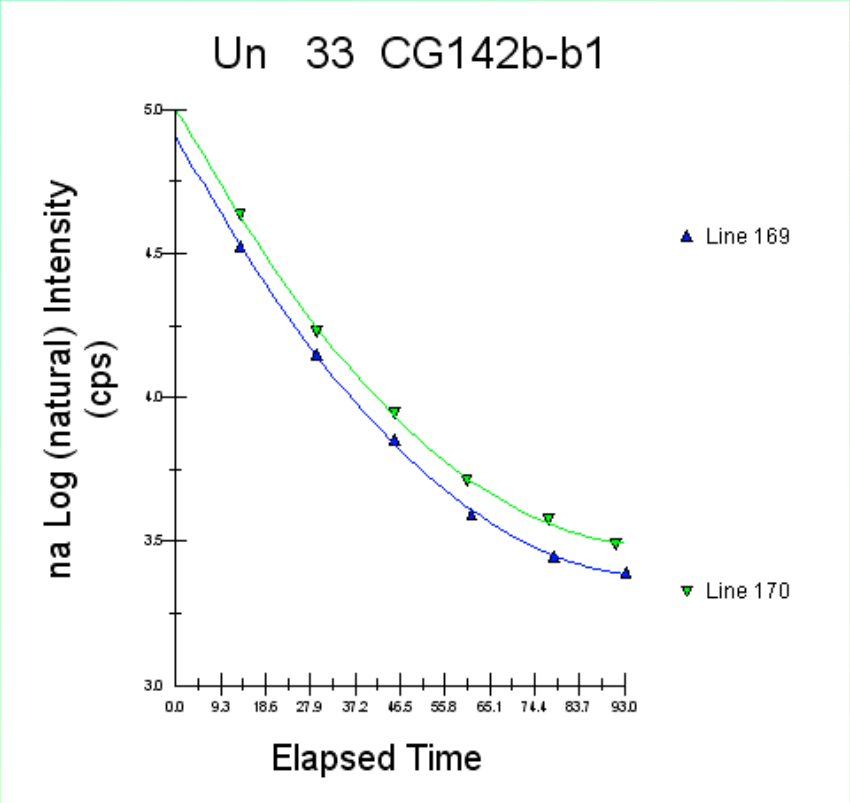
Results in Oxide Weight Percents

| ELEM: | Na2O | SiO2 | Al2O3 | MgO | TiO2 | MnO | P2O5 | Cl | FeO | K2O | CaO | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 169 | 1.140 | 72.895 | 12.112 | .065 | .080 | .052 | .007 | .174 | .502 | 4.323 | .823 | -.039 | 7.867 | 100.000 |
| 170 | 1.267 | 72.815 | 11.824 | .069 | .143 | .032 | -.009 | .172 | .512 | 4.536 | .869 | -.039 | 7.809 | 100.000 |
| AVER: | 1.204 | 72.855 | 11.968 | .067 | .112 | .042 | -.001 | .173 | .507 | 4.429 | .846 | -.039 | 7.838 | 100.000 |
| SDEV: | .090 | .056 | .204 | .003 | .045 | .014 | .011 | .001 | .007 | .150 | .032 | .000 | .041 | |
| SERR: | .064 | .040 | .144 | .002 | .032 | .010 | .008 | .001 | .005 | .106 | .023 | .000 | .029 | |
| %RSD: | 7.5 | .1 | 1.7 | 4.2 | 40.4 | 33.9 | -806.3 | .4 | 1.3 | 3.4 | 3.8 | -.4 | .5 | |
| VOL%: | 96.461 | -2.091 | -1.673 | ---- | ---- | ---- | ---- | ---- | 1.218 | 60.289 | ---- | ---- | ---- | |
| DEV%: | 18.1 | .6 | .8 | ---- | ---- | ---- | ---- | ---- | 5.0 | 6.1 | ---- | ---- | ---- | |
| VOLF: | LINEAR | LINEAR | LINEAR | ---- | ---- | ---- | ---- | ---- | LINEAR | LINEAR | ---- | ---- | ---- | |



# Hyper-exponential Loss




Results in Oxide Weight Percents

| ELEM: | Na2O | SiO2 | Al2O3 | MgO | TiO2 | MnO | P2O5 | Cl | FeO | K2O | CaO | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 169 | 1.790 | 72.897 | 12.121 | .065 | .080 | .052 | .007 | .173 | .501 | 4.318 | .823 | -.039 | 7.213 | 100.000 |
| 170 | 1.969 | 72.817 | 11.833 | .069 | .143 | .032 | -.009 | .172 | .511 | 4.530 | .868 | -.039 | 7.103 | 100.000 |
| AVER: | 1.879 | 72.857 | 11.977 | .067 | .111 | .042 | -.001 | .173 | .506 | 4.424 | .845 | -.039 | 7.158 | 100.000 |
| SDEV: | .127 | .056 | .203 | .003 | .045 | .014 | .011 | .001 | .007 | .150 | .032 | .000 | .078 | |
| SERR: | .090 | .040 | .144 | .002 | .032 | .010 | .008 | .001 | .005 | .106 | .023 | .000 | .055 | |
| %RSD: | 6.7 | .1 | 1.7 | 4.2 | 40.4 | 33.9 | -806.4 | .4 | 1.3 | 3.4 | 3.8 | -.4 | 1.1 | |
| VOL%: | 201.072 | -2.091 | -1.673 | ---- | ---- | ---- | ---- | ---- | 1.218 | 60.289 | ---- | ---- | ---- | |
| DEV%: | 4.0 | .6 | .8 | ---- | ---- | ---- | ---- | ---- | 5.0 | 6.1 | ---- | ---- | ---- | |
| VOLF: | QUADRA | LINEAR | LINEAR | ---- | ---- | ---- | ---- | ---- | LINEAR | LINEAR | ---- | ---- | ---- | |

# Can We Test This Extrapolation?

**Results in Oxide Weight Percents (20 nA)**

| ELEM: | Na2O | SiO2 | Al2O3 | MgO | TiO2 | MnO | P2O5 | Cl | FeO | K2O | CaO | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AVER: | 2.369 | 68.336 | 15.543 | 1.095 | .444 | .041 | .069 | .058 | 2.083 | 4.588 | 2.037 | -.013 | .000 | 96.651 |
| VOL%: | 204.518 | -1.701 | -1.373 | ---- | ---- | ---- | ---- | ---- | -5.860 | 59.030 | ---- | ---- | ---- | |
| DEV%: | 5.2 | .6 | 1.0 | ---- | ---- | ---- | ---- | ---- | 4.0 | 5.9 | ---- | ---- | ---- | |

**Results in Oxide Weight Percents (15 nA)**

| ELEM: | Na2O | SiO2 | Al2O3 | MgO | TiO2 | MnO | P2O5 | Cl | FeO | K2O | CaO | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AVER: | 2.313 | 67.383 | 15.537 | 1.263 | .468 | .018 | .103 | .068 | 2.449 | 4.608 | 2.137 | -.015 | .000 | 96.332 |
| VOL%: | 161.641 | -1.461 | -1.222 | ---- | ---- | ---- | ---- | ---- | -.434 | 49.134 | ---- | ---- | ---- | |
| DEV%: | 4.5 | .4 | .7 | ---- | ---- | ---- | ---- | ---- | 2.8 | 4.5 | ---- | ---- | ---- | |

**Results in Oxide Weight Percents (10 nA)**

| ELEM: | Na2O | SiO2 | Al2O3 | MgO | TiO2 | MnO | P2O5 | Cl | FeO | K2O | CaO | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AVER: | 2.443 | 66.558 | 15.314 | 1.129 | .533 | .031 | .109 | .065 | 2.401 | 4.822 | 2.058 | -.015 | .000 | 95.448 |
| VOL%: | 134.049 | -1.407 | -1.495 | ---- | ---- | ---- | ---- | ---- | -.343 | 36.614 | ---- | ---- | ---- | |
| DEV%: | 3.2 | .6 | .9 | ---- | ---- | ---- | ---- | ---- | 4.5 | 3.2 | ---- | ---- | ---- | |

**Results in Oxide Weight Percents (5 nA)**

| ELEM: | Na2O | SiO2 | Al2O3 | MgO | TiO2 | MnO | P2O5 | Cl | FeO | K2O | CaO | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AVER: | 2.289 | 65.294 | 14.953 | 1.176 | .416 | .055 | .093 | .059 | 2.263 | 5.022 | 2.094 | -.013 | .000 | 93.699 |
| VOL%: | 68.999 | -.940 | -.311 | ---- | ---- | ---- | ---- | ---- | -3.779 | 18.498 | ---- | ---- | ---- | |
| DEV%: | 3.2 | .8 | 1.4 | ---- | ---- | ---- | ---- | ---- | 4.9 | 3.0 | ---- | ---- | ---- | |

**Results in Oxide Weight Percents (20nA, 10um beam size)**

| ELEM: | Na2O | SiO2 | Al2O3 | MgO | TiO2 | MnO | P2O5 | Cl | FeO | K2O | CaO | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AVER: | 2.906 | 66.987 | 15.299 | 1.149 | .457 | .069 | .108 | .069 | 2.380 | 5.114 | 2.159 | -.016 | .000 | 96.681 |
| VOL%: | 74.262 | -.309 | -1.059 | ---- | ---- | ---- | ---- | ---- | .089 | 7.884 | ---- | ---- | ---- | |
| DEV%: | 1.9 | .5 | .5 | ---- | ---- | ---- | ---- | ---- | 2.2 | 1.7 | ---- | ---- | ---- | |

# Matrix Effects from “missing” elements

## No Volatile Correction, No Water By Difference

Results in Oxide Weight Percents

| ELEM: | CaO | K2O | FeO | SiO2 | MgO | Na2O | Al2O3 | TiO2 | P2O5 | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 58 | .411 | 4.900 | .537 | 74.603 | .036 | 2.644 | 11.975 | .073 | .000 | .000 | .000 | 95.180 |
| 59 | .437 | 4.624 | .612 | 75.386 | .033 | 1.841 | 12.024 | .113 | .000 | .000 | .000 | 95.070 |
| 60 | .423 | 4.998 | .526 | 74.715 | .023 | 2.765 | 12.113 | .065 | .000 | .000 | .000 | 95.628 |
| 61 | .423 | 4.853 | .637 | 75.000 | .047 | 2.137 | 12.089 | .055 | .000 | .000 | .000 | 95.240 |
| 62 | .435 | 4.847 | .677 | 74.613 | .048 | 2.561 | 12.089 | .036 | .011 | .000 | .000 | 95.317 |
| *AVER:* | *.426* | *4.844* | *.598* | *74.863* | *.037* | *2.390* | *12.058* | *.068* | *.002* | *.000* | *.000* | *95.287* |
| SDEV: | .011 | .137 | .065 | .333 | .010 | .387 | .057 | .028 | .005 | .000 | .000 | |
| %RSD: | 2.5 | 2.8 | 10.8 | .4 | 27.9 | 16.2 | .5 | 41.5 | 223.6 | 418.3 | .0 | |
| ZCOR: | 1.1202 | 1.1536 | 1.1987 | 1.2061 | 1.4303 | 1.8227 | 1.2568 | 1.1983 | 1.4641 | .0000 | .0000 | |
| KRAW: | .0161 | .3080 | .0057 | 1.0344 | .0003 | .1323 | .7242 | .0006 | -.0004 | .0000 | .0000 | |
| PKBG: | 4.96 | 59.36 | 4.84 | 370.59 | 1.42 | 30.93 | 77.40 | 1.46 | .87 | .00 | .00 | |

## Excel Spreadsheet Subtraction Gives ~ 4.7% H2O

# Volatile Correction Matrix Effects

## With Volatile Correction, No Water By Difference

Results in Oxide Weight Percents

| ELEM: | CaO | K2O | FeO | SiO2 | MgO | Na2O | Al2O3 | TiO2 | P2O5 | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 58 | .411 | 4.867 | .537 | 74.378 | .037 | 3.626 | 12.035 | .030 | .000 | .000 | .000 | 95.921 |
| 59 | .437 | 4.740 | .612 | 75.016 | .034 | 2.426 | 12.063 | .194 | .000 | .000 | .000 | 95.521 |
| 60 | .423 | 4.933 | .526 | 74.057 | .024 | 3.805 | 12.178 | .076 | .000 | .000 | .000 | 96.022 |
| 61 | .423 | 5.220 | .636 | 74.552 | .048 | 3.025 | 12.147 | .077 | .000 | .000 | .000 | 96.128 |
| 62 | .435 | 4.715 | .677 | 74.794 | .049 | 3.503 | 12.146 | .048 | .011 | .000 | .000 | 96.378 |
| *AVER:* | *.426* | *4.895* | *.598* | *74.559* | *.038* | *3.277* | *12.114* | *.085* | *.002* | *.000* | *.000* | *95.994* |
| SDEV: | .011 | .203 | .065 | .379 | .010 | .557 | .062 | .064 | .005 | .000 | .000 | |
| %RSD: | 2.5 | 4.1 | 10.8 | .5 | 27.3 | 17.0 | .5 | 75.6 | 223.6 | .0 | .0 | |
| ZCOR: | 1.1198 | 1.1530 | 1.1983 | 1.2092 | 1.4391 | 1.8180 | 1.2625 | 1.1979 | 1.4627 | .0000 | .0000 | |
| KRAW: | .0161 | .3114 | .0057 | 1.0276 | .0003 | .1819 | .7242 | .0008 | -.0004 | .0000 | .0000 | |
| PKBG: | 4.97 | 60.00 | 4.84 | 369.28 | 1.43 | 42.09 | 77.77 | 1.58 | .87 | .00 | .00 | |
| *VOL%:* | *.000* | *1.135* | *.000* | *-.658* | *.000* | *36.111* | *.000* | *20.283* | *.000* | *.000* | *.000* | |
| DEV%: | .0 | .2 | .0 | .0 | .0 | .4 | .0 | 20.3 | .0 | .0 | .0 | |

## Na, Si, K Intensity Over Time Iteration Gives ~ 4% H2O

# Water By Difference Matrix Effects

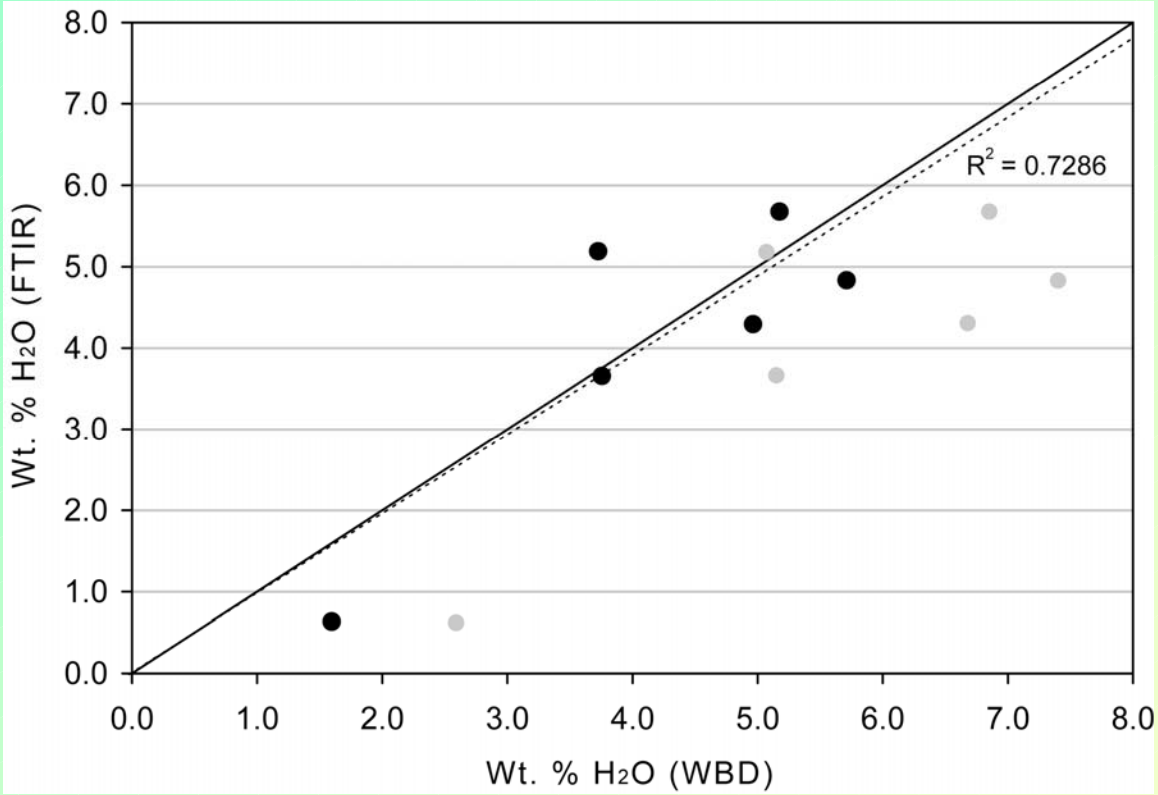
## With Volatile Correction, Water By Difference

Results in Oxide Weight Percents

| ELEM: | CaO | K2O | FeO | SiO2 | MgO | Na2O | Al2O3 | TiO2 | P2O5 | O | H2O | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 58 | .414 | 4.885 | .542 | 74.776 | .039 | 3.668 | 12.139 | .030 | .000 | .000 | 3.506 | 100.000 |
| 59 | .441 | 4.759 | .618 | 75.464 | .036 | 2.457 | 12.181 | .195 | .000 | .000 | 3.849 | 100.000 |
| 60 | .426 | 4.951 | .531 | 74.441 | .026 | 3.848 | 12.281 | .076 | .000 | .000 | 3.420 | 100.000 |
| 61 | .426 | 5.239 | .641 | 74.934 | .050 | 3.058 | 12.249 | .077 | .000 | .000 | 3.327 | 100.000 |
| 62 | .438 | 4.730 | .682 | 75.149 | .051 | 3.539 | 12.240 | .048 | .011 | .000 | 3.112 | 100.000 |
| *AVER:* | *.429* | *4.913* | *.603* | *74.953* | *.041* | *3.314* | *12.218* | *.085* | *.002* | *.000* | *3.443* | *100.000* |
| SDEV: | .011 | .203 | .065 | .385 | .010 | .562 | .057 | .065 | .005 | .000 | .270 | |
| %RSD: | 2.5 | 4.1 | 10.8 | .5 | 25.7 | 16.9 | .5 | 75.6 | 223.6 | -104.6 | 7.9 | |
| ZCOR: | 1.1241 | 1.1571 | 1.2053 | 1.2156 | 1.4515 | 1.8372 | 1.2731 | 1.2037 | 1.4591 | .0000 | .0000 | |
| KRAW: | .0161 | .3114 | .0057 | 1.0276 | .0004 | .1821 | .7244 | .0008 | -.0004 | .0000 | .0000 | |
| PKBG: | 5.03 | 60.00 | 4.89 | 372.20 | 1.46 | 43.35 | 78.99 | 1.58 | .87 | .00 | .00 | |
| VOL%: | .000 | 1.135 | .000 | -.658 | .000 | 36.111 | .000 | 20.283 | .000 | .000 | .000 | |
| DEV%: | .0 | .2 | .0 | .0 | .0 | .4 | .0 | 20.3 | .0 | .0 | .0 | |

Both Na, Si, K Change and Water By Difference Gives 3.4% H2O

# Water By Difference vs. FTIR




Comparison of melt inclusion water contents measured by FTIR in sub-micron melt inclusion water contents estimated as the difference between 100% and microprobe analysis totals or “water by difference” (WBD).

Solid diagonal line indicates 1:1 correspondence, dashed line is a linear regression fixed at the origin. Gray symbols show WBD water content before matrix correction of the analysis and black symbols show matrix-corrected WBD estimates.

From Roman, 2003

# Compound Area Peak Factors

**TakeOff = 40.0  KiloVolt = 12.0  Beam Current = 50.0  Beam Size =  0**

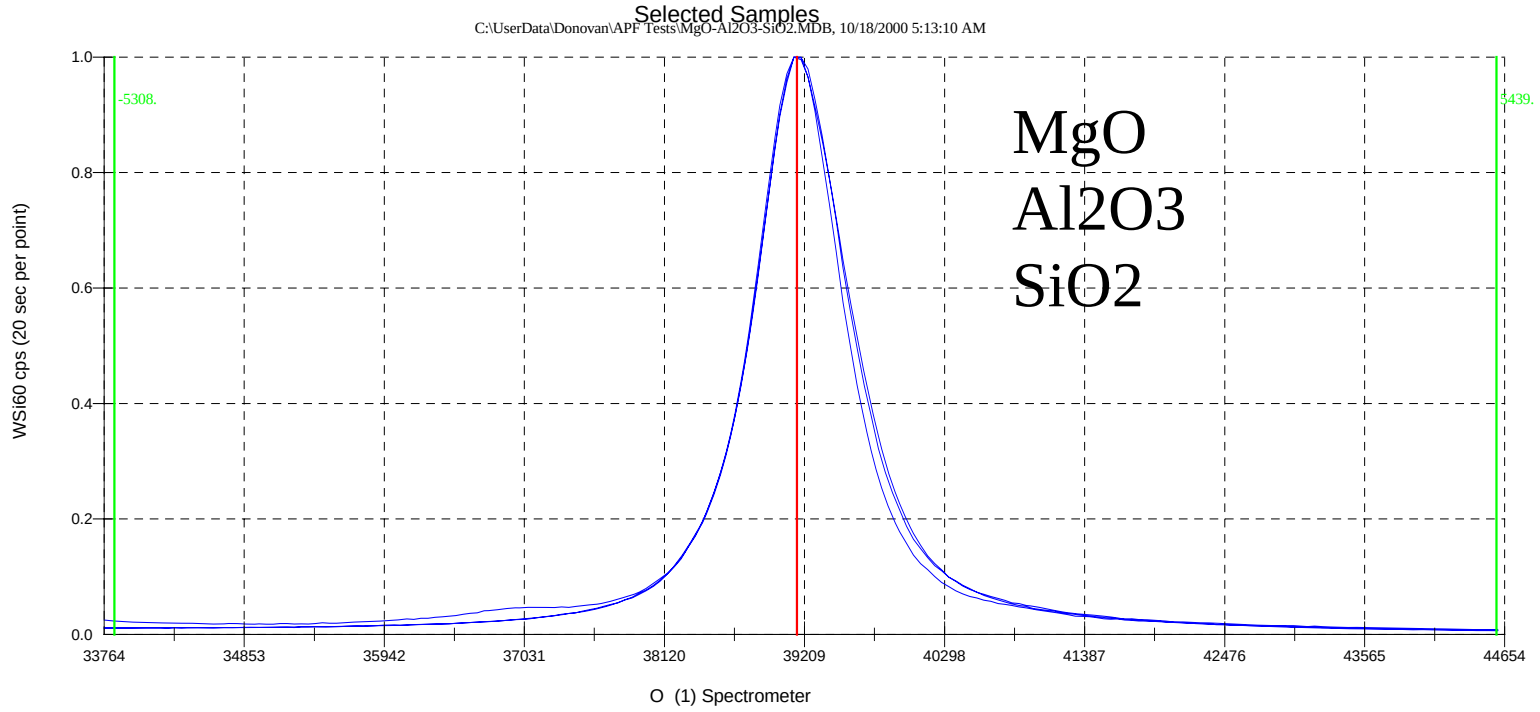
**Results in Oxide Weight Percents**
**SPEC: H2O**
**TYPE: SPEC**

**AVER: .000**
**SDEV: .000**

| ELEM: | SiO2 | MgO | TiO2 | MnO | FeO | Cr2O3 | Al2O3 | O | CaO | SUM |
|---|---|---|---|---|---|---|---|---|---|---|
| 283 | .084 | 2.657 | 6.561 | .926 | 80.498 | .390 | 3.426 | 4.990 | .028 | 99.559 |
| 284 | .088 | 2.660 | 6.633 | .898 | 80.480 | .247 | 3.421 | 5.041 | .033 | 99.501 |
| 285 | .108 | 2.649 | 6.617 | .894 | 80.359 | .189 | 3.392 | 5.003 | .035 | 99.246 |
| 286 | | | | | | | | | | |
| 287 | | | | | | | | | | |
| 288 | | | | | | | | | | |

**AVER:**
**SDEV:**
**SERR:**
**%RSD:**

**INT%:**
**APF:**



# Binary APFs from Bastin

***Oxygen Area Peak Factors (APF)***

**Relative to $Fe_2O_3$ or MgO using W/Si LDE (2d = 59.8)**

| Oxide | Area-Peak Factor (APF) |
|---|---|
| $B_6O$ | 1.0628 |
| MgO | 1.0000 |
| $Al_2O_3$ | 1.0213 |
| $SiO_2$ | 1.0444 |
| $TiO_2$ | 0.9796 |
| $Cr_2O_3$ | 0.9930 |
| $Mn_3O_4$ | 1.0121 |
| $Fe_3O_4$ | 0.9962 |
| CoO | 1.0133 |
| NiO | 1.0153 |
| $Cu_2O$ | 0.9946 |
| CuO | 0.9943 |
| ZnO | 0.9837 |
| $Ga_2O_3$ | 1.0000 |
| $Y_3Fe_5O_{12}$ | 0.9823 |

Bastin, G.F. and Heijligers, H.J.M (1991) Quantitative electron probe microanalysis of ultra-light elements (boron - oxygen), in Electron Probe Quantitation, ed K.F.J. Heinrich and D.E. Newbury, Plenum Press, NY, 145-161

Need to measure these on your own instrument, but any correction (in the right direction) is better than no correction!

# APF Calculations

Binary APF of element i in j

$$APF = \frac{I_U^I}{I_U^P} \cdot \frac{I_S^P}{I_S^I}$$

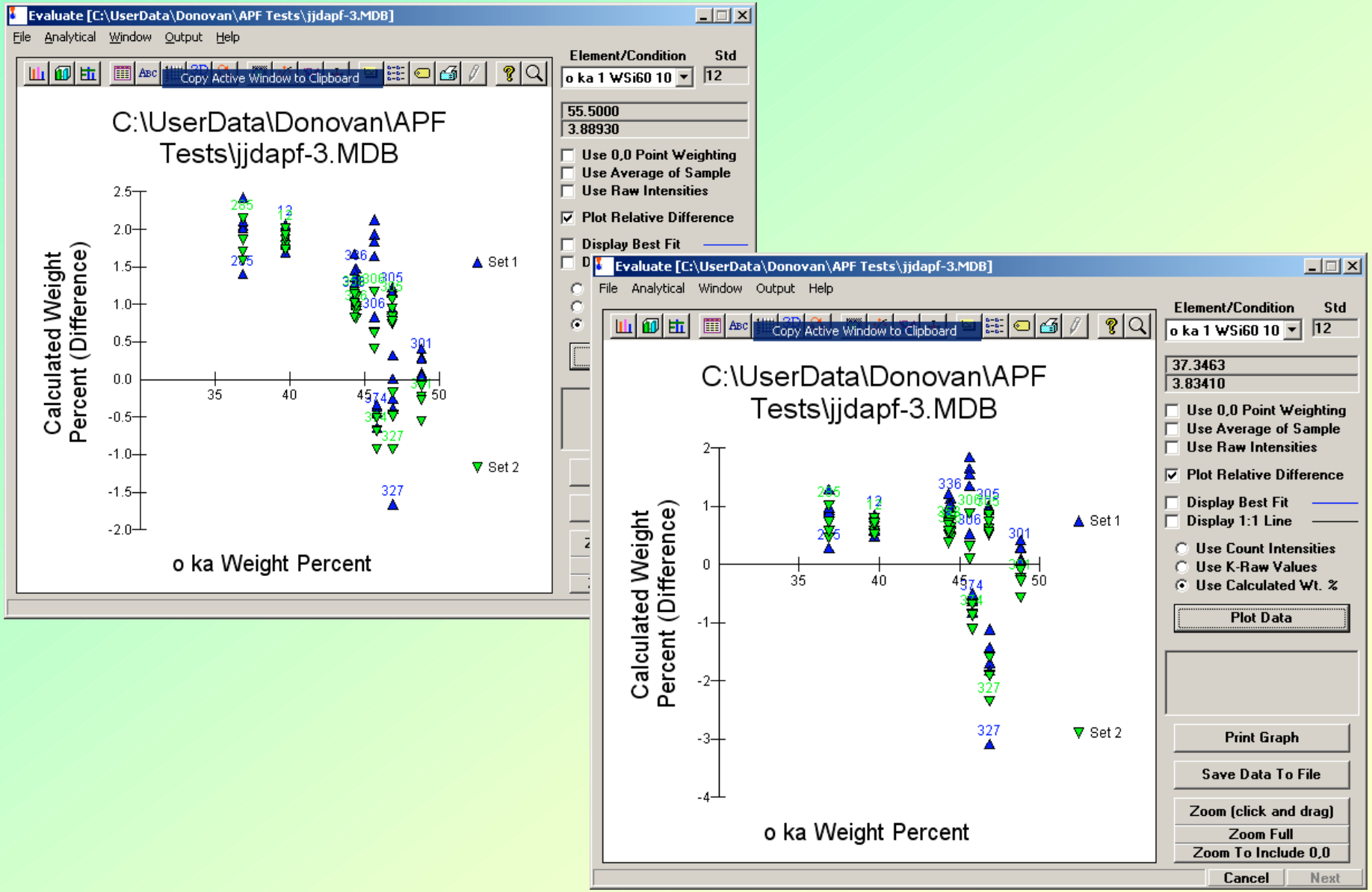
where:

| | |
|---|---|
| $I_U^I$ | is the integrated intensity for the “unknown” |
| $I_U^P$ | is the peak intensity for the “unknown” |
| $I_S^P$ | is the peak intensity for the “standard” |
| $I_S^I$ | is the integrated intensity for the “standard” |

Compound APF of element i in elements j (1 to n)

$$[APF]_{comp} = \sum_{j=1}^{j_n} C_i^j [APF]_i^j$$

# Results for silicate standards



# Conclusions

- Accuracy corrections require quantitative treatment for best results

- Compositionally dependent parameters require iterative correction methods for highest accuracy