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Re-Normalization of Calculation of Compound APFs (Area Peak Factors)

Special case of measuring oxygen in Si-SiO2 nano-particles
(calculation of APF for pure elements when trace elements vary in precision)

To correct for changes in peak shape or peak shift between the standard and unknown, the compound Area Peak Factor is typically calculated from the pure boride, carbide, nitride or oxide end-member APFs (Donovan, 1991) by summing the weight fraction of the element affecting the peak shape or shift of the specified element. This is typically performed as so:

$$APF_{Comp} = \sum APF_j * \frac{W_j}{Sum_{Partial}}$$

Where: APF_j is the binary (end-member) APF for elements other than the affected element

W_j is the weight fraction for elements other than the affected element

$Sum_{Partial}$ is the sum of all elements other than the affected element

This calculation of compound APFs works well on the typical calculation when the affecting element is present is large concentrations as shown here in an oxygen measurement of a magnesium calcium silicate:

```
ELEM:        O      Si      Al      Ca      Na       K       P      Cl      Mg   SUM
    91  44.266  25.925    .016  18.489    .015    .000    .000    .000  11.192  99.903
    92  44.289  25.925    .016  18.489    .015    .000    .000    .000  11.192  99.926
    93  44.016  25.925    .016  18.489    .015    .000    .000    .000  11.192  99.653
    94  44.259  25.925    .016  18.489    .015    .000    .000    .000  11.192  99.896
    95  44.172  25.925    .016  18.489    .015    .000    .000    .000  11.192  99.809

AVER:   44.200  25.925    .016  18.489    .015    .000    .000    .000  11.192  99.837
SDEV:     .112    .000    .000    .000    .000    .000    .000    .000    .000
SERR:     .050    .000    .000    .000    .000    .000    .000    .000    .000
%RSD:       .3      .0      .0      .0      .0      .0      .0      .0      .0

PUBL:   44.316  25.925    .016  18.489    .015   n.a.    n.a.    n.a.   11.192  99.953
%VAR:     -.26     .00     .00     .00     .00     .00     .00     .00     .00
DIFF:    -.116    .000    .000    .000    .000    .000    .000    .000    .000
STDS:       12       0       0       0       0       0       0       0       0

STKF:    .2957   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000
STCT:   4817.4      .0      .0      .0      .0      .0      .0      .0      .0

UNKF:    .2076   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000
UNCT:   3382.0      .0      .0      .0      .0      .0      .0      .0      .0
UNBG:     39.5      .0      .0      .0      .0      .0      .0      .0      .0

ZCOR:   2.1292   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000
KRAW:    .7020   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000
PKBG:    86.97     .00     .00     .00     .00     .00     .00     .00     .00
APF:     1.021    ----    ----    ----    ----    ----    ----    ----    ----
```

However, in the case of trying to analyze a thin film of Si/SiO2 nano-particles it will be necessary to perform a correction due to the peak shift of Si Kα as Si is increasingly oxidized because of the large peak shift of Si Kα. In other words the APF for Si Kα in the presence of oxygen needs to be calculated based on the amount of oxygen present relative to Si.

This means that the line below should be added to the EMPAPF.DAT file to perform the correction for Si to SiO2 peak shift where the compound APF is calculated based on the amount of oxygen present in the sample.

```
 "si"    "ka"    "o"       1.170       "SiO2/Si/PET/8.75"
```

However, in this case since the compound APF is calculated based on the elements other than the affected element (Si), in pure Si metal the calculation is very unstable because the other trace elements (oxygen) can cause the normalized contribution of each fractional APF to vary wildly.

That is, a compound with major oxygen such as SiO2 will be calculated correctly as shown here (note the example below is performed with an additional correction for O $K\alpha$ in the presence of Si relative to MgO):

```
ELEM:        O      Si       S      Fe      Cl      Cu   SUM
   230  54.109  47.224   -.005   -.038    .003    .303 101.595
   231  54.446  47.710   -.002    .076    .030   -.073 102.188
   232  54.116  47.659   -.025    .042   -.009   -.040 101.744

AVER:   54.224  47.531   -.011    .026    .008    .063 101.842
SDEV:     .193    .267    .012    .059    .020    .208
SERR:     .111    .154    .007    .034    .011    .120
%RSD:       .4      .6  -116.7   221.3   244.8   329.0

PUBL:   53.255  46.740   n.a.    n.a.    n.a.    n.a.   99.995
%VAR:     1.82    1.69     .00     .00     .00     .00
DIFF:     .969    .791    .000    .000    .000    .000
STDS:       12     514     730     730     285     529

STKF:    .2962  1.0000   .5369   .4239   .0624   .9972
STCT:   7658.5  7405.4  2705.1  1758.7   392.8   886.0

UNKF:    .3529   .4363  -.0001   .0002   .0001   .0005
UNCT:   9127.0  3230.7     -.5      .9      .4      .4
UNBG:    119.3    11.2     2.1     8.1     3.3    10.2

ZCOR:   1.5363  1.0895  1.1826  1.2611  1.1949  1.3436
KRAW:   1.1917   .4363  -.0002   .0005   .0011   .0005
PKBG:    77.53  290.10     .81    1.14    1.15    1.04
APF:     1.061   1.170    ----    ----    ----    ----
```

But in the case of the pure Si metal, because the APF is summed based on the normalized partial sum of the elements affecting the peak shape or shift (but not the affected element), the presence of minor and trace elements such as the oxygen can cause the correction to become unstable as seen here:

```
ELEM:        O      Si       S      Fe      Cl      Cu
BGDS:      EXP     LIN    HIGH     LIN     LIN     LIN
TIME:    20.00   20.00   20.00   20.00   20.00   20.00

ELEM:        O      Si       S      Fe      Cl      Cu   SUM
   110    .386 114.714    .032    .012    .034    .009 115.187
   111    .383 115.568    .000    .045    .019   -.034 115.982
   112    .326 105.140    .013   -.004    .010    .675 106.161

AVER:     .365 111.807    .015    .017    .021    .217 112.443
SDEV:     .034   5.790    .016    .025    .012    .398
SERR:     .019   3.343    .009    .014    .007    .230
%RSD:      9.2     5.2   106.8   142.9    56.5   183.5

PUBL:    n.a.  100.000   n.a.    n.a.    n.a.    n.a.  100.000
%VAR:      .00   11.81     .00     .00     .00     .00
DIFF:     .000  11.807    .000    .000    .000    .000
STDS:       12     514     730     730     285     529

STKF:    .2962  1.0000   .5369   .4239   .0624   .9972
STCT:   7661.9  7402.8  2686.5  1754.9   384.9   898.4
```

```
UNKF:    .0016  1.1170   .0001   .0001   .0002   .0017
UNCT:     42.6  8269.0      .6      .6     1.1     1.5
UNBG:     47.0    23.5     1.8    12.0     3.7    13.3

ZCOR:   2.2167  1.0010  1.2505  1.2069  1.2313  1.2787
KRAW:    .0056  1.1170   .0002   .0003   .0028   .0017
PKBG:     1.91  352.54    1.33    1.05    1.30    1.16
APF:     1.070   1.117    ----    ----    ----    ----
```

Note that the APF for O Kα is fine (major Si is present), but the APF for Si Kα in oxygen is unstable due to the high variability of the oxygen measurement of the native oxide layer during the iteration.

However, a normalization of the compound APF can be performed by re-normalizing the compound APF based on the partial sum of the elements affecting the calculation. In the case of pure Si, the partial sum is very low and the following expression causes the contribution to be re-scaled based on that small partial sum:

$$APF_{Norm} = 1 + \frac{\left(APF_{Comp} - 1\right)}{\dfrac{1}{\left(\dfrac{Sum_{Partial}}{W_{Affected}}\right)}}$$

Note that this correction is only applied when the absolute value of the scaling factor :

$$\frac{1}{\left(\dfrac{Sum_{Partial}}{W_{Affected}}\right)}$$

is greater than or equal to one to prevent the correction from being over applied to small concentrations. When this correction is implemented the calculation proceeds which much greater stability:

```
ELEM:        O      Si       S      Fe      Cl      Cu
BGDS:      EXP     LIN    HIGH     LIN     LIN     LIN
TIME:    20.00   20.00   20.00   20.00   20.00   20.00

ELEM:        O      Si       S      Fe      Cl      Cu   SUM
   110    .386 100.804    .032    .012    .034    .009 101.277
   111    .383  99.914    .000    .045    .019   -.034 100.327
   112    .326  99.786    .013   -.004    .010    .675 100.807

AVER:     .365 100.168    .015    .017    .021    .217 100.804
SDEV:     .034    .554    .016    .025    .012    .398
SERR:     .019    .320    .009    .014    .007    .230
%RSD:      9.2      .6   106.8   142.9    56.5   183.5

PUBL:    n.a.  100.000   n.a.    n.a.    n.a.    n.a.  100.000
%VAR:      .00     .17     .00     .00     .00     .00
DIFF:     .000    .168    .000    .000    .000    .000
STDS:       12     514     730     730     285     529

STKF:    .2962  1.0000   .5369   .4239   .0624   .9972
STCT:   7661.9  7402.8  2686.5  1754.9   384.9   898.4

UNKF:    .0016  1.0006   .0001   .0001   .0002   .0017
UNCT:     42.6  7407.3      .6      .6     1.1     1.5
UNBG:     47.0    23.5     1.8    12.0     3.7    13.3

ZCOR:   2.2161  1.0011  1.2504  1.2069  1.2313  1.2787
KRAW:    .0056  1.0006   .0002   .0003   .0028   .0017
PKBG:     1.91  316.09    1.33    1.05    1.30    1.16
```

```
APF:     1.070   1.001    ----    ----    ----    ----
```

Note that the APF for Si Kα is very close to 1.0 which makes sense since the contribution of oxygen is small. When SiO2 is calculated (using Si as the primary standard again) the calculation is also reasonable as before and the Si Ka APF in oxygen is similar to the end-member APF as expected:

```
ELEM:        O      Si       S      Fe      Cl      Cu
BGDS:      EXP     LIN    HIGH     LIN     LIN     LIN
TIME:    20.00   20.00   20.00   20.00   20.00   20.00

ELEM:        O      Si       S      Fe      Cl      Cu   SUM
   122  52.891  47.029    .000    .014    .007   -.105  99.837
   123  52.850  46.723   -.018    .012   -.003   -.188  99.376
   124  52.686  46.699    .028   -.057   -.018    .022  99.360

AVER:   52.809  46.817    .004   -.010   -.005   -.090  99.524
SDEV:     .109    .184    .023    .040    .013    .106
SERR:     .063    .106    .013    .023    .007    .061
%RSD:       .2      .4   655.8  -390.2  -272.4  -117.4

PUBL:   53.255  46.740    n.a.    n.a.    n.a.    n.a.  99.995
%VAR:     -.84     .16     .00     .00     .00     .00
DIFF:    -.446    .077    .000    .000    .000    .000
STDS:       12     514     730     730     285     529

STKF:    .2962  1.0000   .5369   .4239   .0624   .9972
STCT:   7640.1  7419.2  2676.1  1746.8   397.9   891.2

UNKF:    .3429   .4300   .0000  -.0001   .0000  -.0007
UNCT:   8846.1  3190.3      .1     -.3     -.2     -.6
UNBG:    113.8    12.5     2.0     8.9     3.3     9.7

ZCOR:   1.5400  1.0888  1.1833  1.2615  1.1955  1.3439
KRAW:   1.1579   .4300   .0001  -.0002  -.0006  -.0007
PKBG:    78.89  259.32    1.35     .97     .94     .94
APF:     1.062   1.170    ----    ----    ----    ----
```

With this new compound APF normalization, the compound area peak factor correction for peak shape and shift works even in end-member situations when the trace elements varying in precision dominate the correction.

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Appendix A

The code for this new correction is show here with the new APF normalization code bolded:

```
' Correct counts on unknown for peak shape changes using APF's (Area Peak
' Factors). Sum weight fraction of APF from each absorber. The sum of APFs
' is calculated from the element weight fractions not including the affected
' element.
If Not sample(1).IntegratedIntensitiesUseFlag% Then
If UseAPFFlag And UseAPFOption% = 0 Then
RowUnkAPFCors!(linerow%, chan%) = 0#
temp! = 0#
For j% = 1 To sample(1).LastChan%
If chan% <> j% Then temp! = temp! + analysis.WtPercents!(j%)    ' calculate partial sum
(not including affected element)
Next j%

If temp! <> 0# Then                 ' was "If temp! > 0# Then" but caused problem when
temp was slightly negative
For j% = 1 To sample(1).LastChan%
If chan% <> j% Then
Call EmpLoadMACAPF(Int(2), sample(1).AtomicNums%(chan%), sample(1).XrayNums%(chan%),
sample(1).AtomicNums%(j%), apf!, tstring$)
If ierror Then Exit Sub
RowUnkAPFCors!(linerow%, chan%) = RowUnkAPFCors!(linerow%, chan%) + apf! *
analysis.WtPercents!(j%) / temp!     ' sum APFs based on relative abundance
End If
Next j%

' Perform APF normalization based on partial sum (added 02/22/2009 to deal with Si Ka
peak shift Si -> SiO2)
If analysis.WtPercents!(chan%) <> 0# Then
temp3! = 1# / (temp! / analysis.WtPercents!(chan%))         ' calculate scaling factor
based on partial sum
If Abs(temp3!) >= 1# Then RowUnkAPFCors!(linerow%, chan%) = 1# +
(RowUnkAPFCors!(linerow%, chan%) - 1) / temp3!
End If

uncts!(chan%) = uncts!(chan%) * RowUnkAPFCors!(linerow%, chan%)     ' perform compound
APF correction to intensities
End If
End If

' Correct using "specified" APF factor for this emitter (and not assigned as the
standard)
If UseAPFFlag And UseAPFOption% = 1 Then
If sample(1).Type% = 2 Or (sample(1).Type% = 1 And sample(1).number% <>
sample(1).StdAssigns%(chan%)) Then
uncts!(chan%) = uncts!(chan%) * sample(1).SpecifiedAreaPeakFactors!(chan%)
End If
End If
End If
```