

Comparison of Detection Limit calculations

This overview of the calculation of the **lower limit of detection** (and the more **useful limit of determination**) is intended for use with the results of wavelength-dispersive spectroscopy on an electron microprobe. It consists of five sections: Definitions, Expressions, Discussion, Examples, and References.

Definitions:

Item	Unit	Symbol	Equivalence
Background counts	counts	N_B	$R_B * T_B$
Standard deviation of bkgd	counts	$\sqrt{N_B}$	
Peak counts	counts	N_P	$R_P * T_P$
Standard deviation of peak	counts	$\sqrt{N_P}$	
net Peak counts	counts	N_{nP}	$N_P - N_B = (R_P * T_P) - (R_B * T_B)$
Time on background	seconds	T_B	N_B/R_B
Time on peak	seconds	T_P	$N_P/R_P \approx T_B$ at limit of detection
Rate of background intensity	counts per second (cps)	R_B	N_B/T_B
Rate of peak intensity	cps	R_P	N_P/T_P
Rate of net peak intensity	cps	R_{nP}	$R_P - R_B$ for equal count times
Concentration in standard	wt% or ppm	C_{std}	
Counts per second per unit of concentration	cps/% or cps/ppm	m	$\frac{R_P - R_B}{C_{std}}$ also: $\frac{1}{m} = \frac{C_{std}}{R_P - R_B}$

Expressions:

Jenkins (1976) p. 111

- Lower limit of detection
$$LLD = \frac{2\sqrt{2}}{m} * \sqrt{(R_B/T_B)} * C_{std} = \frac{2\sqrt{2} * \sqrt{N_B} * C_{std}}{N_{np}}$$

Toya and Kato (1983) p. 81

(JEOL training manual)

- Minimum detectability limit
$$MDL = \frac{2\sqrt{2} * \sqrt{R_B} * C_{std}}{(R_P - R_B) * \sqrt{T_B}} = \frac{2\sqrt{2} * \sqrt{N_B} * C_{std}}{N_{np}}$$

$2\sqrt{2} \approx 2.82843; \approx 3 * 94.2809\%$.

Potts (1992) p. 11

- Minimum detection limit
$$MDL = \frac{3\sqrt{N_B} * C_{std}}{N_{np}} = \frac{3\sqrt{(R_B * T_B)} * C_{std}}{R_P * T_P - R_B * T_B}$$

Long (1995) p. 18

- Detection limit
$$DL = \sqrt{2} * \frac{3\sqrt{N_B}}{T_B} * \frac{C_{std}}{R_{np}} = \sqrt{2} * \frac{3\sqrt{N_B} * C_{std}}{N_{np}}$$

This reference therefore overestimates the limit of detection by $\sqrt{2}$; compare Potts (1992).

Goldstein et al. (2003) p. 446

- Concentration at DL
$$C_{DL} = \frac{3\sqrt{N_B} * C_{std}}{N_P - N_B}$$

Reed (2005) p. 139

- Detection Limit
$$DL = \frac{3\sqrt{(R_B * T_B)} * C_{std}}{(R_P * T_P) - (R_B * T_B)} = \frac{3\sqrt{(R_B * T_B)} * C_{std}}{(R_{np} * T_P)}$$

John Fournelle, PowerPoint 11/8/10

This is the most rigorous formulation.

(Madison Geology 777)

$$K_{Ca-mdl} = 3 * \frac{\sqrt{bkgcts_{Ca}^{unk}}}{(pkcts - bkgcts)_{Ca}^{std}} * \frac{ZAF_{Ca}^{unk}}{ZAF_{Ca}^{std}} * C_{Ca}^{std} \quad \begin{matrix} ZAF_{Ca}^{ol} = 1.1087 \\ ZAF_{Ca}^{std} = 1.080 \end{matrix}$$

$bkgcts = N_B, pkcts = N_P, C^{std} = C_{std}$; formulation given above for determination of Ca in olivine.

For N_B of the unknown = N_B of the standard, and for similar ZAF values for both the standard and unknown for the element of interest, this is approximately:

$$C_{DL} \approx \frac{3\sqrt{N_B} * C_{std}}{N_{np}}$$

Note: conditions of $N_{B(unknown)} = N_{B(standard)}$, and $ZAF_{unknown} = ZAF_{standard}$ are probably not true in cases of widely different matrices.

Discussion:

With the exception of Long (1995), all of the above expressions essentially recommend that the lower limit of detection be placed at about three times the standard deviation of the background above the average background counts. This is at 95% confidence. "It is important to emphasize

that quantitative analysis is not possible at the concentration represented by the lower limit of detection” (Potts 1992). According to Potts (1992), a more useful criterion is the Limit of Determination, a concentration equivalent to six standard deviations of the background above the mean background counts, or twice the lower limit of detection as defined here.

Note that some authors will adopt different definitions of the Limit of Determination (e.g., three times the lower limit of detection – Jenkins 1976).

Example 1

Standard data – output from JEOL software on JXA-8900 Superprobe for an obsidian analytical session. Measurement Condition, Measurement Order, Standard Data and Standard Intensity shown.

Operating conditions: 15 kV, 10 nA, 10 μ m beam.

Measurement Condition

WDS elements

	Element	X-ray	Crystal	CH	Acc.v	Peak Pos.	(Angstrom)	BG_L	BG_U (mm)
1	K	Ka	PET	(1)	15	121.345	3.7414	2.5	2.5
2	Na	Ka	TAP	(2)	15	129.599	11.9101	0	3
3	Ca	Ka	PETH	(3)	15	107.871	3.35839	2	2
4	Si	Ka	TAPJ	(4)	15	78.086	7.12542	0	3
5	Fe	Ka	LIFH	(5)	15	132.832	1.93604	4	4
6	Ti	Ka	PET	(1)	15	89.444	2.74851	2	2
7	Mg	Ka	TAP	(2)	15	107.671	9.89	0	3
8	P	Ka	PETH	(3)	15	197.79	6.157	4	2
9	Al	Ka	TAPJ	(4)	15	91.209	8.33934	0	2
10	Mn	Ka	LIFH	(5)	15	144.254	2.10182	0	1.5

	Element	T _P Peak	T _B Back		Pksk	Gain	High.V	Base.L	Window.W	Mode
1	K	20	10	(sec)	2	64	1710	1	6.6	(V) Dif
2	Na	20	10	(sec)	2	64	1706	1	8	(V) Dif
3	Ca	20	10	(sec)	0	16	1700	2	7	(V) Dif
4	Si	20	10	(sec)	0	64	1660	1	7	(V) Dif
5	Fe	20	10	(sec)	2	32	1760	1.5	6.2	(V) Dif
6	Ti	20	10	(sec)	2	64	1674	0.5	7	(V) Dif
7	Mg	20	10	(sec)	0	64	1696	0.8	9	(V) Dif
8	P	20	10	(sec)	2	32	1690	0.8	6.9	(V) Dif
9	Al	20	10	(sec)	0	64	1664	1	7	(V) Dif
10	Mn	20	10	(sec)	2	32	1750	0.8	7	(V) Dif

Measurement Order of WDS

Order	Channel 1	2	3	4	5
1	K*3	Na*1	Ca*7	Si*1	Fe*2
2	Ti*1	Mg*1	P*5	Al*2	Mn*1

Standard Data

	Oxide	Standard	C _{std} Wt.(%)
1	K2O	sanidine	12.11
2	Na2O	albite	11.59
3	CaO	hawaii-basalt	9.3
4	SiO2	obsidian	73.93
5	FeO	hematite	89.7113
6	TiO2	rutile	100
7	MgO	hawaii-basalt	5.08
8	P2O5	apatite	40.87
9	Al2O3	obsidian	13.12
10	MnO	rhodonite	36.85

Standard Intensity of WDS

Element	Curr.(A)	R _{nP} Net(cps)	R _{B1} Bg-(cps)	R _{B2} Bg+(cps)	S.D.(%)	Date
1 K	1.00E-08	616.9	4.8	4.1	0.52	Aug 6 18:11 2013
2 Na	1.01E-08	371.1	0	2.2	0.52	Aug 6 15:57 2013
3 Ca	1.02E-08	1143.6	21.9	20.3	0.34	Aug 7 8:22 2013
4 Si	1.01E-08	6317	0	13.4	0.14	Aug 6 15:49 2013
5 Fe	1.01E-08	4659.4	24.6	21.8	0.15	Aug 6 15:24 2013
6 Ti	1.01E-08	4371.5	21	17.7	0.15	Aug 6 16:06 2013
7 Mg	1.02E-08	267	0	3.6	0.69	Aug 7 8:22 2013
8 P	1.00E-08	898.5	3.5	5.6	0.38	Aug 6 18:02 2013
9 Al	1.01E-08	1217.4	0	8.9	0.32	Aug 6 15:49 2013
10 Mn	1.03E-08	1697.3	0	20.9	0.17	Aug 2 13:39 2013

Calculation of Lower Limit of Detection:

Our standard practice is to measure a background on either side of the peak, with each background measured for half as long as the peak measurement. The total time spent counting background is therefore the same as for the peak: $T_B = T_P$.

In the case of “one-sided backgrounds”, twice the rate of the background that is greater than zero has been adopted here for convenience. From the formulas tabulated above and using the usual JEOL output, a convenient approximation for the lower limit of detection is:

$$LLD = \frac{3\sqrt{(R_B * T_B) * C_{std}}}{(R_{nP} * T_P)}$$

It is often assumed that the backgrounds measured on the standards are directly comparable (equal) to those of the unknowns. The lower limits of detection can thus be calculated from the data for the standards:

Obsidian		R_{nP}	R_{B1}	R_{B2}	T_P	T_B		C_{std}	LLD
	Element	Net(cps)	Bg-(cps)	Bg+(cps)	Peak	Back	Oxide	Wt.(%)	Wt.(%)
1	K	616.9	4.8	4.1	20	10	K2O	12.11	0.03
2	Na	371.1	0	2.2	20	10	Na2O	11.59	0.03
3	Ca	1143.6	21.9	20.3	20	10	CaO	9.3	0.03
4	Si	6317	0	13.4	20	10	SiO2	73.93	0.03
5	Fe	4659.4	24.6	21.8	20	10	FeO	89.711	0.06
6	Ti	4371.5	21	17.7	20	10	TiO2	100	0.07
7	Mg	267	0	3.6	20	10	MgO	5.08	0.02
8	P	898.5	3.5	5.6	20	10	P2O5	40.87	0.07
9	Al	1217.4	0	8.9	20	10	Al2O3	13.12	0.02
10	Mn	1697.3	0	20.9	20	10	MnO	36.85	0.07

Example 2

Standard data – output from JEOL software on JXA-8900 Superprobe for an olivine analytical session.

Operating conditions: 20 kV, 20 nA, 2 μm beam.

Olivine		R_{nP}	R_{B1}	R_{B2}	T_P	T_B		C_{std}	LLD
	Element	Net(cps)	Bg-(cps)	Bg+(cps)	Peak	Back	Oxide	Wt.(%)	Wt.(%)
1	Cr	16735.2	107.3	90.2	60	30	Cr2O3	100	0.02
2	Mg	5977	0	10.4	60	30	MgO	51.63	0.01
3	Ca	11797.3	76.8	70.6	60	30	CaO	25.74	0.01
4	Si	6499.4	0	20.3	60	30	SiO2	40.85	0.01
5	Mn	7432.5	0	69.9	40	20	MnO	36.85	0.02
6	Ti	15819	59.6	56.8	60	30	TiO2	100	0.02
7	Al	3744	23.2	16.7	60	30	Al2O3	22.51	0.01
8	P	2790.6	11.9	16.1	60	30	P2O5	40.87	0.02
9	Fe	15637.1	74.5	65.4	40	20	FeO	66.94	0.02
10	Ni	35255.4	308.6	391	40	20	NiO	127.2526	0.03

Calculation of Limit of Determination:

The limit of determination is “the smallest signal which can be quantitatively measured (as opposed to qualitatively recognized) above background... The ideal error in measurements at this signal level is 16.7% relative (one sigma). The limit of determination represents the threshold below which measurements become increasingly qualitative.” (Potts 1992). The limit of determination (the six-sigma limit) is twice the magnitude of the lower limit of detection.

Note: The standards and unknowns must be analyzed at the same accelerating voltage.

If the current used was different for the standards and the unknowns, then the count rates for the standards should be adjusted by the appropriate multiplier (e.g., two times higher current).

Similarly, if the counting times were different on the standards and unknowns, this must be taken into account in the calculations.

Example 3

Trace-element data – output from JEOL software on JXA-8900 Superprobe for a zircon analytical session. Standards for U and Th are UO₂ and ThO₂. Backgrounds are from the zircon analyzed. Net peak count rates are from the standards. Operating conditions: 15 kV, 200 nA, 2 μm beam.

Element	Standard R_{NP} Net(cps)	Zircon R_{B1} Bg-(cps)	Zircon R_{B2} Bg+(cps)	T_P Peak	T_B Back	Oxide	C_{std} Wt.(%)
U	52023.2	462.9	237	600	300	UO ₂	99.06
Th	14606.4	67.1	59.5	600	300	ThO ₂	100.00

Material	U ZAF	Th ZAF
Zircon	1.4097	1.4822
UO ₂	1.3230	
ThO ₂		1.6363

The expression of J. Fournelle is used here, because of the considerable difference between the standards and the unknown:

$$3 \cdot \frac{\sqrt{bkgcts^{unk}}}{(pkcts - bkgcts)^{std}} \cdot \frac{ZAF^{unk}}{ZAF^{std}} \cdot C^{std} \quad bkgcts = N_B, pkcts = N_P, C^{std} = C_{std}$$

Lower limits of detection for U and Th in zircon from these data are 0.0046 and 0.0060 wt% oxide, respectively. These correspond to 41 ppm U and 53 ppm Th.

The limits of determination for U and Th in this zircon are therefore 82 and 106 ppm, respectively.

References:

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