CRB
Analyse Service GmbH

GeoPT11 - certification project OU-6, Penrhyn Slate

Veranstalter: International Association of Geoanalysts and Geostandards Newsletter - GeoPT11

Ringversuchsmaterial: certification project OU-6, Penrhyn Slate

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Literatur: Report of the IAG on the Certification of Penrhyn Slate OU-6

Hauptelemente [MA%]

	CRB	RV	1sRV	Z-Score
Na_2O	1,69	1,759	0,043	---
MgO	2,4	2,419	0,034	---
Al_2O_3	20,47	10,45	0,201	---
SiO_2	57,53	57,35	0,469	---
P_2O5	0,116	0,117	0,008	---
K_2O	3,05	3,031	0,046	---
CaO	0,78	0,738	0,024	---
TiO_2	0,997	0,995	0,019	---
Fe_2O_3 tot.	8,88	8,945	0,142	---
MnO	0,281	0,284	0,006	---

Spurenelemente [µg/g]

	CRB	RV	1sRV	Z-Score
Ba	476	478	13,6	---
Ce	67	77,1	13,6	---
Co	31	29,1	1,39	---
Cr	70	70,7	4,06	---
Cu	38	40,4	2,78	---
Ga	26	24,2	1,16	---
Hf	4,8	4,7	0,035	---
Nb	15	14,5	0,77	---
Ni	45	40,17	2,12	---
Pb	31	28,8	1,13	---
Rb	132	121,2	3,77	---
Sr	130	131,7	4,88	---
V	125	129,8	5,04	---
Y	29,8	27,8	1,16	---
Zn	116	111,5	4,5	---
Zr	168	173,5	4,58	---

Legende

CRB: Ergebnisse CRB – **RV:** Ergebnisse Ringversuch -- **1s-RV:** Standardabweichung Ringversuch

Z-Score: Differenz des Messwertes vom Mittelwert des Ringversuchs -- * Wert nicht zertifiziert

To all participants in the OU-6 certification:

Let me try again, since the attachments apparently were not attached to the first try with this message.

It was wonderful to see so many of you at Geoanalysis 2003 last month in Rovaneimi and to be able to share with you then the progress in certifying the slate material OU-6. Attached is the formal report on the project, which will be submitted to Geostandards Newsletter: the Journal of Geostandards and Geoanalysis. The project was most successful, and various sections of the report will be greatly condensed to form the final Certificate of Analysis to accompany the material in distribution by IAG.

It is my intention to submit the report for publication in GSN, but before doing so, I wanted to give all of you, without whose analytical work there would be no project at all, an opportunity to review the report and recommend edits. Please send comments to me before August 15, so that I can complete revisions before the August 31 submission deadline for the Geoanalysis 2003 symposium volume. Attached are three files, one a Word (Office 2000) document which is the text, and references, with Tables 4a, 4b and 5 imbedded. The second is an Excel file in which the remaining tables (1,2,3,6,7) are concatenated. The third is the Summary table of all of the contributed laboratory averages for both OU-6 and JSI-1. This will appear as the appendix to the report, with an additional section fully identifying all contributing laboratories. I believe that all of the errors in the tables that were distributed before Geoanalysis 2003 have been corrected, but please verify that for your laboratory's data.

I'm most grateful to each and every laboratory for its contribution to this project. It has been an outstanding effort, which has accomplished a huge amount for the geoanalytical community at large. I've been privileged to be a part of this.

My best wishes,

Jean Kane

Table 6

Certified Values and Their Uncertainties (95% confidence intervals) for IAG CRM OU-6

	Certified Value	U=t*u (see text and Table 7)
SiO2 % m/m	57,350	0,3093
TiO2 % m/m	0,995	0,0772
Al2O3 % m/m	20,450	0,3216
Fe2O3T % m/m	8,945	0,2373
FeO3(calc) % m/m	7,115568	
Fe(II)O % m/m	1,645	0,1423
MnO % m/m	0,284	0,0758
MgO % m/m	2,412	0,0799
CaO % m/m	0,741	0,0771
Na2O % m/m	1,758	0,0899
K2O % m/m	3,031	0,0830
P2O5 % m/m	0,118	0,0761
H2O- %m/m	0,143	0,1312
H2O+ %m/m		
CO2 %m/m	0,226	0,1241
LOI % m/m	3,617	0,0987
TOTAL	99,516	
As mg/kg	13,234	0,656049
Ba mg/kg	479,713	13,11814
Be mg/kg	2,525	0,311324
Ce mg/kg	77,072	2,66319
Co mg/kg	29,166	1,059362
Cr mg/kg	70,672	2,1344
Cs mg/kg	8,098	0,276065
Cu mg/kg	40,415	4,906695
Dy mg/kg	5,061	0,138246
Er mg/kg	2,930	0,221967
Eu mg/kg	1,355	0,05483
Ga mg/kg	24,169	0,731291
Gd mg/kg	5,302	0,37669
Hf mg/kg	4,700	0,319965
Ho mg/kg	1,038	0,050996
La mg/kg	33,216	1,836731
Li mg/kg	95,295	4,544566
Lu mg/kg	0,451	0,022497
Nb mg/mg	14,491	0,576165
Nd mg/kg	30,178	1,480841
Ni mg/kg	40,165	1,305957
Pb mg/kg	28,798	0,791979
Pr mg/kg	7,910	0,257839
Rb mg/kg	121,311	3,858616
Sb mg/kg	0,563	0,130752

Sc mg/kg	23,073	3,15662
Sm mg/kg	6,014	0,423055
Sn mg/kg	2,670	0,189225
Sr mg/kg	131,691	2,597759
Ta mg/kg	1,022	0,119293
Tb mg/kg	0,859	0,039936
Th mg/kg	11,311	1,017531
Tl mg/kg	0,538	0,055929
Tm mg/kg	0,451	0,01893
U mg/kg	1,924	0,088791
V mg/kg	129,839	5,146149
Y mg/kg	27,748	0,738686
Yb mg/kg	2,981	0,101942
Zn mg/kg	111,427	3,38249
Zr mg/kg	174,169	5,660151

Report of the IAG on the Certification of Penrhyn Slate, OU-6

Jean S. Kane and 31 participating laboratories

Abstract

The IAG has certified a slate sample, OU-6, for 12 major/minor constituents and 35 trace elements through an interlaboratory programme conducted in close compliance with ISO Guide 35 (1989). Information values are provided for an additional 7 constituents where certification criteria were not met. Uncertainties developed in accordance with GUM (Eurachem 2000) and representing the 95% confidence interval of the certified and information values are reported for all 49 constituents. The material is immediately available for distribution by the IAG.

Introduction

Reference materials are critical to geoanalytical laboratories, as calibration materials for instrumental techniques and as materials for quality assurance and control. While these RMs have played an extensive role in the continual improvement of the capabilities of geoanalytical laboratories, many do not fully meet modern metrological demands. Few of the available RMs are accompanied by Certificates of Analysis providing uncertainties as defined by the Guide on Uncertainty in Measurement (GUM) (Eurachem 2000), making it difficult to meet modern metrological traceability of measurement requirements.

Recently IAG embarked on a certification programme to make available to geoanalysts CRMs that have been prepared in close compliance with ISO Guide 35 (1989) requirements. The goals of the certification effort were two-fold. First, IAG wished to demonstrate that it could function as a certifying body, operating as BCR does, to set certification goals, select participants, plan the measurement protocol, and perform data analysis, leading to certified values and their uncertainties. Second, IAG wished to demonstrate that IAG member laboratories could provide analyses of the quality required to accomplish a certification in accordance with ISO (1989) Guidelines.

This report describes the certification of OU-6 Penrhyn Slate by the IAG carried out in the spring of 2003 which accomplished both of these certification goals. Certified values and their uncertainties are presented for 12 major/minor constituents and 35 trace elements; information values are presented for an additional 7 elements. Traceability of the certified values is demonstrated for most of the certified values, based on concurrent analyses of the existing RM JSI-1 issued by the GSJ (Imai et al 1996).

1) Identification of qualified laboratories

Historically, laboratories have been self-selecting in their participation in interlaboratory characterizations of geochemical RMs. GeoPT™, the IAG's international proficiency testing program, provides a starting point for prequalifying laboratories for participation in certification programmes. In conducting the PT programme (IAG 2001), each laboratory is given a z-score indicating the quality of a laboratory's performance on every analysis that the laboratory performs. The z-score is determined using the Horwitz factor (Horwitz and Albert 1995), or target precision for GeoPT, which describes the expected deviation between laboratories analyzing a common sample, and is a function of concentration. It is derived from experience with thousands of analytical results developed in method validation studies conducted by AOAC and similar organizations. Z-scores in the range -3<z<3 are considered satisfactory.

$H_a = X_a^{0.8495}$ for pure geochemistry laboratories

and $H_a = 2X_a^{0.8495}$ for applied geochemistry laboratories.

$z = (X - X_a)/H_a$ where X is the contributed result and X_a the assigned value
and H_a is the appropriate one for the contributing laboratory

Seventy-four laboratories participated in GeoPT9. Very few had satisfactory z-scores for all major oxides and trace elements for which assigned values could be derived. Several, however, had satisfactory z-scores for either all (or all but one) major oxide or all (or all but one) of the trace elements, and all of these laboratories, 30 in total, were considered "qualified" to participate in the certification programme. This prequalification is designed to eliminate the submission of inaccurate data that would require rejection before deriving the certified values and their uncertainties from the contributed data.

Prequalification of laboratories based on the quality of their GeoPT9 performance is possible only for the 12 major and 41 trace elements for which assigned values were developed. Thus, some elements of interest to individual laboratories cannot be considered for certification.

In addition to the participants qualified through their GeoPT9 performance, three current producers of geoanalytical RMs (CRPG, GSJ, USGS) were invited to participate in the certification of OU-6. These laboratories were deemed qualified based on their extensive RM characterization activities. A number of IDTIMS laboratories were also invited to participate. IDTIMS is a definitive method, and thus should provide the highest possible level of accuracy in a certification program. However, even definitive methods require validation; agreement between three to five laboratories using the technique is thus desired to provide that validation; only one IDTIMS data set has been submitted to date. Thirty-one laboratories returned data to the IAG Certification Committee; one data set could not be accepted because the submitting laboratory did not follow the requested experimental design.

2) Establishment of target uncertainties for certified values

It can be seen that the Horwitz factor provides a means of establishing target uncertainties for certified values. Uriano and Gravatt (1977) suggested that uncertainties of certified values be three to ten times smaller than the uncertainties for routine laboratory measurements. Assuming that the Horwitz factor is a reasonable estimate of laboratory uncertainty generally, then the target uncertainty for certification should be one-third to one-tenth the magnitude of the Horwitz factor. Targets were thus set for uncertainties (u) of each certified value to be established for OU-6 through this certification. The Horwitz factor for each analyte was calculated using the assigned value obtained through the GeoPT9 program as the analyte concentration. See Table 1.

3) Establishment of analytical protocol for the certification

In order to achieve certified value uncertainties that are most likely to meet the targets tabulated in Table 1, it is desirable to have 15 or more laboratories (ISO Guide 35 1989) providing data obtained by more than one method of analysis. Further, the two or more methods should be as independent as possible (Epstein 1991), and should produce accurate data. The number of selected laboratories should provide adequately sized data sets for most, if not all, analytes. A review of the GeoPT9 report (Potts et al. 2001) showed that the selected laboratories had in fact used a range of methods, and their prequalification assured that the data would be of adequate accuracy, but gave no information about repeatability of measurement within any of the laboratories.

To be able to assess uncertainties of measurement for each laboratory prior to compiling the data for the derivation of certified values, each laboratory was asked to analyze two samples prepared from each of three splits of OU-6 twice, with the measurement runs separated by a week or more. Participants were also required to analyze an existing RM to demonstrate traceability of analysis. The Japanese slate JSl-1 (Terashima et al 1990, Imai et al 1996) was selected for the purpose, as it and JSl-2 provided the closest matrix match available among existing RMs.

Before considering the certification data itself, it is helpful to review briefly the sample itself, the homogeneity test done on the sample as the material for GeoPT9, and the assigned values that resulted from the test.

4) GeoPT9, OU-6 Penrhyn Slate

OU-6 Penrhyn Slate was obtained from the Penrhyn Slate Quarries, Bethesda, North Wales as powdered material prepared as a commercial product. The slate quarry is located in a north-south trending belt that cuts across part of Snowdonia. The slate is fine-grained, purplish grey, well-cleaved and of Cambrian age. The rock was originally deposited as a mud and was recrystallized during low grade metamorphism. Caldonian deformation aligned fine-grained mica in the rock to produce the slatey cleavage. The rock is minerallogically homogeneous on a fine scale, with the exception of occasional green reduction spots (Fe^{+2}) and crystals of pyrite.

The Open University obtained the material from Penrhyn Quarries and prepared it for distribution as a sample, GeoPT9, in the IAG's international proficiency testing programme. The preparation involved homogeneity testing preliminary to packaging for distribution. The homogeneity test was based on the Harmonized Protocol (Thompson and Wood 1993, Fearn and Thompson 2001). The statistical analysis of the homogeneity test data is summarized in Potts et al. (2001). It is necessary to identify any inhomogeneity of such a magnitude that it would interfere with interpretation of proficiency test results.

If within-packet variance is very small, the classical F-test might return a conclusion that the sample is inhomogeneous when the sample variance was actually insignificant in comparison to the Horwitz factor H_a which determines the z-score. In this case, despite the F-test result, the sample is considered homogeneous for PT testing purposes unless the ratio of sampling variance is more than 0.3 times H_a.

Alternatively, if the within-packet variance is very large, the classical F-test would not detect inhomogeneities that were sizable in comparison to H_a. This might occur either if mineralogical inhomogeneity occurs within packets as well as between them, or because the homogeneity test method is generally imprecise, as when measurements are being made close to the detection limit. This factor is taken into account by requiring that the analytical (within-packet) variance is smaller than 0.4 times H_a.

Once the suitability of the sample was established through the homogeneity testing, the sample was packaged. The quantity of material was sufficient for the GeoPT™ program, with an additional 350 +/-units that were stored for potential future certification as a CRM. The sample was distributed in March, 2001, to participating laboratories. In accordance with the GeoPT™ protocol (IAG 2001), each laboratory performed a single analysis of the sample using the routine laboratory method. The results were submitted to the IAG for evaluation in May 2002. Robust means and their standard deviations were calculated as assigned values and uncertainties for all analytes for which 1) a sufficient number of laboratories had reported data for the analyte, and 2) the data approximated a normal distribution, i.e., that it showed a single central tendency. Z-scores were calculated for each result from all laboratories. A report was distributed to participants in July, 2001 (Potts et al. 2001) that included assigned values and their uncertainties and a tabulation of all z-scores. The assigned values for 12 major oxides and 41 trace elements in OU-6 appear in Table 2. These values represent the first iteration in establishing certified values. Further analyses according to the certification protocol

should enable the establishment of uncertainties for the final certified values that can be developed in accordance with the Guide to Uncertainty in Measurement (GUM) (Eurachem 2000).

5) Statistical Analysis of Data Submitted for the Certification of OU-6 Penrhyn Slate as a CRM

The rationale for, and details of, the statistical protocol for processing the certification data is given in the IAG (2003) Draft Protocol for the Certification of Reference Materials. Only a brief summary follows.

Laboratory averages and standard deviations for each analyte reported were calculated for the OU-6 and JSI-1 data submitted by each laboratory. (See the Appendix for a tablulation of laboratory means for all elements determined in both samples.) Additionally analysis of variance (anova) was performed on each laboratory's OU-6 data, to examine homogeneity of the CRM, and to determine whether or not there were significant day to day or preparation-to-preparation components to the laboratory's analytical variance.

Before proceeding to the derivation of certified values, each individual laboratory average for each analyte in OU-6 was compared to the GeoPT9 assigned value. Similarly, the laboratory average for each analyte in JSI-1 was compared to the certified value. Any average laboratory result for either sample that was not within ± 3z of the expected value, using H_a for pure geochemistry, was considered for possible rejection. The goal of the laboratory selection process was to avoid any need for data rejection that could not be justified technically. This goal was largely met, as rejection rates were 4% for OU-6 data and 6% for JSI-1 data, with little covariance between the rejections.

For the anova, a nested design was used for those laboratories (25 of 30) that followed the protocol exactly, making two separate analytical runs at intervals of a week or more of their OU-6 samples. Variances between splits, between duplicate preparations from each split and between the two days on which analyses were performed were assessed. Some laboratories (4), however, made only one analytical run, and in these cases, the data allowed only a simple one-way analysis of variance, with split as the classification variable. Because the technique is so much more labor-intensive than instrumental ones, the one laboratory providing IDTIMS data followed a unique protocol, reporting four replicates for OU-6 and duplicates only for JSI-1. No analysis of variance was done for the IDTIMS data. Between split variances were used to confirm and expand on the homogeneity testing performed as part of the GeoPT9 exercise using OU-6, as discussed below in the section on establishing uncertainties for the certified values.

5b) Statistical treatment of the compiled laboratory averages

After completing these analyses of the data from individual laboratories, the data were compiled, and the means and standard deviations of data from all laboratories were calculated for both OU-6 and JSI-1. Also, the individual laboratory standard deviations for OU-6 were pooled to provide s_w, which is needed for users to properly assess their own data in comparison to certified values, as outlined in ISO Guide 33 (2000). The JS1-1 data were used to establish traceability to the fullest extent possible, and the OU-6 data were used to develop the certified values and their uncertainties for this CRM.

5b1) Traceability

Traceability has been established to the fullest extent possible using the Japanese slate JSI-1 (Imai et al 1996) for many of the elements being certified. Generally, the IAG mean for a constituent in JSI-1 agreed with the original GSJ certified value, as shown in Table 3. In some cases, the agreement was immediately obvious, and statistical analysis was not necessary. In other cases, agreement had to be demonstrated through anova. Results showed that the two agencies obtained "the same" values for all major and minor oxides except CaO and CO_2. To evaluate the analytical significance of the statistically significant differences, the absolute differences between the GSJ certified values (Imai et al

1996) for JSI-1 and the IAG mean were compared to the stated accuracy requirements for major/minor oxides given in Shapiro (1975). See Table 4a. Thus traceability is demonstrated for CaO despite the lack of statistical agreement of the IAG mean with the certified value. However, the CO_2 difference indicates a serious analytical error in either the IAG certification data set or the IAG data set or both.

For trace elements, where there are no comparable accuracy requirements to use for reference, demonstration of traceability through the analysis of JSI-1 required agreement between the GSJ certified value (Imai et al 1996) and the IAG consensus mean, after rejection of outliers. Again, in some cases. the agreement was obvious from simply looking at the data; Ba provides an example. In other cases it was necessary to use anova to determine the significance of the differences between the GSJ certification and the IAG data sets.

When significant differences were found, as for example in the case of Er, the GSJ data certification data set alone was carefully examined. In this instance, the inability to establish traceability stems from the quality of the original certification, rather than from problems with the IAG data. For Er, the GSJ certification was based on too few (n=3) data; this was also the case for As, Dy, Ho, Sb, Sn, Ta, U and Tm (n ≤8). Alternatively the certified value was based on data that did not produce agreement between methods (As, Ta, U, Zr). IAG has IDMS data to provide missing traceability link for the elements Dy and Er, since IDTIMS is a definitive method. For the other elements, the agreement of IAG laboratory results between two or more independent methods for OU-6 provides traceability to the fullest extent possible. It is this agreement that metrology laboratories often use in establishing traceability to SI of their certified values established using comparative rather than definitive methods. See Table 4b.

5b2) Derivation of certified values and their uncertainties

Certified values for OU-6 are the means of the laboratory averages, after rejection of the very few outliers identified. The mean is used as the least squares best fit of normally distributed data. Normality of all data sets was verified using the Kolmogorov-Smirnov D value, and by verifying the absence of either skewness or kurtosis in the data sets. The Chi-square test for normalcy is less useful, since for all data sets, n<30.

The certified values are based on no fewer than ten individual laboratory results obtained using at least two methods of analysis that are in agreement. While this is less than n=15 recommended by ISO Guide 35 (1989), it appears sufficient, given the other checks through traceability, and the requirement that data be available from at least two independent methods and that the means for those methods be in statistical agreement. The most desirable situation would be to have had an equal number of laboratories providing data for each of the methods, but that was the exception rather than the rule. See Table 5.

Uncertainties have been developed to include components that address random variability within and between laboratories, bias when random between-laboratory variance is insufficient to account for it, material variability where it is quantifiable using data from more than one of the certification laboratories, and non-reproducibility of sample weighing form. Each of the components included in the uncertainty is discussed in the IAG Protocol for Certification under development (IAG 2003) and is summarized below.

The approach taken is less rigorous than that recently outlined by IRMM (Pauwels et al. 1998, van der Veen and Pauwels 2000, van der Veen et al 2001a, 2001b, among others). However, it is in the spirit if not the letter of ISO Guide 35 (1989), and is necessary until geochemical laboratories individually are more experienced in reporting uncertainties according to GUM practices (Eurachem 2000). Briefly, uncertainty has been based on three components of variance for most elements in this certification. These components have been combined in quadrature, and then expanded with the appropriate factor to give a 95% confidence interval. The factor is slightly greater than 2, and variable from one constituent to another, because n<30.

The first component, the standard deviation of the mean of the contributed laboratory results, collects together the random within and between laboratory variances. Between-laboratory anova showed highly significant differences between results from individual laboratories, using

either the same techniques or different ones. This implies bias in results between laboratories and methods. However, because none of the contributed laboratory means used in establishing certified values fell outside the range of mean ± 3z range, it was considered appropriate to treat these biases as random, so long as the final expanded uncertainty of the certified value included all method means based on data from two or more laboratories. Exceptions will be discussed below.

The material variance component is derived from the within-laboratory anovas, with split as the classification variable, and was calculated for each laboratory from the anova tables. When two or more laboratories, including also the laboratory that provided original GeoPT™ homogeneity test measurements, found quantifiable material variance, these material variances were compiled and evaluated statistically.

The median value of material variance rather than the mean was used in calculating overall uncertainty of the certified value for several reasons. First, more than half of all contributing laboratories found material variance to be zero (i.e. F <1), with the one exception of the element copper, for which 10 of 14 laboratories found non-zero material variance. This may have resulted because within-split material variance was larger than between-split material variance, as can often be the case when material variance is due to mineralogical factors. None of these zero material values are included in the mean, so that the mean overstates material variance considerably. Second, the mean values of material variance are themselves highly uncertain; the 95% confidence interval of the mean material variance generally included zero, again suggesting that the mean inflates the true material variance. Finally, the quantifiable material variances did not vary in any predictable way with test portion mass, as theory predicts they would (Ingamells and Pitard 1986), if well-defined.

While current practice requires that an instability component of variance (van der Veen et al. 2001b), it is generally believed that geological materials are stable in storage and shipment, so that any variance due to instability will be immeasurably small in comparison to other components of variance. This belief is based on the fact that materials like G-1 and W-1 have been in use for more than 50 years, contributing greatly to a continual improvement in measurement quality among geoanalytical laboratories, without any updating of the original certified values over that time. To be sure, analysts are able to measure elements today in these materials that could not be measured originally, and values have been developed for these. But the original reference values remain valid after more than 50 years. Thus, the stability component of variance that is included for this certification effort is based entirely on the potential difference between laboratories in establishing a dry rather than wet weight of the material for reporting purposes. Most laboratories in the certification study determined moisture content, in order to then report analyses on a dry weight basis. The between-laboratory uncertainty in determining moisture is taken as the instability component of variance. It is applied only in calculating the uncertainties of the major oxides, as it is too small in comparison to other components of trace element uncertainty to have impact.

There are a few elements for which the bias between method averages is great enough that the above approach seems to underestimate the certified value uncertainty. An alternative method of estimating uncertainty (Schiller 1996), combines in quadrature all Type A component of variance. This Type A variance is expanded, after which the maximum deviation of any method mean from the certified value is added linearly to provide the certified value uncertainty. This procedure applies well to NIST certifications, where each method is employed in-house, but requires significant modification to apply to IAG interlaboratory certifications. After such modification, the 95% confidence interval so obtained is wider than the range of all contributed data, which result seems to overestimate uncertainty, rather than under-estimating it as before.

The Pauwels et al (1998) approach is better suited to interlaboratory certifications. Analysis of variance between laboratories demonstrates significant differences in results between laboratories. However, this difference is already accounted for in the standard deviation of the interlaboratory mean, as discussed above. A second anova was run between methods, using the laboratory average results. This anova showed zero variance between methods (F<1) for many elements, and no statistically significant differences between method means ($1<F<F_{crit}$) for most others. In some cases however, F exceeded F_{crit}, showing significant between-method differences. Whenever U as originally calculated failed to include all method averages (n ≥2 labs using the method), the between method variance obtained from the anova was added in

quadrature to the original components of variance to estimate u for expansion to U. This approach appears to neither underestimate nor overestimate the uncertainty, and is the one taken for the OU-6 certification.

Those elements (FeO, Be, Li, Sb, Tl) that were determined by fewer than ten laboratories, or by a single method (Tm), or for which traceability could not be demonstrated in any manner (CO_2), were assigned information values rather than certified values. In most cases, however, element concentrations have been certified. The certified and information values and their uncertainties (U, 95% confidence interval, =t*u) for all elements determined in OU-6 appear in Table 6. The individual components of variance which were summed before taking the square root to obtain u, and the expansion factor, t, leading to each final U appear in Table 7, along with values for s_w and σ_{LM}, required for users to apply statistical tests given in ISO Guide 33 (2000) in evaluating their CRM data.

It will be noted that in many cases, certification proceeded, despite the fact that uncertainties exceed the target uncertainties (u) (Table 1) established for the certification. The final expanded uncertainties for this CRM are better established and generally smaller than for most other CRMs and RMs issued for use by geoanalytical laboratories, despite exceeding pre-certification targets. The result, however, requires a re-examination of how target uncertainties are established for future certifications. In the process, it would be advisable to compare the uncertainties of metrology laboratory certified values to similarly established targets.

6) Conclusion

IAG has completed the certification of the slate sample OU-6 for 12 major and minor constituents and 35 trace elements, complying with ISO Guidelines in the process to a greater extent than has been achieved with any other geological RM, except for the few produced by NIST (e.g., basalt SRM 688 and obsidian SRM 278). Traceability has been established as fully as possible, using a combination of approaches, including concurrent analysis of an existing RM, use of a definitive technique (gravimitry, IDTIMS), and agreement of results between two or more comparitive methods. Furthermore, validity of the certification for major oxides is obtained through the summation of the major and minor oxides to 100%. The material is now available for distribution and may be obtained by contacting…..

Table 4a   Demonstration of traceability for major oxides based on Shapiro (1975) accuracy requirements. IAG data for JSI-1 in comparison to GSJ certified values.

	Difference GSJ-IAG		Accuracy requirement for major oxides		Conclusion
	absolute, %m/m	relative, %	absolute, or % m/m	relative,%	
SiO_2	0.25	0.42		1	IAG result sufficiently accurate
TiO_2	0.001		0.02		to be found traceable
Al_2O_3	0.093	0.53		1	ditto
Fe_2O_3	0.042		0.10		ditto
FeO	0.29		0.10		ditto
MnO	0.0001		0.02		ditto
MgO	0.025		0.10		ditto
CaO	0.026		0.10		ditto
Na_2O	0.023		0.10		ditto
K_2O	0.028		0.10		ditto
P_2O_5	0.008		0.02		ditto
CO_2	2.644		0.02 or 0.10 depending on whether GSJ or IAG value is "correct"		cannot establish accuracy of IAG result

Table 4b		Demonstration of traceability of OU-6 data through agreement of independent method results		

Element	Overall Mean	IAG Method Means		P
As	13.24	13.19	NAA (2)	0.938
		13.29	XRF (6)	
		13.63	hydride AAS (1)	
		13.05	ICPMS (3)	
Dy	5.061	5.047	ICPMS (14)	0.942
		5.110	ICPAES (2)	
		5.023	IDTIMS (1)	
Er	2.930	2.969	ICPMS (14)	0.190
		2.728	ICPAES (2)	
		2.845	IDTIMS (1)	
Ho	1.027	1.180	NAA (1)	0.092
		1.017	ICPMS (14)	
		1.018	ICPAES (2)	
Sn	2.67	2.728	ICPMS (8)	0.174
		2.435	XRF (10)	
Ta	1.022	1.087	NAA (2)	0.160
		1.12	ICPMS (13)	
Tm	0.451	0.488	ICPMS (13)	0.415
		0.478	ICPAES (1)	
U	1.923	1.914	ICPMS (13)	0.309
		2.028	NAA (1)	
Zr	173.470	174.058	XRF (11)	0.782
		172.375	ICPMS (10)	
		176.0	NAA (1)	
		175.417	ICPAES (1)	

P is the risk of making an error in rejecting the null hypothesis, which states that the difference between the IAG mean and the GSJ certified value is zero.

Table 5   Methods used for OU6 certification analyses and probability that all method means are the same

Oxide/element (no. labs)	Number and identification of methods		P value[*]
SiO_2 (24)	3 methods	XRF(19) ICPAES(4) GRAV(1)	P=0.522
TiO2 (24)	2 methods	XRF(19) ICPAES(5)	P=0.065
Al_2O_3 (24)	3 methods	XRF(19) ICPAES(4) GRAV(1)	P=0.512
Fe_2O_3 (28)	4 methods	NAA(2) XRF(19) ICPAES(6) GRAV(1)	P=0.014
MnO (27)	4 methods	XRF(19) AAS(1) ICPMS(1) ICPAES(6)	P=0.488
MgO (23)	2 methods	XRF(17) ICPAES(6)	P=0.083
CaO (22)[**]	2 methods	XRF(18) ICPAES(4)	P=0.854
Na_2O (25)	5 methods	NAA(2) XRF(15) AAS(1) ICPAES(6) Fl. Photom.(1)	P=0.709
K_2O (24)	5 methods	XRF(16) AAS(1) ICPAES(5) Fl. Photom (1) IDTIMS 1)	P=0.539
P_2O_5 (24)	3 methods	XRF(17) ICPAES(6) COLOR(1)	P=0.294

As (12)**	4 methods	NAA(2) XRF(6) AAS-hydride(1) ICPMS	P=0.938
Ba (24)	5 methods	NAA(2) XRF(8) ICPMS(9) ICPAES(4) IDTIMS(1)	P=0.318
Ce (24)	4 methods	NAA(2) XRF(6) ICPMS(15) IDTIMS(1)	P=0.534
Co (20)	4 methods	NAA(2) XRF(7) ICPMS(8) ICPAES(3)	P=0.968
Cr (21)	4 methods	NAA(2) XRF(9) ICPMS(4) ICPAES(6)	P=0.834
Cs (17)	3 methods	NAA(2) XRF(1) ICPMS(14)	P=0.038
Cu (14)	3 methods	XRF(7) ICPMS(3) ICPAES(4)	P=0.067
Dy (17)	3 methods	ICPMS(14) ICPAES(2) IDTIMS(1)	P=0.942
Er (17**	3 methods	ICPMS(14) ICPAES(2) IDTIMS(1)	P=0.905
Eu (19)	4 methods	NAA(2) ICPMS)14) ICPAES(2) IDTIMS(1)	P=0.572
Ga (16)	2 methods	XRF(8) ICPMS(8)	P=0.301
Gd (16)	3 methods	ICPMS(13) ICPAES(2) IDTIMS(1)	P=0.105
Hf (16)	3 methods	NAA(2) XRF(1) ICPMS(13)	P=0.144
Ho (17)**	3 methods	NAA(1) ICPMS(14) ICPAES(2)	P=0.191
La (21)	5 methods	NAA(2) XRF(3) ICPMS(14) ICPAES(1) IDTIMS(1)	P=0.067
Lu (16)	4 methods	NAA(2) ICPMS(12) ICPAES(1) IDTIMS(1)	P=0.117
Nb (22)	2 methods	XRF(9) ICPMS(13)	P=0.598
Nd (23)	5 methods	NAA(2) XRF(4) ICPMS(13) ICPAES(3) IDTIMS(1)	P=0.349
Ni (20)	3 methods	XRF(9) ICPMS(5) ICPAES(6)	P=0.344
Pb (22)	3 methods	XRF(10) ICPMS(11) ICPAES(1)	P=0.185
Pr (17)	3 methods	XRF(1) ICPMS(14) ICPAES(2)	P=0.062
Rb (26)	4 methods	NAA(2) XRF(10) ICPMS(13) IDTIMS(1)	P=0.983
Sc (16)	4 methods	NAA(3) XRF(2) ICPMS(5) ICPAES(6)	P=0.008

Sm (18)	4 methods	NAA(2) ICPMS(13) ICPAES(2) IDTIMS(1)	P=0.151
Sn (18)	2 methods	XRF(10) ICPMS(8)	P=0.382
Sr (27)	4 methods	XRF(12) ICPMS(10) ICPAES(4) IDTIMS(1)	P=0.783
Ta (15)**	2 methods	NAA(2) ICPMS(13)	P=0.141
Tb (18)	3 methods	NAA(2) ICPMS(14) ICPAES(2)	P=0.348
Th (23)	4 methods	NAA(2) XRF(6) ICPMS(14) ICPAES(1)	P=0.096
U (14)**	2 methods	NAA(1) ICPMS(13)	P=0.26
V (19)	3 methods	XRF(8) ICPMS(4) ICPAES(7)	P=0.526
Y (23)	3 methods	XRF(8) ICPMS(12) ICPAES(3)	P=0.082
Zn (23)	4 methods	NAA(2) XRF(11) ICPMS(4) ICPAES(6)	P=0.787
Zr (23)**	4 methods	NAA(1) XRF(11) ICPMS(10) ICPAES(1)	P=0.859

* P is the risk of making an error in rejecting the null hypothesis, which states that the differences between the two or more method means are zero.

** elements for which traceability cannot be established through the analysis of JSl-1; see Table 4a

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Table 1   Horwitz values and target uncertainties based on them for certification of OU-6

Oxide/element	Horwitz expected betw-lab. precision		Target uncertainty (u)- maximum value	
SiO2	0,625059		0,208353	in % m/m
Al2O3	0,260217		0,086739	
Fe2O3	0,129321		0,043107	
MnO	0,006864		0,002288	
MgO	0,042042		0,014014	
CaO	0,015485		0,005162	
Na2O	0,032607		0,010869	
K2O	0,051586		0,017195	
TiO2	0,019965		0,006655	
P2O5	0,003255		0,001085	
As	0,706797	7,07E-05	0,235599	in ug/g
Ba	15,08537	0,001509	5,028457	
Be	0,183627	1,84E-05	0,061209	
Ce	3,111719	0,000311	1,03724	
Co	1,401857	0,00014	0,467286	
Cr	2,985162	0,000299	0,995054	
Cs	0,468917	4,69E-05	0,156306	
Cu	1,821497	0,000182	0,607166	
Dy	0,313355	3,13E-05	0,104452	
Er	0,149003	1,49E-05	0,049668	
Eu	0,103858	1,04E-05	0,034619	
Ga	1,203726	0,00012	0,401242	
Gd	0,32823	3,28E-05	0,10941	
Hf	0,297815	2,98E-05	0,099272	
Ho	0,080662	8,07E-06	0,026887	
La	1,559472	0,000156	0,519824	
Li	3,748307	0,000375	1,249436	
Lu	0,040589	4,06E-06	0,01353	
Nb	0,788657	7,89E-05	0,262886	
Nd	1,397765	0,00014	0,465922	
Ni	1,829695	0,000183	0,609898	
Pb	1,365363	0,000137	0,455121	
Pr	0,457967	4,58E-05	0,152656	
Rb	4,676047	0,000468	1,558682	
Sb	0,048132	4,81E-06	0,016044	
Sc	1,109331	0,000111	0,369777	
Sm	0,362316	3,62E-05	0,120772	
Sn	0,19		0,06327	
Sr	5,027037	0,000503	1,675679	
Ta	0,084042	8,4E-06	0,028014	
Tb	0,069669	6,97E-06	0,023223	
Th	0,637358	6,37E-05	0,212453	
Tl	0,046641	4,66E-06	0,015547	
Tm	0,039821	3,98E-06	0,013274	
U	0,141668	1,42E-05	0,047223	
V	4,976747	0,000498	1,658916	
Y	1,329521	0,000133	0,443174	

Yb	0,203383	2,03E-05	0,067794
Zn	4,376225	0,000438	1,458742
Zr	6,407144	0,000641	2,135715

Table 2   Assigned values for OU6 from GeoPT9

Oxide/element	Robust Mean in % m/m	standard er of robust m	standard error of robust mean
SiO2	57,513	0,095	0,095
TiO2	0,998	0,004	0,004
Al2O3	20,5	0,032	0,032
Fe2O3 total	9,001	0,033	0,033
FeO	1,65	0,019	0,019
MnO	0,284	0,001	0,001
MgO	2,398	0,010	0,010
CaO	0,74	0,005	0,005
Na2O	1,778	0,016	0,016
K2O	3,051	0,012	0,012
P2O5	0,118	0,002	0,002
LOI	3,604	0,011	0,011
	in ug/g m/m		in ug/g m/m
As	13,00	0,45	0,45
Ba	477,24	4,80	4,80
Be	2,66	0,11	0,11
Ce	74,42	1,11	1,11
Co	29,11	0,48	0,48
Cr	70,87	1,39	1,39
Cs	8,02	0,13	0,13
Cu	39,62	1,05	1,05
Dy	4,99	0,07	0,07
Er	2,98	0,03	0,03
Eu	1,36	0,02	0,02
Ga	24,33	0,29	0,29
Gd	5,27	0,07	0,07
Hf	4,70	0,09	0,09
Ho	1,01	0,02	0,02
La	33,00	0,51	0,51
Li	92,65	2,64	2,64
Lu	0,45	0,01	0,01
Nb	14,79	0,31	0,31
Nd	29,01	0,52	0,52
Ni	39,83	0,71	0,71
Pb	28,22	0,50	0,50
Pr	7,80	0,13	0,13
Rb	120,20	0,9	0,9
Sb	0,55	0,02	0,02
Sc	22,10	0,43	0,43

Sm	5,92	0,08	0,08
Sn	2,72	0,11	0,11
Sr	130,89	1,16	1,16
Ta	1,06	0,02	0,02
Tb	0,85	0,01	0,01
Th	11,51	0,17	0,17
Tl	0,53	0,02	0,02
Tm	0,44	0,01	0,01
U	1,96	0,02	0,02
V	129,35	1,63	1,63
Y	27,35	0,47	0,47
Yb	3,00	0,02	0,02
Zn	111,18	1,4	1,4
Zr	174,15	1,59	1,59

Table 3   IAG mean, standard deviation and standard deviation of the mean
in comparison to the GSJ certified values (Imai et al. 1996) for JSI-1.

	IAG Data				GSJ Reference Values	Comparison
Oxide	Mean	sigma	n	Sigma(Xbar)	Certified	P1
SiO2	59,72	0,196	24	0,125	59,47	0,259
TiO2	0,726	0,0071	25	0,0041	0,725	
Al2O3	17,69	0,080	26	0,051	17,60	
Fe2O3TOT	6,81	0,044	28	0,024	6,764	
FeO	4,23	0,021	4	0,013	4,523	0,327
MnO	0,060	0,0012	27	0,00042	0,0599	
MgO	2,39	0,021	26	0,016	2,413	0,763
CaO	1,51	0,013	27	0,0095	1,479	0,035
Na2O	2,21	0,025	28	0,014	2,184	
K2O	2,87	0,021	28	0,016	2,845	
P2O5	0,194	0,0025	24	0,0020	0,202	0,206
H2O-	0,575	0,023	3	0,018	0,654	
CO2	3,41	0,011	5	0,0060	0,769	
LOI	4,91	0,144	17	0,084		
As mg/kg	13,84278	0,730812	9	0,243604	14,9	0,035
Ba mg/kg	307,2031	11,99924	24	2,449335	305	
Be mg/kg	2,137916	0,119186	9	0,039729	2,28	0,110
Ce mg/kg	58,56666	2,454649	21	0,535648	60,6	0,059
Co mg/kg	15,77206	1,109977	18	0,261624	15,5	0,583
Cr mg/kg	59,9961	3,771668	21	0,823045	60,9	0,808
Cs mg/kg	8,052472	0,340209	17	0,082513	7,6	0,214
Cu mg/kg	39,94627	2,900081	15	0,748798	40,8	0,448
Dy mg/kg	4,829913	0,197963	16	0,049491	5,11	0,119
Er mg/kg	2,840586	0,178827	16	0,044707	1,15	<0.0001
Eu mg/kg	1,239655	0,095661	18	0,022547	1,22	
Ga mg/kg	21,1453	0,988364	16	0,247091	20,7	

Gd mg/kg	5,035146	0,302925	15	0,078215	4,84	
Hf mg/kg	4,541544	0,312531	18	0,073664	4,63	
Ho mg/kg	1,001303	0,067194	18	0,015838	0,688	<0.0001
La mg/kg	28,23641	0,807666	18	0,190369	29,3	
Li mg/kg	51,74682	1,937548	7	0,732324	50,7	
Lu mg/kg	0,438336	0,022941	15	0,005923	0,442	
Nb mg/mg	9,570851	0,58731	21	0,128162	9,53	
Nd mg/kg	27,25884	1,570027	21	0,342608	28,8	
Ni mg/kg	37,11959	2,26029	19	0,518546	37,6	
Pb mg/kg	18,58902	1,112105	18	0,262126	17,4	
Pr mg/kg	6,681856	0,401797	14	0,107385	6,07	
Rb mg/kg	113,5856	4,144236	24	0,845939	117	
Sb mg/kg	0,918788	0,105891	7	0,040023	0,933	0,93
Sc mg/kg	16,48734	1,176845	16	0,294211	16,7	
Sm mg/kg	5,611607	0,29682	18	0,069961	6,02	
Sn mg/kg	2,50256	0,150187	7	0,056765	2,5	0,724
Sr mg/kg	189,479	6,277157	26	1,231052	193	
Ta mg/kg	0,733132	0,062796	14	0,016783	0,842	0,078
Tb mg/kg	0,800473	0,043729	17	0,010606	0,717	
Th mg/kg	9,906693	0,575858	23	0,120075	9,97	
Tl mg/kg	0,559532	0,037033	5	0,016562	0,633	
Tm mg/kg	0,435494	0,035945	14	0,009607		
U mg/kg	2,588355	0,145028	15	0,037446	2,63	
V mg/kg	135,1846	5,744674	17	1,393288	131	0,11
Y mg/kg	28,92232	1,466236	24	0,299294	30	
Yb mg/kg	2,90037	0,156906	18	0,036983	2,81	
Zn mg/kg	108,5386	5,466898	24	1,115926	108	
Zr mg/kg	169,4388	5,150463	21	1,123923	174	0,334

P is not calculated is some instances when visual inspection alone provides valid conclusion (REF ISO
P is risk in rejecting the null hypothesis that the difference between two values, the IAG mean and the G
Differences are significant when P < 0.05.

P1 is risk in rejecting equality of means between IAG data and GSJ certified value.
P2 is risk in rejecting equality of method means or GSJ certification data only.

Table 6

Certified Values and Their Uncertainties (95% confidence intervals) for IAG CRM OU-6

	Certified Value	U=t*u (see text and Table 7)
SiO2 % m/m	57,350	0,3093
TiO2 % m/m	0,995	0,0772
Al2O3 % m/m	20,450	0,3216

e2O3T % m/m	8,945	0,2373
CO3(calc) % m/m	7,115568	
Fe(II)O % m/m	1,645	0,1423
MnO % m/m	0,284	0,0758
MgO % m/m	2,412	0,0799
CaO % m/m	0,741	0,0771
Na2O % m/m	1,758	0,0899
K2O % m/m	3,031	0,0830
P2O5 % m/m	0,118	0,0761
H2O- %m/m	0,143	0,1312
H2O+ %m/m		
CO2 %m/m	0,226	0,1241
LOI % m/m	3,617	0,0987
TOTAL	99,516	
As mg/kg	13,234	0,656049
Ba mg/kg	479,713	13,11814
Be mg/kg	2,525	0,311324
Ce mg/kg	77,072	2,66319
Co mg/kg	29,166	1,059362
Cr mg/kg	70,672	2,1344
Cs mg/kg	8,098	0,276065
Cu mg/kg	40,415	4,906695
Dy mg/kg	5,061	0,138246
Er mg/kg	2,930	0,221967
Eu mg/kg	1,355	0,05483
Ga mg/kg	24,169	0,731291
Gd mg/kg	5,302	0,37669
Hf mg/kg	4,700	0,319965
Ho mg/kg	1,038	0,050996
La mg/kg	33,216	1,836731
Li mg/kg	95,295	4,544566
Lu mg/kg	0,451	0,022497
Nb mg/mg	14,491	0,576165
Nd mg/kg	30,178	1,480841
Ni mg/kg	40,165	1,305957
Pb mg/kg	28,798	0,791979
Pr mg/kg	7,910	0,257839
Rb mg/kg	121,311	3,858616
Sb mg/kg	0,563	0,130752
Sc mg/kg	23,073	3,15662
Sm mg/kg	6,014	0,423055
Sn mg/kg	2,670	0,189225
Sr mg/kg	131,691	2,597759
Ta mg/kg	1,022	0,119293
Tb mg/kg	0,859	0,039936
Th mg/kg	11,311	1,017531
Tl mg/kg	0,538	0,055929
Tm mg/kg	0,451	0,01893
U mg/kg	1,924	0,088791
V mg/kg	129,839	5,146149

Y mg/kg	27,748	0,738686		
Yb mg/kg	2,981	0,101942		
Zn mg/kg	111,427	3,38249		
Zr mg/kg	174,169	5,660151		

Table 7   Standard deviations summed in quadrature to produce u, expansion
and other statistics related to expanded uncertainty U=t*u

Oxide	n labs	sd(mean)	u(bias)	s(matl) median	s(stabil)	t
SiO2 % m/m	24	0,098		0,107	0,037	2,064
TiO2 % m/m	24	0,004		0,005	0,037	2,064
Al2O3 % m/m	24	0,042	0,141986	0,029	0,037	2,064
Fe2O3T % m	28	0,027	0,078198	0,048	0,037	2,048
FeO %m/m	4	0,025			0,037	3,182
MnO % m/m	27	0,001		0,001	0,037	2,052
MgO % m/m	25	0,009		7,85E-03	0,037	2,06
CaO % m/m	23	0,005		2,54E-03	0,037	2,069
Na2O % m/m	26	0,009		2,19E-02	0,037	2,056
K2O % m/m	25	0,009		1,32E-02	0,037	2,06
P2O5 % m/m	25	0,002		1,17E-03	0,037	2,06
H2O- %m/m	4	0,018			0,037	
H2O+ %m/m	2				0,037	3,182
CO2 %m/m	6	0,031			0,037	2,571
LOI %m/m	19	0,029			0,037	2,101
As mg/kg	12	0,215		0,207 na- see text		2,201
Ba mg/kg	24	2,845	23,2091	2,983		2,069
Be mg/kg	9	0,048		0,126		2,306
Ce mg/kg	24	0,727		1,062		2,069
Co mg/kg	20	0,318		0,394		2,093
Cr mg/kg	21	0,901		0,486		2,086
Cs mg/kg	17	0,090		0,094		2,120
Cu mg/kg	14	0,772		2,136		2,160
Dy mg/kg	17	0,055		0,035		2,120
Er mg/kg	17	0,043	0,008144	3,15E-02		2,120
Eu mg/kg	19	0,020		1,63E-02		2,101
Ga mg/kg	16	0,298		1,70E-01		2,131
Gd mg/kg	16	0,078	0,02007	7,19E-02		2,131
Hf mg/kg	16	0,091		1,20E-01		2,131

Ho mg/kg	18	0,020		1,34E-02	2,110
La mg/kg	21	0,292	0,517	4,16E-01	2,086
Li mg/kg	7	1,439		1,17E+00	2,447
Lu mg/kg	16	0,008		6,93E-03	2,131
Nb mg/mg	22	0,167		0,221	2,080
Nd mg/kg	23	0,330	0,2439	0,396	2,074
Ni mg/kg	20	0,486		0,391	2,093
Pb mg/kg	22	0,247		0,290	2,080
Pr mg/kg	17	0,094		0,078	2,110
Rb mg/kg	26	0,746		1,718	2,060
Sb mg/kg	6	0,024		0,045	2,571
Sc mg/kg	16	0,396	1,912	0,354	2,131
Sm mg/kg	18	0,068	0,02119	0,120	2,110
Sn mg/kg	10	0,084			2,262
Sr mg/kg	27	0,957		0,825227	2,056
Ta mg/kg	15	0,018	0,002702	0,010	2,131
Tb mg/kg	18	0,015		0,012	2,101
Th mg/kg	23	0,121	0,1706	0,236	2,074
Tl mg/kg	6	0,021			2,571
Tm mg/kg	14	0,009		0,007	2,160
U mg/kg	14	0,028		0,029791	2,160
V mg/kg	19	1,189		2,141	2,101
Y mg/kg	23	0,247		0,257	2,074
Yb mg/kg	19	0,037		0,032	2,101
Zn mg/kg	23	0,955		1,322	2,074
Zr mg/kg	23	1,266		2,418	2,074

s(w) is pooled within-laboratory standard deviation

sigma(LM) is between-laboratory standard deviation

       and should be similar in value to the Horwitz factor Ha (Table 1)

sd(mean)=sigma(LM)/square root(n-1)