The trials and tribulations of certifying geological reference materials using the GeoPT proficiency testing programme.

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#### Outline

- Why are reference materials important in geochemical research.
- Earlier approaches to the characterization of geological reference materials.
- GeoPT proficiency testing programme.
- Opportunities for certification of RMs provided by ISO Guide 35.
- The way in which GeoPT complies with these certification requirements.

#### **Other considerations**

ISO/REMCO Guide 35 is currently under revision (ISO TC334).

Issues in the interpretation of documentation.

Period	Geochemical research	Technical innovation	Use to which data was put
1920s-	Major elements	Classical then rapid methods	Classification of rock types.
1960s-			
1970s-			
1980s-			
1990s-			
2000s-			

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1980s-	Radiogenic isotope geochemistry	TIMS	Age of geological processes.
1990s-			
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1980s-	Radiogenic isotope geochemistry	TIMS	Age of geological processes.	
1990s-	Stable isotope geochemistry	High resolution ICP-MS	Climate and environmental change over geological time scales.	
2000s-	All above in an individual mineral scale	Microbeam techniques (LA-ICP-MS, SIMS)	Assessment of the above phenomena on a mineral scale.	

#### Elements involved in geochemical research

Major elements	SiO <sub>2</sub> , TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> T, MnO, MgO, CaO, Na <sub>2</sub> O, K <sub>2</sub> O, P <sub>2</sub> O <sub>5</sub>
<b>Trace elements (XRF)</b>	Ni, Cu, Zn, Ga, Rb, Sr, Y, Nb, Zr, Ba, Pb
REE (INAA)	La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu (+ Ta, Hf, Th)
Radiogenic isotopes	Nd/Sm, Rb/Sr, U/Th/Pb
Stable isotopes	H, C, N, O, S, Fe, Cu, Zn, Mo
Modern lab (routine use of ICP-MS, XRF and ICP- AES)	SiO <sub>2</sub> , TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> T, MnO, MgO, CaO, Na <sub>2</sub> O, K <sub>2</sub> O, P <sub>2</sub> O <sub>5</sub> , Ag, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Li, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Tl, Tm, U, V, W, Y, Yb, Zn and Zr.

#### **Development of geological reference materials**

## G1 (Granite) and W1 (Diabase).

One of the most important early investigations (1940s-1950s) in the characterization of geological reference materials was undertaken by the US Geological Survey/MIT/Carnegie Institute

**Reason:** To develop a well characterized RMs for the calibration of dc arc OES.

**Programme:** Samples distributed and 34 laboratories from 10 countries who reported results (mainly by classical methods).

Results of interlaboratory study (Fairburn et al., USGS Bulletin 980, 1951):

- Significant interlaboratory bias.
- "The normative variation was so extreme that in the absence of direct evidence to the contrary, there would be little reason to suppose that all the analyses submitted were of the same two rocks" (Chayes, 1951).

See also AMC Technical Brief No.26 (2006) - How good were analysts in the good old days before instrumentation?

## What followed the G1/W1 study?

- The need for geological reference materials recognized.
- Indeed, because of the importance of *matrix matching (especially the mineralogy)*, ideally a RM for every known rock type.
- The benefits of participation in *interlaboratory trials* recognized (no PT schemes yet!).
- There then followed a *free for all* (unregulated) period in which many geological reference materials were issued.
- *Early contributors:* US Geological Survey (*Father Flanagan*), Geological Survey of Japan (*Terashima and others*), Centre de Recherches Pétrographiques et Géochimiques, France (*Raj Govindaraju*), National Institute for Metallurgy, South Africa (*T.W. Steele*), Geological Survey of Canada (*Sidney Abbey*)

## During this period (1970s-1990s), how were geological reference materials characterized?

- (i) Using a limited amount of data from the *survey's own laboratories*.
- (ii) Data from *selected labs* invited (or paid) to participate.
- (iii) Data from any lab who wished to contribute (*no assessment of competence*).
- (iv) In at least one case, new (potential) RMs were issued with guide values, but no properly assessed reference values at all.
- (v) At the same time, there developed a practice of *compiling data published in the research literature* to derive reference values. These compilations were often undertaken by independent researchers (not the RM producer).

There are difficulties in demonstrating current ISO-REMCO compliance with some of these approaches!

But, ISO REMCO was not established until 1975 and the first (?) edition of ISO-REMCO Guide 35 (Certification of reference materials – General and statistical principles) was not published until 1989.

#### **ISO-REMCO – Committee on reference materials – TC334**

- Established in 1975.
- To establish concepts, terms and definitions related to reference materials.
- To specify the basic characteristics of reference materials as required by their intended use.
- To propose actions on reference materials required to support other ISO activities.
- To **prepare guidelines** for ISO technical committees when dealing with reference material issues.
- To communicate with other international organizations on reference material matters.
- To advise the ISO Technical Management Board (TMB) on reference material issues.
- ISO REMCO was an advisory committee that published Guides but is now a formal ISO Technical Committee with the authority to develop new standards.

#### Why all this interest in <u>Certified</u> Reference Materials?

#### **Definitions from VIM3 (under review):**

## **5.13** (6.13) **reference material RM**

material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in **measurement** or in examination of **nominal properties** 

#### **5.14** (6.14) certified reference material CRM

**reference material**, accompanied by documentation issued by an **authoritative body** and providing one or more specified property values with associated **uncertainties** and **traceabilities**, using valid procedures Therefore, a CRM represents a higher metrological standard because property values must be accompanied by **uncertainties** and a statement of **traceability**.

#### **2.26** (3.9)

#### measurement uncertainty

non-negative parameter characterizing the dispersion of the **quantity values** being attributed to a **measurand**, based on the information used

## **2.41** (6.10) metrological traceability

property of a **measurement result** whereby the result can be related to a reference through a documented unbroken chain of **calibrations**, each contributing to the **measurement uncertainty** 

#### ISO-REMCO Guide 35 – Use of Proficiency Testing for Certification Characterisation Studies

**ISO Guide 35:2017** (Reference materials – Guidance for characterization and assessment of homogeneity and stability).

The 2017 Guide accepted (for the first time) that proficiency testing could in some circumstances by used in certification studies.

#### After listing all the disadvantages of doing so:

"Nonetheless, it can be useful to consider **combining characterization studies for RMs with other studies to save costs**, providing that due care is taken to avoid the principal disadvantages and that certain conditions are met. A.3.2 provides guidance on the principal disadvantages; clause A.3.3 provides conditions for combination of such studies with RM characterization".

#### ISO-REMCO Guide 35 – Use of Proficiency Testing for Certification Characterisation Studies

• Are there opportunities to use the GeoPT Proficiency Testing Programme for the certification of geological reference materials?

#### **GeoPT Proficiency Testing Programme**

- Established in 1994 and now operated by the International Association of Geoanalysts
- Designed for laboratories that **routinely measure silicate rocks** for the major elements and a wide range of trace elements.
- No requirement for laboratories to demonstrate competence before participating.
- Laboratories are sent test materials twice a year.
- Typically, over **100 laboratories** world-wide participate in each round.
- Reports from previous rounds are available on the IAG web site.

(https://www.geoanalyst.org/geopt-previous-rounds/).

## What do we know of GeoPT participants?

1. Please indicate which of the following categories best describes the function (0 of your organisation. point)



#### Type of establishment.

2. Please indicate your role in the organisation that you represent. (0 point)

#### **GeoPT contact.**

Technical	23
Quality Control	16
Managerial	17
Other	6



Main analytical activity of organization.

## **Details of GeoPT participants**

Please indicate the extent to which the following activities form part of your (0 analytical workload.



## **Details of GeoPT participants**

4. Please indicate the length of your experience of the GeoPT scheme . (0 point)

- 2 years or less experience of the... 10
- 3 to 6 years experience of the G... 14
- Over 6 years experience of the ... 38



Number of years participating in GeoPT.

5. Please indicate any experience you may have of other PT schemes. (0 point)

Experience of other GeoPT schemes.

- No experience of other PT sche... 28
- Some experience of other PT sc... 34



#### **Details of GeoPT participants**

7. Please tell us if your analytical laboratory is accredited? (0 point)

33

Accreditation

key words.

Yes, for all procedures involved i... 10

- Yes, for some procedures involv... 14
- Yes, but not for any procedures i... 5
- No methods are accredited



Is your lab accredited?

7 respondents (27%) answered ISO/IEC for this question.



#### **Details of GeoPT participants**

13. How important to you are the following benefits of participating in GeoPT? (0 point)

Very important

Moderately important

■ Not important ■ Irrelevant

Confirmation of your analytical capabilities

Recognition of specific analytical shortcomings

Ongoing improvement of the general performance of your...

Demonstrating your capabilities to clients

Satisfying accreditation requirements

Acquisition of well characterised samples



#### Benefits of participating in GeoPT.

#### What sort of material is distributed to GeoPT participants?

Finely ground silicate rock powder (at least 125 x 40 g). Options:

- (1) An established RM or CRM (Ideal but rarely possible *commercial cost could be more than £15,000 per round*).
- (2) -
- (3) -

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- (2) A material prepared from high purity chemical reagents (Although such a material might match the chemical composition of a silicate rock, it cannot match the mineralogy).

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#### What sort of material is distributed to GeoPT participants?

Finely ground silicate rock powder (at least 125 x 40 g).

**Options:** 

- (1) An established RM or CRM (Ideal but rarely possible commercial cost could be more than £15,000 per round).
- (2) A material prepared from high purity chemical reagents (Although such a material might match the chemical composition of a silicate rock, it cannot match the mineralogy).
- (3) A representative silicate rock, the composition of which is assessed from the results submitted by participating laboratories (Only practical option).

# Assessing the composition from the results submitted by participating laboratories.

- As a consequence, data distributions must be assessed to derive **consensus values** that are judged to be the best estimates of the true composition.
- In GeoPT, practical experience has led to procedures based on **robust statistical procedures** with the use of **expert judgement** to assess the quality of data distributions.
- Precision targets (the standard deviation for proficiency testing) is set by a modified form of the Horwitz function.
- *(see AMC Technical Brief No.17 (2004) The amazing Horwitz function).*
- Experience has also led to circumstances where **analytical bias** can be detected in contributed data distributions.

#### Assessing GeoPT data distributions

#### **Example of 'good' GeoPT data distributions**

Data plotted in increasing order of magnitude as the difference between individual values and the consensus value.



- Majority of data is within the inner tram lines (z=+/-2).
- Mix of procedures contribute to this section.
- Clearly defined point of inflection corresponding to the consensus value.
- No distracting tails.
- Estimators converge.

AD – acid digestion FD – fusion disk (XRF) PP – powder pellet (XRF) FM/AD – fusion followed by acid digestion. AD/FM – Acid digestion followed by fusion of residue. Si - sintering

```
Sample preparation
```

6	estimator	S					
	analyte	n	median	robust	Rmode mean	Mike's mode	Mike's mode boot
	Cu	79	52.4	52.509	52.725	52.511	52.201

# Examples of distributions judged to be not sufficiently good to allocate an 'assigned' value.

GeoPT46 - HG-1 - Grandodiorite 600 z'= 2 z = 2 500 gy/gm prep outlier AD PP FD FM AD 400 SI other AD FM laboratory code

- Data distribution fails the Horwitz precision target test.
- Poorly defined point of inflection.
- Consensus value only suitable as an information value.

AD – acid digestion.
PP – powder pellet (XRF).
FD – fusion disk (XRF).
FM/AD – fusion followed by acid digestion.
Si – sintering.
AD/FM – Acid digestion followed by fusion of residue.

Sample preparation

#### Examples of distributions judged to demonstrate analytical bias



# Rigorous criteria for allocating 'assigned value' status to a GeoPT consensus value.

- Sufficient laboratories (15 or more) had contributed data to the region of the distribution from which the consensus value was evaluated.
- Visual assessment gave confidence that a substantial proportion of the results distribution was symmetrically disposed about the consensus.
- The **ratio of the uncertainty** in the location estimate to the target precision was an acceptably small value.
- An evaluation of measurement results by procedure including both methods of measurement and sample preparation indicated no significant **procedural bias** among the results from which the consensus was derived.

# Some issues on how GeoPT complies with ISO/REMCO Guide 35 as a certification scheme'

"Decide, before the start of a study, *which subset of data from specified laboratories will be used for value assignment.*"

Note that there is no requirement for laboratories to demonstrate their competence to participate in the GeoPT proficiency testing scheme.

**Evaluation of competence was undertaken on GeoPT round 39** 

**Test Material:** Syenite SyMP-1

**Co-analysed CRM:** nepheline syenite CGL 006 (LNS).

102 laboratories contributed to SyMP-1

	Laboratory selection criteria	Rationale for selection criteria
1	Use data from labs that participated in at <b>least three of the last four GeoPT proficiency testing rounds</b> .	Regular participation means lab has effective quality control procedures and has had an opportunity to respond to z-score feedback.
2		
3		
4		
5		
STEREDT		

	Laboratory selection criteria	Rationale for selection criteria
1	Use data from labs that participated in at least three of the last four GeoPT proficiency testing rounds.	Regular participation means lab has effective quality control procedures and has had an opportunity to respond to z-score feedback.
2	Use data from labs that reported <b>at least 70% 'satisfactory'</b> according to the GeoPT z-score criterion whereby $-2 < z < 2$ .	Competent laboratories should consistently contribute satisfactory data.
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3	Use data from labs that reported <b>at least 70% 'satisfactory'</b> measurement results (according to the GeoPT z-score criterion whereby $-2 < z < 2$ ) <b>on the co-analysed CRM</b> .	Competent laboratories should consistently contribute satisfactory data. In this case the evaluation is based on the CRM results.
4		
5		

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3	Use data from labs that reported at least 70% 'satisfactory' measurement results (according to the GeoPT z-score criterion whereby $-2 < z < 2$ ) on the co-analysed CRM.	Competent laboratories should consistently contribute satisfactory data. In this case the evaluation is based on the CRM results.
4	Use data from laboratories that <b>reported satisfactory data</b> (according to the GeoPT z-score criterion whereby $-2 < z < 2$ ) <b>on the co-analysed CRM</b> , restricting measurands to only those that gave such satisfactory data.	If measurement results on the CRM are satisfactory, it is likely that those on the test sample will be as well.
5		

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3	Use data from labs that reported at least 70% 'satisfactory' measurement results (according to the GeoPT z-score criterion whereby $-2 < z < 2$ ) on the co-analysed CRM.	Competent laboratories should consistently contribute satisfactory data. In this case the evaluation is based on the CRM results.
4	Use data from laboratories that reported satisfactory data (according to the GeoPT z-score criterion whereby $-2 < z < 2$ ) on the co-analysed CRM, restricting measurands to only those that gave such satisfactory data.	If measurement results on the CRM are satisfactory, it is likely that those on the test sample will be as well.
5	No selection criteria – <b>use the full GeoPT data set</b> for the assessment of consensus values.	The rationale for this approach is that when measurement results are assessed from a large number of laboratories operating independently of one another, errors will cancel out.





#### **Conclusion:**

No advantage was observed in using a sub-set of labs participating in GeoPT round 39, compared with evaluating consensus values and uncertainties from the full data set.





An Evaluation of Methods for Assessing the Competence of Laboratories Based on Performance in the Geo*PT* Proficiency Testing Scheme

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The original certification protocol, published by the International Association of Geoanalysts in 2003, specified that the competence of laboratories selected as competent to contribute certification measurements should be evaluated from their performance in the GeoPT proficiency testing programme. Round 39 of the IAG GeoPT proficiency testing programme provided an opportunity to examine four methods of evaluating laboratory competence based largely on the use of proficiency testing z-scores as performance indicators. This opportunity arose because two test materials were co-analysed by participating laboratories in this round: a syenite, SyMP-1, supplied by the USGS, and an established CRM, the nepheline syenite, CGL 006. The performance of laboratories was assessed in four ways; in each case, consensus values and their uncertainties as derived from selective data sets of competent laboratories were compared with results derived from the routine GeoPT data assessment, involving all submitted measurements. An overall comparison of results showed no significant statistical differences in either consensus values or unextrainties between these data sets. This conclusion was unexpected and calls into question the widely held assumption that 'better' consensus data would be obtained from a subset of laboratorize judged to be competent on the basis of proficiency testing performance indicators.

Keywords: reference material certification, laboratory competence, laboratory selection, GeoPT, proficiency testing, USGS SyMP-1, syenite, CGL 006.

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As an alternative to demonstrate the competence of participating laboratories, is it possible to demonstrate the <u>competence of the proficiency testing scheme itself</u>?

Specifically, by comparing GeoPT consensus values with certified values on the small number of occasions when Certified Reference Materials have been used as GeoPT test materials.

## **GeoPT versus CRM comparison**

GeoPT round	Origin	Name	Rock type	Certified by
GeoPT9	IAG (International Association of Geoanalysts)	OU-6	Penrhyn Slate	IAG Certification Protocol (Competent labs selected by PT and asked to submit certification quality data)
GeoPT12	MGL (Central Geological Laboratory, Mongolia)	GAS	Serpentine	IAG Certification Protocol
GeoPT14	MGL (Central Geological Laboratory, Mongolia)	OShBO	Alkaline Granite	IAG Certification Protocol
GeoPT16	NIST	SRM 688	Basalt	NIST standard procedures (mainly primary methods)
GeoPT25	Instituto di Geociencias (Campinas, Brazil)	BRP-1	Basalt	In collaboration with the US Geological Survey
GeoPT27	MGL (Central Geological Laboratory, Mongolia)	AND	Andesite	Accredited procedures, CGL, Mongolia



Figure 1. Comparison of certified and assigned values with lines of equality for (a) IAG OU-6, (b) MGL-GAS, (c) MGL-OShBO, (d) NIST SRM 688, (e) BRP-1, (f) MGL-AND.

# GeoPT versus CRM comparison

**X** axis: Certified value.

Y axis: GeoPT consensus value.

Major and trace elements plotted on a **log scale.** 



Figure 2. Comparison of uncertainties on assigned values and on certified values showing the lines of equality for (a) IAG OU-6, (b) MGL-GAS, (c) MGL-OShBO, (d) NIST SRM 688, (e) BRP-1, (f) MGL-AND.

# GeoPT versus CRM comparison

X axis: Uncertainty in certified value.

**Y axis:** GeoPT uncertainty in GeoPT consensus value.

Major and trace uncertainty data plotted on a **log scale.** 

#### **GeoPT versus CRM comparison - Conclusions**

- A statistical analysis of these data showed that the difference between individual assigned and certified values **seldom reached significance**, except for a few values in two of the six CRMs (MGL-OShBO and NIST SRM 688).
- More importantly, when differences were **scaled** according to the respective GeoPT fitness-for-purpose criteria, there was no suggestion of differences of a consequential magnitude.
- GeoPT assigned values are a **reliable estimate** of the true quantity value derived from the rigorous certification process and are fit for purpose for use in the GeoPT scheme.

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The Reliability of Assigned Values from the Geo*PT* Proficiency Testing Programme from an Evaluation of Data for Six Test Materials that have been Characterised as Certified Reference Materials

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Assigned values derived from the GeoPT proficiency testing programme were compared with certified values for six carfield reference materials that have been used as test materials in the GeoPT programme. Statistical analysis showed that there were few significant differences between these sets of data and that these differences had no significant impact on the GeoPT assessment when fitnessfloe-purpose criteria were taken into account. Les valeurs attribuées dérivées du programme de test d'aptitude GeoPT ont téé comparés avec les valeurs certifiées pour six matéricaux de référence certifiés qui ant été utilsés comme matériaux de test dans le programme GeoPT. L'analyse statistique a montré qu'IJ y avait peu de différences significatives entre ces ensembles de données, et que ces différences significatives entre ces ensembles de données, et que ces différences significative sur l'appréciation GeoPT quand les critères d'usage on téé pris en compte.

Mots-clés : test de compétence, valeur attribuée, valeur certifiée, GeoPT, analyse statistique, aptitude à l'emploi

Keywords: proficiency testing, assigned value, certified value, GeoPT, statistical analysis, fitness for purpose Received 25 Sep 14 – Accepted 19 Mar 15

The GeePT proficiency testing scheme is organised by the International Association of Geoanalysts (IAG) and has been in operation since 1995. The scheme is designed for the evolucion of the performance of laboratories involved in the routire analysis of slicate rads and is undertaken in accordance with a published protocal (Thompson 2002), which was written to demonstrate compliance with the URAC international homonisate protocal (Thompson 2002) and the principal aim is to provide each participating laboratory with information to decide whether analytical performance is judged to be satisfactory or may be subject to unsuspected analytical bias. Full details of the scheme may be found in Thompson (2002), Posts et al. (2013) and the various. GeoPT reports cide below.

Although this proficiency testing scheme is designed to provide quality control information to participating laboratories, it is accessionally used for the selection of laboratories judged to have satisfactory performance to contribute to the

certification of aeological reference materials using the IAG certification protocol (Kane et al. 2003). The IAG protocol was designed to establish good practice in the certification of geological reference materials by complying to the fullest extent possible with ISO Guide 35 (2006). Certified reference values and associated uncertainties obtained for CRMs produced according to the IAG protocol are essentially the most reliable values currently available, representing the current best estimates of locations of possible true composition values. Six samples, to date, have been both circulated as GeoPT proficiency testing samples and certified as reference materials. These samples are IAG OU-6 (Penrhyn slate), MGL-GAS (serpentinite), MGL-OShBO (alkaline aranite), NIST SRM 688 (basalt), BRP-1 (basalt) and MGLAND (andesite). Of these, NIST SRM 688, BRP-1 and MGLAND were independently certified before being made available for circulation as GeoPT test samples and were distributed anonymously, so that GeoPT participating laboratories had no prior knowledge of the compositions.

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Geostandards and Geoanalytical Research (2015), 39, 407-417).

## **GeoPT and traceability**

Values that are certified using the GeoPT certification protocol are primarily traceable to a rigorously assessed consensus values derived from this well characterized proficiency testing scheme itself, noting:

#### PROs

- Over 100 participating laboratories.
- A rigorous assessment of consensus values from the distribution of submitted results is undertaken in GeoPT that has allowed the recognition of **method bias**.
- GeoPT consensus values agree with certified values when **CRMs** have been available as test materials.
- The GeoPT certification scheme requires the **co-distribution of an established matrixmatched CRM**.

#### CONs

- Traceability to a **consensus value** is controversial.
- Lack of clarity in ISO-REMCO Guide 35 in the use of proficiency testing schemes for certification creating uncertainty in some aspects of the present proposal.

#### However:

#### The last word on GeoPT and traceability?

Abraham Lincoln quote	Measurement science equivalent
You can fool all of the people some of the time.	Reporting measurement results with an incomplete uncertainty budget.

## GeoPT and traceability – the last word?

Abraham Lincoln quote	Measurement science equivalent
You can fool all of the people some of the time.	Reporting measurement results with an incomplete uncertainty budget.
You can fool some of the people all of the time.	A reference to those laboratories that do not participate in proficiency testing??

## GeoPT and traceability – the last word?

Abraham Lincoln quote	Measurement science equivalent
You can fool all of the people some of the time.	Reporting measurement results with an incomplete uncertainty budget.
You can fool some of the people all of the time.	A reference to those laboratories that do not participate in proficiency testing??
But you cannot fool all of the people all of the time	"A properly developed consensus from a proficiency test is, for all practical purposes, interchangeable with a certified value derived from an interlaboratory comparison" (Thompson 2018)

#### And finally – A summary of GeoPT as a certification scheme

- The candidate CRM and an independently certified CRM (matrix matched) are circulated as test materials in the same GeoPT round.
- Consensus values are evaluated using **robust statistics** from the **full set of data** submitted by participating laboratories for both test materials.
- A comparison is made between certified and GeoPT consensus values for the established CRM to establish the **absence of significant bias**.
- Consensus values in the candidate CRM are considered to qualify as certified values if they comply with the **rigorous criteria as GeoPT 'assigned' values**.

This scheme is currently being applied to the certification of a Meissen Granite.

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GEOSTANDARDS and GEOANALYTICAL RESEARCH

The GeoPT Proficiency Testing Programme as a Scheme for the Certification of Geological Reference Materials

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ISO Guide 35:2017 provides, for the first time, an alternative way of characterising certified reference materials using proficiency testing. In this paper, the properties of assigned values derived from the vell-established GeoPT proficiency testing scheme are examined. This scheme, designed for laboratories that undertake the routine analysis of silicate rocks and related materials, routinely has over 100 participants contributing results. Following a detailed assessment of the metrological properties of GeoPT assigned values, provided a number of criteria are met. These criteria include the following: a demonstration of sufficient homogeneity of the candidate CRM; circulation, when judged to be appropriate, of an established matrix-matched CRM for co-analysis in that round; the robust statistical analysis of data sets using GeoPT established criteria; a decision whether assigning a value is justified (including a requirement of a minimum of fifteen value sculls); and an expert group to manage the certification and the maintenance of appropriate records. In summary, the GeoPT proficiency testing scheme, subject to the arrangements summarised above, is considered to be competent for the certification of geological reference materials.

Keywords: certification protocol, proficiency testing, GeoPT, ISO Guide 35, assigned values, certified value.

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