

On the precision of electron microprobe data: a new test for the homogeneity of mineral standards

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Abstract

The precision of electron microprobe analyses has been investigated as a function of elemental concentration and a rigorous derivation is presented for the K-factor equation $K = S/\sqrt{C}$ (where S is the measured standard deviation and C the element oxide concentration). It is shown that K is not a constant, but is dependent on element sensitivity and counting times. If counting times for each element are adjusted, for example, such that 50,000 counts would be accumulated at the 10% oxide level, then it is shown that for a homogeneous material, Poisson counting errors in any element at any concentration level will fall within the limits of $0.014 \sqrt{C} \leq S \leq 0.042 \sqrt{C}$.

This relationship has been tested by the analysis of homogeneous minerals. Further data are presented to show that this expression can be used to discriminate inhomogeneous mineral phases and that it is fully compatible in this respect with Boyd's homogeneity index. The equations apply equally to X-ray fluorescence analytical data where counting errors are also controlled by Poisson counting statistics.

Introduction

The electron microprobe has gained wide acceptance in the field of geological sciences as an essential tool in the quantitative analysis of minerals (Sweatman and Long, 1969). To facilitate this, a considerable amount of work has been undertaken to investigate correction procedures to convert apparent to true elemental concentrations. Nevertheless, there is a general consensus that it is desirable to calibrate such instruments using minerals of similar composition to the samples to be analyzed thus minimizing matrix correction uncertainties (Reed, 1975, p. 187; Jarosewich *et al.*, 1980; Smellie, 1972).

Silicate mineral standards must satisfy rigorous criteria. As well as being stable under the electron beam and capable of taking a high degree of polish, suitable minerals must be both homogeneous and have an independent chemical analysis representative of the material down to the micron level. In consequence, there are few internationally available sources of calibrated mineral standards.

This work presents a new criterion for assessing the precision of microprobe data which can further be used to evaluate the homogeneity of mineral standards.

Background

The generally accepted test for mineral homogeneity in microprobe analysis was proposed by Boyd *et al.* (1967). Their method involves the calculation of a homogeneity index equal to S^1/\sqrt{N} ; where S^1 is the standard deviation of analyzed count data and N is the total number of X-ray

counts accumulated during an individual measurement. \sqrt{N} therefore represents the ideal Poisson counting statistical error (Bertin, 1975, p. 474). Boyd *et al.* reasoned that if, for a representative number of analyses, this factor did not exceed three, then a sample could be considered to be homogeneous.

However it is not always convenient to calculate this homogeneity index from sets of full mineral analyses on modern computer-interfaced microprobe systems many of which do not automatically provide total accumulated count data. Nor is it obvious how to apply this index to some energy dispersive systems where such data are not routinely provided at all.

An alternative approach is to investigate the application of a precision factor which has been proposed for use in whole rock X-ray fluorescence analysis (Jenkins, 1976, p.118; Lynch and de Koning, 1977). This is based on the work of Johnson (1967) who described the results of an interlaboratory analysis of steel and ferrous alloys using a wide variety of techniques. Johnson showed empirically that a linear relation existed between S and \sqrt{C} where C is the mean concentration of an element. Data from chemically homogeneous materials were effectively bracketed by two lines having values of the proportionality constant K between 0.009 and 0.047. Johnson further showed that the same relationship held in data obtained during a comparable analysis of ceramic materials (Bennett and Hawley, 1961) but with the magnitude of K now in the range 0.050 to 0.400. It has been suggested (Lynch and de Koning, 1977) that the greater range for ceramics

indicates that either these materials are not as easy to analyze as steels or are *less chemically homogeneous*.

As will be discussed below, the magnitudes of K-factors determined by these workers are not necessarily independent of the counting strategies adopted by the analyst.

The aim of this paper is therefore to: (1) Establish a rigorous derivation of the equation $K = S/\sqrt{C}$. (2) Discuss the conditions under which this equation may be used as an indicator of analytical precision for electron microprobe analyses. (3) Demonstrate the application of K-factors as homogeneity indices for prospective electron microprobe standards and compare it with Boyd *et al.*'s (1967) criteria.

Methods

All analyses presented here were performed on a Cambridge Instruments Microscan 9 electron microprobe using two wavelength dispersive spectrometers under computer control. Operating conditions were 20 kV accelerating voltage, 30 nA beam current with the probe beam defocused to about 15 μm diameter to reduce the effects of decomposition in beam sensitive minerals. The instrument was calibrated for quantitative analysis using the mineral standards listed in Table 1. Count times were selected so that during calibration, a minimum of 100,000 X-ray counts per element were accumulated on each mineral standard. For the analysis of unknowns, a compromise between precision and analysis time was achieved by programming count times such that a total of 50,000 counts would be accumulated for an element present at the 10% oxide level.

Derived count times were then rationalized to 30 or 50 seconds as appropriate to make best use of analysis time as dictated by the computer operating system. All count rates were automatically corrected for dead-time and probe current drift effects. Particular care was taken to enhance instrument stability by maintaining the probe in a

temperature controlled environment and by fitting a Cartesian manometer to the flow counter gas supply. One complete analysis for 10 elements including on-line ZAF correction could be completed in approximately 12 minutes. The instrument was normally recalibrated daily and the consistency of data was checked by analyzing as an unknown an in-house multi-element secondary mineral standard selected to match the composition of the mineral type under study.

Data presented here was obtained from one of the in-house secondary standards—a basaltic glass A11 93-11-5 (Staudigel 1979); from four mineral standards obtained from the Smithsonian Institution: olivine (San Carlos) USNM 111312/444, plagioclase (labradorite) USNM 115900, Kanakui augite USNM 122142 and Kanakui anorthoclase USNM 133868 (Jarosewich *et al.*, 1980) and finally from three minerals circulated for homogeneity screening by Ingamells (1980); pyroxene PSU 5-180, pyroxene PSU 5-182 and biotite R2208. Representative grains of these minerals were mounted in epoxy resin at one end of a brass tube and polished down to a 1 μm diamond finish before being carbon coated for analysis.

Derivation of K-factor equation

A derivation of the equation $K = S/\sqrt{C}$ is found in the Appendix where it is shown that for a given element in a homogeneous material,

$$\sqrt{f} \leq [K = S/\sqrt{C}] \leq 3\sqrt{f}$$

providing errors arise from Poisson counting statistics only.

f is a constant for a specified element and specified analytical conditions and may be regarded as a sensitivity factor. It is equal to:

$$f = C_s^1 \cdot \text{CPR} \cdot \frac{T_s}{(N_P - N_B)_s} \cdot \frac{1}{T_U} \cdot \frac{\text{ZAF}_s}{\text{ZAF}_U}$$

Table 1. Details of mineral standards and K-factor normalization parameters

ELEMENT	MINERAL STANDARD	C_s %	CPR	T_s (s)	ELEMENT COUNT RATE ON STANDARD (s^{-1})	ZAF_s	T_U^{-1} (s)	T_U (s)	$\sqrt{f^1}$
Si	wollastonite	24.05	2.139	20	10250	0.3222	30	25	0.013
Ti	rutile	59.95	1.668	15	34500	0.4349	30	15	0.010
Al	jadeite	13.28	1.889	30	4300	0.2836	30	29	0.014
Fe	fayalite	52.95	1.286	30	5150	0.4375	50	66	0.016
Mn	metal	100	1.291	20	11050	0.4853	50	58	0.015
Mg	forsterite	25.52	1.658	30	4700	0.2281	30	45	0.017
Ca	wollastonite	34.16	1.399	20	21600	0.3895	30	11	0.009
Na	jadeite	11.20	1.348	40	1040	0.2093	30	73	0.022
K	synthetic KCl	52.45	1.205	15	27800	0.3627	30	11	0.009

For identification of symbols - see Appendix 1.

T_U^{-1} is the count time actually used to determine data presented here.

T_U is the count time required to accumulate 50,000 counts if 10% of the element were present.

f^1 equals f (Equation 2, Appendix) with $\text{ZAF}_s/\text{ZAF}_U$ set to unity and T_U set to T_U^{-1} (see text for details).

(See Equation 2, Appendix)

(See Appendix for the definition of symbols)

This expression may be greatly simplified by setting individual element count times equal to:

$$T_u = \frac{50,000}{10} \cdot C_s^1 \cdot \text{CPR} \cdot \frac{T_s}{(N_P - N_B)_s}$$

(see Equation 7, Appendix)

T_u now represents the count time required to accumulate 50,000 counts on a mineral containing 10% of the element oxide. These figures have been arbitrarily chosen to afford adequate counting precision in routine electron microprobe analysis; alternatives are listed in the Appendix.

Under these conditions, the value of f simplifies such that $\sqrt{f} = 0.014$ and therefore:

$$0.014 \leq [K = S/\sqrt{C}] \leq 0.042$$

or

$$0.014 \sqrt{C} \leq S \leq 0.042 \sqrt{C}$$

(see Equation 9, Appendix)

This form of the equation is now applicable to all elements at any concentration level providing the specified pre-conditions are met.

It should be noted that as well as being necessary in order to simplify the form of the K-factor equation, the prerequisite of adjusting count times as described is a useful practice in any general analytical strategy since as a consequence, all elements at equivalent concentration levels are determined to equivalent counting precision.

From the above equation it may be predicted that the measured standard deviation (S), will be a linear function of \sqrt{C} , with a high probability that for homogeneous materials, all data will plot between two lines representing limiting gradients of $K = 0.014$ and $K = 0.042$ providing measured counting errors arise from Poisson counting statistics only.

Conversely it is possible to use this K-factor relationship to predict the magnitude of the Poisson counting error from element concentration alone and hence allow identification of additional errors due to instrumental or sample inhomogeneity effects.

The relationships presented above apply equally to X-ray fluorescence data since errors in this technique are also governed by Poisson statistics. The general form of the K-factor equation may also be applied to energy dispersive microprobe data although in this case it is not possible to simplify the expression by adjusting individual element count times.

It should be emphasized that throughout these argu-

ments, it has been assumed that background counts are insignificant in comparison with peak counts and that differences in the ZAF correlation factors between standards and unknowns are negligible.

Testing the hypothesis

Precision in routine analysis

The validity of the K-factor equation was tested on minerals of known homogeneity under two sets of circumstances. First, the *same grain* of basaltic glass (A11-93-11-5) was analyzed over a 5 month period and the mean of 54 such determinations is listed in Table 2. These data represent typical day to day precision levels taking into account both long term instrumental drift and calibration discrepancies. As a second indicator, the precision obtained within single operating sessions from the analysis of different grains of minerals of proven homogeneity was measured by analyzing 10 to 12 individual grains of each of the four USNM standards described previously. Data for plagioclase (USNM 115900) are listed in Table 2 as representative of the worst case for these minerals.

Data in Table 2 show that for all elements present at above 1% oxide, analyzed means agree with expected data to within the measured 2S limits except for Al and Na where there appears to be a small but systematic bias. This is of no consequence to the arguments to be developed below but illustrates the problem in relying on the accuracy of an individual and possibly non-representative mineral grain as a standard. Data for both K-factors and Boyd's homogeneity index are also listed in Table 2. These data suggest that a higher degree of homogeneity was obtained from the analysis of the single grain of basaltic glass than from the 10 to 12 grains of plagioclase. However for elements present in significant concentrations, Boyd's index in general lies within the specified limit of 3.

As has already been noted, it is only possible to compare directly K-factors for different elements if count times have been adjusted to give comparable counting precision. This criterion was only appreciated at a late stage in this work and all data presented here were analyzed using the instrumental conditions listed in Table 1 with unknown count times rationalized to optimize operating efficiency. Therefore to allow direct comparison between precision and concentration for different elements, the measured standard deviation (S) was normalized by multiplying by the ratio $0.014/\sqrt{f^1}$ where f^1 is the value of f calculated from the actual parameters used to analyze a particular element (Table 1) and 0.014 represents the value of \sqrt{f} for 50,000 counts per 10% element oxide.

The resulting plot of S^1 against \sqrt{C} (Fig. 1) demonstrates the linear trend between these data with almost all points lying between two lines of gradient $K = 0.014$ ($S^1 = 1\sigma$) and $K = 0.042$ ($S^1 = 3\sigma$). There is some indication

Table 2. Analysis and homogeneity indices of selected minerals

	DSDP BASALTIC GLASS A11 93-11-5					PLAGIOCLASE USNM 115900					PYROXENE PSU 5-180				
	Known composition	\bar{C} (n=54)	S	K	BOYD	Known composition	\bar{C} (n=12)	S	K	BOYD	Known composition	\bar{C} (n=11)	S	K	BOYD
SiO ₂	51.52	51.53	0.241	0.037	2.42	51.25	50.82	0.313	0.048	3.31	49.34	49.30	0.524	0.082	5.82
TiO ₂	1.30	1.32	0.025	0.031	2.29	0.05	0.06	0.009	0.056	2.98	0.70	0.36	0.205	0.490	30.91
Al ₂ O ₃	15.39	15.01	0.098	0.025	1.62	30.91	30.27	0.176	0.032	2.50	1.04	0.99	0.058	0.059	3.83
FeO	9.12	9.05	0.067	0.019	1.28	0.46	0.42	0.018	0.025	1.78	21.14	20.32	0.575	0.111	7.89
MnO	0.17	0.18	0.013	0.028	2.44	0.01	0.02	0.007	0.044	4.19	0.48	0.54	0.026	0.032	1.81
MgO	8.12	7.96	0.079	0.023	1.43	0.14	0.10	0.013	0.033	1.87	7.96	7.99	0.142	0.042	2.71
CaO	11.31	11.15	0.076	0.037	2.63	13.64	13.42	0.117	0.052	3.64	18.93	19.18	0.372	0.139	9.41
Na ₂ O	2.48	2.76	0.045	0.017	0.92	3.45	3.78	0.076	0.025	1.37	-	0.23	0.027	0.036	1.61
K ₂ O	0.09	0.07	0.005	0.034	3.37	0.18	0.11	0.010	0.050	1.70	-	-	-	-	-
TOTAL	99.50	99.03				100.09	99.00				99.59	98.91			

(1) Concentration units = wt.% oxide

(2) Expected compositions are from the following sources: basaltic glass, Staudigel [1979]; plagioclase, Jarosewich *et al.* [1980]; pyroxene, C.O. Ingamells [person. comm.].

(3) \bar{C} is the mean analysed value of n determinations, (this work); S is the standard deviation, K the K-factor normalized to standard counting conditions (see text) and 'Boyd' the homogeneity index after Boyd *et al.* [1967].

that data for values of $C \leq 0.1\%$ exceed the upper limit as would be expected for measurements where background counts are not negligible. Four data points (2 for Si and 2 for Ca) slightly exceed the $S^1 = 3\sigma$ limit at higher concentration levels. We would correlate this with larger than expected standard deviations due to instrumental errors, associated with the mechanical re-alignment of the wavelength spectrometers.

We would therefore propose that overall, these measurements derived from minerals of known homogeneity under the specified preconditions fully support the K-factor relationship:

$$0.014 \leq [K = S/\sqrt{C}] \leq 0.042$$

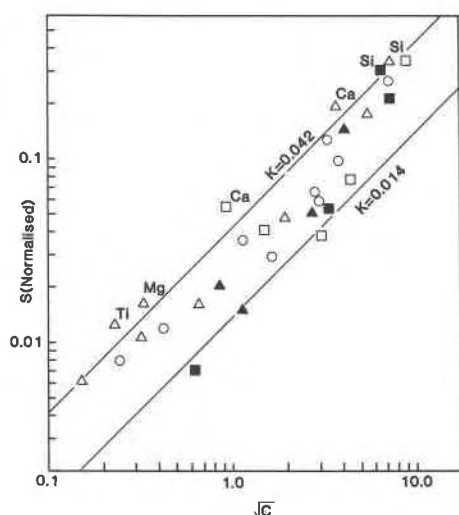


Fig. 1. Plot of normalized standard deviation (S) (see text) against \sqrt{C} for data from five homogeneous minerals: \circ basaltic glass (A11-93-11-5), \blacksquare olivine (USNM 111312/444), \triangle plagioclase (USNM 115900), \blacktriangle Kanakui augite (USNM 122142) and \square Kanakui anorthoclase (USNM 133868).

for errors derived only from Poisson counting statistics, under the analytical conditions noted previously.

The K-factor as a homogeneity index

If the above arguments are accepted, then it is possible to use the K-factor as a mineral homogeneity indicator since the worst acceptable elemental counting precision on our instrumentation is represented by the value $K = 0.042$. To test this hypothesis, three further minerals were analyzed (biotite R2208, pyroxene PSU 5-180 and pyroxene PSU 5-182). These are minerals which, having been distributed for screening as possible standards, were subsequently rejected on the grounds of doubtful homogeneity (Ingamells, 1981). Mean data from 12 randomly selected grains of one of this group (pyroxene PSU 5-180) are presented in Table 2 and the large increase in magnitude of the homogeneity index for some elements is immediately apparent.

To investigate the discrimination afforded by the K-factor in comparison with Boyd's homogeneity index, data for both these parameters taken from all eight analysed minerals are plotted in Figure 2. In this instance the value if K has been normalized by the sensitivity constant $\sqrt{F^1}$ (see Table 1) so that $K/\sqrt{F^1} = 1$ when $S^1 = 1\sigma$ and $K/\sqrt{F^1} = 3$ when $S^1 = 3\sigma$. This allows direct comparison to be made with Boyd's index.

There is good correlation between these two indices with all data plotting about the line of equivalence. Exact equivalence has not been achieved because ZAF correction differences and the effect of background counts have both been ignored in calculating K. Boyd *et al.* proposed a limit of three as the point at which errors became unacceptably large. Whereas most of the data for homogeneous phases lie within this limit, we would suggest a more realistic limit of four for data where instrumental effects may make some contribution to measured counting errors. This threshold corresponds to a value of $K = 0.056$ ($S = 4\sigma$).

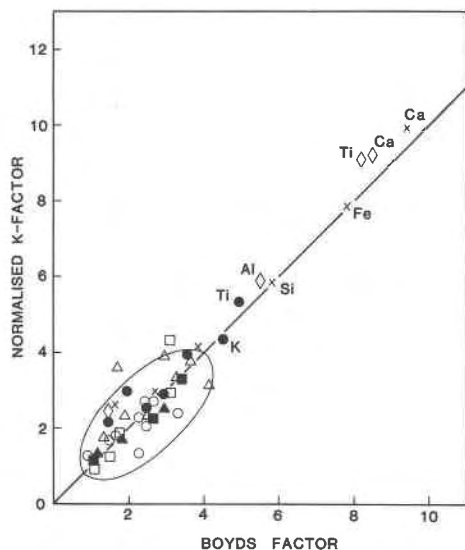


Fig. 2. Homogeneity discrimination plot: normalized K-factor (see text) vs. Boyd's homogeneity index for eight minerals: \times pyroxene PSU 5-180, \diamond pyroxene PSU 5-182 and \bullet biotite R 2208 plus the homogeneous phases identified in Fig. 1. One point (Ti) for pyroxene PSU 5-180 plotted off the top right hand corner of this diagram (see Table 1 for values). Data points enclosed in circled area represent analyses of elements which are homogeneously distributed in mineral phase.

As can be seen from Figure 2, there is clear discrimination between points lying below this threshold and data for the elements Si, Ca, Fe and Ti in PSU-180 and Ca, Al and Ti in PSU-182 which lie well outside the field of acceptability of either homogeneity criterion. Data for the elements Ti and K in biotite R2208 (Fig. 2) represent a more marginal case but clearly this mineral cannot be considered to be completely homogeneous. Thus the K-factor is fully equivalent to Boyd's index in discriminating homogeneous minerals.

Conclusions

(1) A rigorous derivation of the equation $K = S/\sqrt{C}$ has been presented showing that contrary to assumptions made by some previous workers, K is not a constant independent of element sensitivities unless specified pre-conditions are met.

(2) It has been shown that by adopting an analytical strategy which equalizes element sensitivities, the K-factor equation may be used for predicting counting errors in the determination of any element at any concentration level providing such errors originate only from Poisson counting statistics.

(3) As an extension of this concept, K-factors may further be used as a microprobe mineral homogeneity index, fully equivalent in this respect to Boyd's criterion.

Acknowledgments

The authors gratefully acknowledge the following for donation of mineral samples: E. Jarosewich (Smithsonian Institution), C. O. Ingamells (Amex Corporation) and R. G. Pritchard (University of Bochum, F.D.R.). We should also like to thank Pam Owen for typing the manuscript, John Taylor for drafting the diagrams, and the referee for his comments which stimulated further derivations of the concepts described here.

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Manuscript received, May 25, 1982;
accepted for publication, April 11, 1983.

Appendix

Derivation of the K-factor equation

Let:

- K = the "K-factor"
 C^1 = element concentration, C = oxide concentration (both expressed as wt%)
 N_p = total accumulated peak counts

- N_B = total accumulated background counts
 S = measured standard deviation derived from concentration
 S^1 = measured standard deviation derived from total accumulated peak - background counts
 σ = "true" standard deviation derived from Poisson statistics
 T = count time
 ZAF = ZAF correction factor
 CPR = compound ratio (to convert % element to % oxide)
 subscript u = relating to unknown analysis
 subscript s = relating to standard analysis

Then the concentration of an element oxide analyzed against a standard by electron microprobe analysis is given by:

$$C_u = \frac{(N_P - N_B)_u}{(N_P - N_B)_s} \cdot \frac{T_s}{T_u} \cdot C_s^1 \cdot CPR \cdot \frac{ZAF_s}{ZAF_u} \quad (1)$$

(c.f. Long, 1977, Equation 6, p. 300)

$$= f(N_P - N_B)_u$$

where f is a constant for a given element at any concentration under constant calibration and analytical conditions given by

$$f = C_s^1 \cdot CPR \cdot \frac{T_s}{(N_P - N_B)_s} \cdot \frac{1}{T_u} \cdot \frac{ZAF_s}{ZAF_u} \quad (2)$$

From the definition of standard deviation (see, for example, Bertin, 1975, Equation 11.5, p. 463)

$$S = \left[\frac{\sum(C_u - \bar{C}_u)^2}{n - 1} \right]^{1/2}$$

substituting for C_u :

$$S = f \left[\frac{\sum\{(N_P - N_B)_u - \overline{(N_P - N_B)_u}\}^2}{n - 1} \right]^{1/2} \quad (3)$$

Thus from Equation 1 and 3, and given the relation

$$K = \frac{S}{\sqrt{C}}$$

$$K = \sqrt{f} \left[\frac{\sum\{(N_P - N_B)_u - \overline{(N_P - N_B)_u}\}^2}{n - 1} \right]^{1/2} \cdot \frac{1}{[(N_P - N_B)_u]^{1/2}} \quad (4)$$

But by definition

$$S^1 = \left[\frac{\sum\{(N_P - N_B)_u - \overline{(N_P - N_B)_u}\}^2}{n - 1} \right]^{1/2} \quad (5)$$

and according to Poisson counting statistics (see Bertin, 1975, p. 474, Equation 11.20)

$$\sigma = (\overline{N_P + N_B})^{1/2} \quad (6)$$

If the magnitude of background counts may be neglected in comparison with peak counts then substituting Equations 5 and 6 into Equation 4:

$$K = \sqrt{f} \left(\frac{S^1}{\sigma} \right) = \sqrt{f} \text{ (BOYD)}$$

where BOYD is Boyd's factor expressed in terms of net peak area.

Examining now the constant f (Equation 2).

Assuming $ZAF_s/ZAF_u = 1$ and if T_u is adjusted to the time required to accumulate 50,000 counts at the 10% element oxide level (or alternative analytically acceptable values) then:

$$T_u = \frac{50,000}{10} \cdot C_s^1 \cdot CPR \cdot \frac{T_s}{(N_P - N_B)_s} \quad (7)$$

Substituting this value of T_u into Equation 2, the value of f now equals 0.0002 and $\sqrt{f} = 0.014$

Under these conditions:

$$K = \frac{S}{\sqrt{C_u}} = 0.014 \cdot \frac{S^1}{\sigma} \quad (8)$$

Applying the same criteria proposed by Boyd *et al.*, (1967) and applied by other workers (Jarosewich *et al.*, 1980), the acceptable limit to the value of S^1 if errors are caused by Poisson counting statistics alone is $S^1 \leq 3\sigma$.

Therefore from a practical point of view, limits may be placed on Equation 8 as follows:

$$0.014 \leq \left[K = \frac{S}{\sqrt{C_u}} \right] \leq 0.042$$

or

$$0.014 \sqrt{C_u} \leq S \leq 0.042 \sqrt{C_u} \quad (9)$$

If different counting criteria were adopted, the limits of the K -factor would vary according to the number of counts accumulated at the 10% oxide level as follows:

50,000 counts accumulated:	$0.014 \leq K \leq 0.042$
100,000 counts accumulated:	$0.010 \leq K \leq 0.030$
200,000 counts accumulated:	$0.007 \leq K \leq 0.021$
500,000 counts accumulated:	$0.004 \leq K \leq 0.013$