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Empirical Approach for Estimating Reference Material Heterogeneity and Sample Minimum Test Portion Mass for "Nuggety" Precious Metals (Au, Pd, Ir, Pt, Ru)

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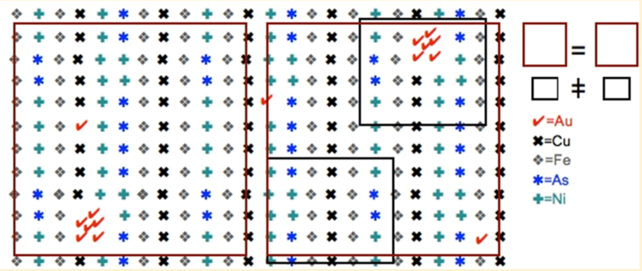

ABSTRACT: Quantification of precious metal content is important for studies of ore deposits, basalt petrogenesis, and precious metal geology, mineralization, mining, and processing. However, accurate determination of metal concentrations can be compromised by microheterogeneity commonly referred to as the "nugget effect", i.e., spatially significant variations in the distribution of precious metal minerals at the scale of instrumental analytical beam footprints. There are few studies focused on the spatial distribution of such minerals and its detrimental effects on quantification of the existing suite of relevant reference materials (RM). In order to assess the nugget effect in RM, pressed powder pellets of MASS-1, MASS-3, WMS-1a, WMS-1, and KPT-1 (dominantly sulfides) as well as CHR-Pt+ and CHR-Bkg (chromite-bearing) were mapped with micro-XRF. The number of verified nuggets observed was used to recalculate an effective concentration of precious metals for the analytical aliquot, allowing for an empirical estimate of a minimum mass test portion. MASS-1, MASS-3, and WMS-1a did not contain any nuggets; therefore, a convenient small test portion could be used here (<0.1 g), while CHR-Pt+ would require 0.125 g and WMS-1 would need 23 g to be representative. For CHR-Bkg and KPT-1, the minimum test portion mass would have to be ~80 and ~342 g, respectively. Minimum test portions masses may have to be greater still in order to provide detectable analytical signals. Procedures for counteracting the detrimental manifestations of microheterogeneity are presented. It is imperative that both RM and pristine samples are treated in exactly the same way in the laboratory, lest powders having an unknown nugget status (in effect all field samples for analysis) can not be documented to be representing a safe minimum mass basis.

Gold, Pt, Pd, Ru, and Ir are important elements in many geoscience and cosmochemical studies, for example, as tracers of early planetary histories because of their siderophile nature, e.g.,[1] and play an especially important role in economic geology. The precious metals (Au, Pd, Ir, Pt, Ru) are studied in order to understand how important types of ore deposits form and are also of interest as proxies of geochemical processes in general petrology. Accurate determination of the abundance of these elements in whole rock and mineral analysis is therefore of significant interest.

However, estimating the concentration of these elements within an analytical sample is often difficult for three reasons: (1) a lack of an adequate number of reference materials (RM) for calibration and quality control, and (2) many of the current RM show some significant heterogeneity (nugget effects), due to the presence of small grains of platinum group metals (PGM) or clusters thereof. The nugget effect becomes increasingly important when lower mass test portions are used in analytical techniques including isotope dilution, often limiting the possible mass to less than a gram. (3) The status of the analytical aliquot itself often constitutes the most critical element in the full field-to-analysis pathway in that typically nothing is known regarding the heterogeneity of PGM mineral grains (size(s), spatial distribution) in the field specimen and very often neither of the subsamples derived on the path to the aliquot. Savard et al.[2] showed that, for some samples, the use of a "too small" mass test portion can introduce large uncertainties in estimates of precious metal concentrations. It is necessary to follow the stipulations governing representative primary, secondary, and tertiary sampling and subsampling, in all steps lest the possibility to document a representative relationship between the aliquot and the original field rocks is forfeit.[3−5] When considering the uncertainty of metal abundance estimates for a given sample, it is not only necessary to be in command of representative sampling principles but also critical to consider the relevant lower limit for the mass test portion that should be used. As such, reliable determination of nugget presence and abundance will provide a more realistic estimate of the minimum mass test portion than convenient models based on assumptions that may not be realistic for most samples (see further below).

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Table 1. Description of Reference Materials (RM)[a]

		critical phases			
RM	petrography	mineral	formula	maximum nugget size (mm)	reference
CHR-Pt+	chromitite from a dunite pod	sperrylite	$PtAs_2$	250	14
		gemkinite	$(Pt,Pd)_4Sb_3$		
		hongshiite	PtCuAs		
		alloy	Pt−Pd−Cu		
		alloy	Pt−Pd−Au−Cu		
CHR-Bkg	serpentinized chromite-bearing dunite	laurite	RuS_2	ND	14
		irarsite	(Ir,Ru,Rh,Pt)AsS		
MASS-1	precipitated amorphous sulfide		$(Fe,Cu,Zn)S\ H_2O$	ND	39
MASS-3	precipitated amorphous sulfide		NiS	ND	40
WMS-1	massive sulfide (pyrrhotite 60%, clinochlore 11%, pentlandite 9%, clinopyroxene 6%, chalcopyrite 4%)	sperrylite	$PtAs_2$	145	29, 30
		sudburyite	(Pd,Ni)Sb	13	
		kotulskite	Pd(Te,Bi)	10	
WMS-1a	same as WMS-1	same as WMS-1			29, 30
KPT-1	quartz diorite	unknown		ND	34

[a] Note: ND = not determined.

In most geological samples, precious metals are substituted in base metal sulfides or oxides or make up discrete phases where precious metals are the main constituents and which, if present in low concentrations, are prone to show a nugget effect, e.g.[6−13] In some RM, such as CHR-Pt+,[14] the presence of precious metal-rich phases such as sperrylite ($PtAS_2$) and laurite ($(Ru,Os,Ir)S_2$) is well documented.[15] The presence of such low abundance-high concentration phases are the main cause of localized heterogeneities for low mass test portions. Heterogeneity is a function of the modal composition of the material involved, and the presence or absence of such discrete phases in the analytical aliquot will significantly impact the measured concentration. Also, the grain size distribution(s) is a part of the heterogeneity status. For example, a single 10 μm Pt nugget can increase the estimated Pt concentration by more than 10 ng/g for a 1 g test mass portion. Characterization of the nugget effect potential is therefore critical for valid analysis of the precious metals (Au, Pd, Ir, Pt, Ru) and is also the only guarantee for an accurate estimate of the relevant total measurement uncertainty. There are several compositional systems not only in the geosciences but also in technology and industry, in which analogous nugget effects may be on the agenda as well, which to a large extent can be treated with the same approach as the one brought forward here.

Potts[16] calculated minimum mass test portions at defined uncertainty levels for Au and Zr. His calculations were based on the assumption that all Au or Zr is held in discrete phases. However, mass balance studies of sulfide ores show that this is seldom the case, e.g.[7−9,12,13,17−20] Moreover, it is also *assumed* that such phases can be *perfectly* pulverized into *round* fragments that are *distributed evenly* throughout all subsamples. Actual samples are often very different from such *ideal assumptions* as shown by the experience of many analytical laboratories that assess precious metal concentrations; see, e.g., Lyman[21,22] for an in-depth discussion of this feature from the point of view of the Theory of Sampling (TOS). In order to estimate heterogeneity at analytical scales, Potts[16] made an initial *approximation* regarding the effect of a calculated sample weight required to achieve a predetermined sampling precision (0.1−20% at one standard deviation), based on a Poisson *model* for discrete mineral phases (*identically sized* spherical particles containing *all* the minor/trace elements in question), *assumed* to be present with a *random spatial distribution*. While these assumptions are simplistic with regards to the real-world heterogeneity of ground mineral fragments, such calculations nevertheless do provide a useful *first order* indication of minimum mass test portions needed to counteract heterogeneity effects at test mass portion scales, but this is not enough.

In real world samples, even the finest ground mineral fragment powder assemblages display a nontrivial size distribution range, not a uniform fragment size. This will, in all likelihood, contribute toward segregation and/or local clustering (grouping) effects as a function of significant density contrasts, which will be exacerbated with respect to analysis to the degree that different grain sizes carry different elemental concentrations. Assumptions of random spatial distribution are inherently false given the ubiquitous residual heterogeneity displayed by all naturally occurring materials.[3,23] Poisson model assumptions may or may not correspond to the reality of heterogeneity distributions of elements within real world samples;[24] it is certainly not satisfactory to rely on such model assumptions without corroborating evidence.

Potts et al.[14] highlighted this in their report that evaluated homogeneity within the RM CHR-Pt+ and CHR-Bkg (both chromite-bearing ($(Fe, Mg)Cr_2O_4$) samples). Despite diligent statistical testing, these RM defied attempts to resolve severely diverging analytical results from analytical laboratories (in fact, no recommended values could be established for most precious metals). In conclusion, it was noted that for CHR-Pt+ the results reflected lingering heterogeneity effects *in* and *between* the prepared 100 g delivery batches. These issues can only be fully understood when it is acknowledged that all characterizations of heterogeneity require a consideration of the contributions from both compositional and spatial heterogeneity (see, e.g., Esbensen and Wagner;[5] Esbensen et al.[25]).

In the present work, it is proposed that detailed chemical maps of realistically pulverized RM with the purpose of quantifying discrete phases (nuggets) will improve estimates of an appropriate minimum mass test portion that will in turn

Table 2. Concentrations from Certificate of Analysis of Major Elements and Selected Precious Metals for the RM Studied[a]

	CHR-Pt+	CHR-Bkg	MASS-1	MASS-3	WMS-1	WMS-1a	KPT-1
SiO_2	21.75	15.27			4.50	10.05	54.14
TiO_2	0.07	0.14			0.07	0.13	0.9
Al_2O_3	7.43	12.91			1.07	2.55	14.41
Fe_2O_3(total)	13.41	13.87	22.30		69.62	64.90	12.24
CaO	0.23	0.07			1.60	4.32	6.89
MgO	27.97	23.47			0.20	0.55	4.3
MnO	0.15	0.14	0.03		0.06	0.08	0.14
Na_2O			3.3		0.05	0.13	2.61
P_2O_5					0.03	0.04	0.17
K_2O					0.08	0.12	1.65
S	0.00467		27.6	30	31.32	28.17	1.043
Cr (μg/g)	12.94	18.41					
Cu (μg/g)	0.04		13.4		1.24	1.4	0.11
Ni (μg/g)	0.55	0.19		40	3.50	3.02	0.11
Zn (μg/g)	0.02	0.02	21				
Au (μg/g)	4.3	0.028	47		0.29	0.3	0.037
Ir (μg/g)	6.2	0.028	46.2	65.5	0.25	0.322	0.00662
Pd (μg/g)	80.8	0.07		58	1.2	1.45	0.123
Pt (μg/g)	58	0.05	51.9	33.8	1.8	1.95	0.097
Ru (μg/g)	9.2	0.067		67.3	0.1	0.145	0.017
reference	14	14	39	40	29	29	34

[a] Results in %m/m unless otherwise indicated.

reduce the uncertainty of effective measurements. Proper use of RM requires that material consumption should be minimized[26] further emphasizing the importance of defining a minimum mass test portion for RM.

The present paper is a companion study to Bédard and Néron[27] in which an analytical procedure and data analysis (named spatial geochemistry) to characterize heterogeneity at scales relevant to aliquots were defined. Their data analysis used statistics and an image analytical erosion protocol based on microXRF chemical maps so as to define a minimal mass test portion and a proximity number to quantify heterogeneity. Their proximity number quantifies the spatial distribution of elements of high concentrations that group together various elements that are evenly distributed over the mapped area. The minimal mass test portion is defined with respect to an a priori uncertainty level and a number of beam footprints defining a volume that is converted to a mass. From their analysis, they proposed a minimal test portion for the same suite of RM as this study. However, for their mathematical analysis to be applicable, a large number of results above the detection limit is required. In the case of precious metals, very few of their results (below 10 in all samples) were above detection limits precluding the use of their mathematical analysis. As such, for precious metals, a different approach had to be developed, which is presented in this study.

■ METHODS AND MATERIALS

Micro-XRF. Sulfide and oxide RM (Tables 1 and 2) can be mapped with micro-XRF.[27] There are many advantages to the use of micro-XRF: a small sampling volume (beam diameter of 50 μm), relatively fast measurements, and the capacity to revisit anomalous result locations as this is a nondestructive technique. 2-D mapping of the RM surface (pressed pellets, fused disks, in situ thin rock slabs) is also fully automated so that sample preparation, instrument loading, and data extraction all take less than an hour per sample, although mapping time is much longer. Because the nuggets involved are small, their analytical signal is weak. However, the nondestructive nature of the method allows for revisiting all first foray indicated anomalous spots to ensure that nugget signals are valid and reproducible. Microbeam techniques that have beams less than 10 μm (SEM, EPMA) will be potentially much more effective in microscale characterization of heterogeneity but will inevitably take an unreasonably long time when mapping large areas. For a more realistic and practical approach, micro-XRF mapping allows for characterization of single nuggets of commensurate size(s), as well as clusters hereof, and ensures that the test portion is of sufficient mass so as to be representative. This realistic estimation of the effective number of nuggets within a sample should increase the confidence level for calculations of the minimal mass test portion.

Reference Materials. Since ores are among the most problematic materials for which to calibrate valid analytical procedures, a series of ore and mineralization relevant RM of varying composition were selected for the present method development pilot study (Tables 1 and 2) to evaluate the presence/intensity of nugget heterogeneity. Sample MASS-1 (((Fe,Cu,Zn)S); previously named PS-1[28]) is used in laser ablation although concerns have been raised here regarding possible heterogeneity issues. The newly produced MASS-3 (NiS) is also included. All precious metals values (Table 2) for MASS-1 and MASS-3 are preliminary values. WMS-1 and WMS-1a[29] are used for PGE-hosting mineral deposit studies. Au, Pd, and Pt are certified values (Table 2), and Ir and Ru are provisional values. They also offer the opportunity to look at the complete process from field sampling to RM production in replicate form as WMS-1a represents a *resampling* of the same deposit in order to provide a replacement for WMS-1. The Wellgreen deposit, where WMS-1(a) samples were taken, can contain a few large PGM (as nuggets), up to 145 × 145 μm,[30] certainly visible in microXRF maps. CHR-Pt+ and CHR-Bkg are chromite-bearing samples[2,14,31−33] and are rare examples of RM for this type of matrix. CHR-Pt+ precious metal values are recommended while those of CHR-Bkg are provisionals. A mafic rock containing disseminated sulfides (KPT-1[34]) was also included to provide an analogue for more routine sample types used in mining exploration. This sample is believed to be "homogeneous" for major and trace elements[34] but not for precious metals (preliminary values).[2] Reference materials were provided in the form of satchels, vials, or small containers. Great effort was taken to ensure that RM sample preparation and processing mirrored the typical workflow in analytical laboratories as closely as possible, although there are very few descriptions in the literature on exactly *how* RM are aliquoted. Referring to protocols in many laboratories known to the present authors and incorporating the experiences of analytical colleagues, RM were mixed vigorously (shaken in their specific containers) for "homogenization" and subsequently mass-reduced by multiple passes through a small riffle splitter (5 cm side with four riffles). Several laboratories use an alternative approach relying on a spatula to extract the required mass from the top of the vial or container more or less in one extraction. N.B. this is the dreaded *grab sampling* in TOS' parlance, which is a decidedly inferior procedure relative to microsplitting; see, e.g., Petersen et al.,[35] Esbensen and Wagner,[5] and DS 3077.[36] Grab sampling can never be accepted, ibid. As microsplitting is used by a fair proportion of high-level laboratories, this approach was deemed the most appropriate for the present study. The danger of significant segregation of particles due to density or size differential is small when particles are below 75 μm but can not be eliminated completely for the large(st) nuggets; however, as these issues are involved in all routine work, they were simply left in order to increase the realism of the backdrop of the present studies.

Aliquots of sulfide powder samples were pressed into pellets of about 1 cm diameter and 5 mm thickness (20 tons pressure for 2 min). Sulfides autobind when pressed, so no binder was used. For oxide and silicate samples, which were pressed into pellets of 2 cm diameter and 5 mm thickness, poly(vinyl alcohol) was added to help binding. Measurements were carried out using an Eagle III (EDAX, Mahwah, New Jersey, USA) dispersive energy micro-XRF instrument with a voltage of 40 kV and a current of 40 mA to maintain a dead time of 25−30%. X-rays were produced by a Rh tube focused with a poly capillary lens at nominally 50 μm. For each sample, between 8000 and 10 000 measurements, each lasting 10 s, were undertaken on a grid covering ~25 mm^2. Each analysis point was juxtaposed to the next without overlap between beam footprints. Some grids were rectangular to avoid surface damage previously caused by LA-ICPMS. The results were used as net intensity counts (background corrected) to ensure minimal data modifications of the signal. Repeatability of the analytical technique was measured by collecting 1000 determinations at the same point under similar conditions. After collection, results were mapped with a geographic information system (GIS) software to ensure no trends or localization problems could arise. For each sample, basic signal statistics (average, relative standard deviation, maximum and minimum values, kurtosis, and skewness) were compiled to detect any spurious effects related specifically to analytical issues. Since precious metal concentrations in the selected RM are very often near background (below lower limit of detection), variations in net intensity may be due either to the presence of a true nugget or to a spurious signal (analytical noise or interference). To ensure that nugget quantification limits were well-defined, *all* high net intensity signal localizations were *revisited*. An area of at least 32 × 25 beam diameters (approximately $1200 \times 1000\ \mu$m, with beam overlap) was mapped with the EDAX mapping software to ensure that the nugget could be clearly reidentified. For example, in sample WMS-1, "point 6127", where Pd has an intensity of 16.5 cps (Figure 1), was more closely investigated by making a localized map to confirm this was indeed a valid nugget signal (Figure 1). However, these validation results were not used for nugget calculation. Other problems could also be assessed through this approach, such as Sb interference on Te or Zn on Pt (Figure 1). If a high concentration point could not be detected on the second visit, it was considered to be random instrumental noise and discarded. Typically, but not in every case, a nugget was found to be present if the signal was above 10 counts per second (cps), which represents the average background (typically 1.5 cps) plus 12 standard deviations ($\sigma = 0.7$ cps). No Os and Rh nuggets were detected with the micro-XRF approach and were therefore not included in this study. Many reasons could explain their absence: (1) there were no Os- or Rh-bearing nuggets present, (2) the nuggets were too small to be detected, (3) they did not pass the remapping validation, or (4) they were eliminated because of interference. The exclusion of Os and Rh does not invalidate this study. It was never meant to be exhaustive, but it intends to present a comprehensive first exposuré of a new empirical approach only.

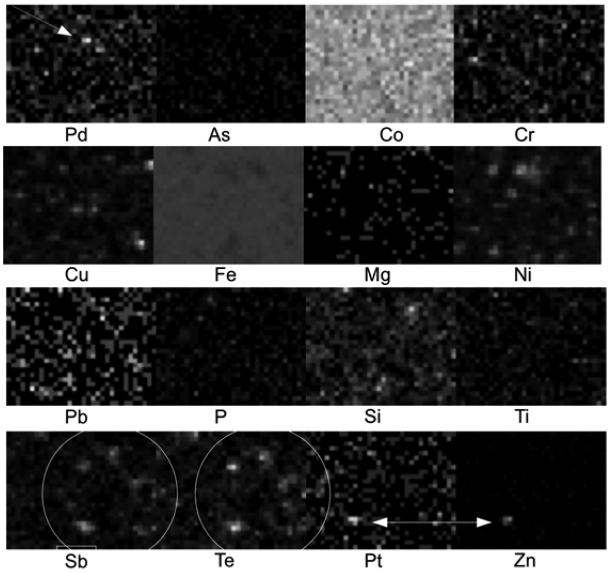

Figure 1. Detailed map of sample WMS-1 for verification of anomalous values of Pd and Pt. The anomalous value for Pd represents a real nugget as the elevated values could be repeatedly recorded. The anomalous value for Pt represents a Zn anomaly. Similar non-nugget anomalies are recorded for Sb and Te.

■ RESULTS AND DISCUSSION

RM Heterogeneity. Results can be presented in a so-called *unfolded* form: a juxtaposition of successive pixel-lines from top to bottom, transforming a 2-dimensional image into a 1-dimensional signal (Figure 2). For Ir, Au, and Pt, a few anomalies higher than approximately 10 cps (average +12 σ) are present and are interpreted as nuggets. For Pd, the background and standard deviations are higher, and hence, higher counts are necessary to produce an anomaly or nugget; however, in Figure 2, most anomalies can not be replicated and

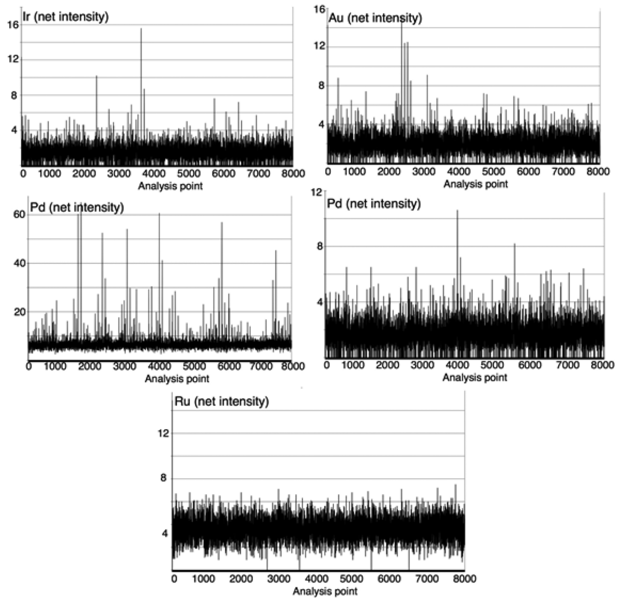

Figure 2. *Unfolded* results of mapping for Au, Ir, Pd, Pt, and Ru (sample CHR-Bkg). Results are presented as analysis numbers (cps). Potential nuggets are easily detected as vertical spikes, although these spikes must be verified through a second mapping in order to be considered as real signals produced by nuggets.

only one is considered valid. For Ru, no anomalous values have been identified in this sample.

Nugget Identification. In order to calculate the minimum test portion mass, some parameters have to be estimated (e.g., a minimum detectable nugget threshold). Precious metals were assumed to be in the most likely mineral such as sperrylite ($PtAs_2$) for Pt, laurite (RuS_2) for Ru, and Au as native gold (Table 1). Sample density was determined using the immersion balance technique. The analyzed volume (escape volume) in XRF will vary with sample density and has to be calculated for each matrix−element combination. The analyzed volumes were calculated (Table 3) from first-principles using data from Goldstein et al.[37] Considering six standard deviations of the background in the studied matrixes, a detection limit of about 1000 μg/g was estimated. The size of a nugget in the calculated analyzed volume (50 μm beam) necessary to produce a signal of about 1000 μg/g is 10 μm. Therefore, a nugget threshold size of 10 μm (cubic) was chosen for all calculations. The maximum number of nuggets expected in a sample (calculated) was determined by assigning all precious metals to nuggets (Table 4), in order to furnish a worst-case scenario.

Table 3. Analyzed Volumes (10^{-6}cm^3) for Au, Ir, Pd, Pt, and Ru Computed from First-Principles Using Mass Absorption Coefficients from Goldstein et al.[37]

	density g/cm^3	Au	Ir	Pd	Pt	Ru
		Lα	Lα	Lα	Lα	Kα
CHR-Pt+	3.3	1.5	1.3	0.13	14	10
CHR-Bkg	3.5	1.3	1.1	0.14	1.2	9
MASS-1	1.5	1.4	1.8	0.19	2	9
MASS-3	2.0	1	0.88	0.14	0.94	6.7
WMS-1	4.3	0.67	0.58	0.09	0.62	4.5
WMS-1a	3.7	0.83	0.71	0.11	0.77	0.6
KPT-1	2.8	2.8	2.4	0.18	5.6	20

In RM samples MASS-1 and MASS-3, no nuggets are detected suggesting that essentially any "small mass test portion" can be used. Such a result is expected for samples that have been prepared as *precipitated* sulfides and confirms their suitability, in terms of heterogeneity, as RM for microbeam techniques.

Sample WMS-1 and its replacement WMS-1a show differing behaviors however. Pd nuggets are detected in sample WMS-1 while none are detected in sample WMS-1a suggesting a better preparation of the latter. The presence of nuggets (Table 4) reflects, therefore, suboptimal sample preparation (crushing, pulverizing, and subsampling mass reduction) and/or incomplete mixing and "homogenizing". Both CHR-Bkg and CHR-Pt+ are known to be very heterogeneous,[2,14,31−33] and both RM contain nuggets (Table 4).

Calculation of Minimum Mass Test Portion. Estimation of minimum test portion masses was done using Moore's third equation[38]:

$$\text{C.V.} = \sqrt{\frac{\pi \rho D^3}{600 W p}}$$

where C.V. is the coefficient of variation, ρ is the particle density in g/cm^3, D is the particle diameter in μm, W is sample weight in g, and p is the concentration in μg/g.

This equation estimates the analytical sample weight necessary taking into consideration nugget size and density, element concentration, and a sampling error acceptance threshold. Using 10 μm nuggets (calculated from the detection limit determined above), applying a sampling error level of 5%, and assuming that all precious metals are held in nuggets, our predicted analytical sample weights are reported in Table 5. An alternative simple estimation has been computed (Table 5) assuming a Poisson distribution (assuming that nuggets are randomly distributed in the matrix and the test portion is small compared to the lot). Relative standard deviation (S_r) of the expected number of nuggets follows a simple equation: $S_r = \frac{1}{\sqrt{n_{\text{nuggets}}}}$ where n_{nugets} is the number of nuggets. Given $S_r = 5\% = 0.05$, that sample must contain a minimum number of nuggets $n_{\min} = \frac{1}{S_r^2} = \frac{1}{0.05^2} = 400$. Then, the minimum sample mass test portion is $\text{SMTP}_{\min} = \frac{400}{[\text{el}]} \cdot m_{\text{nugget}}$ where [el] is the concentration of the element of interest, m_{nugget} is the mass of the nugget which is $m_{\text{nugget}} = f \times V_{\text{nugget}} \times \rho_{\text{el}}$ where f is Gy's shape factor[3] (0.5 for spheric), V_{nugget} is the nugget volume (10^3 μm^3, as defined previously), and ρ_{el} is the density of the element. Intuitively, it corresponds to the mass of sample that will contain 400 nuggets at the measured concentration of that element. Both estimations (using Moore's equation or Poisson distribution (Table 5)) agree for a high concentration of precious metals, but Moore's equation gives the mass test portion for low concentration samples. However, mass test portion estimated for the low concentration samples is so high that it will be unrealistic for most analytical techniques.

These masses are minimum estimates only and apply only to the elements of this study (while the outlined principles apply to all elements found partly or wholly in similar nugget-forming phases). For other elements (Co, Cr, Cu, Fe, Ni, S, Si, Ti, and Zn), Bédard and Néron[27] proposed minimal mass test portions, lower than those presented in Table 5 as these elements do not

Table 4. Nuggets Detected versus Nuggets Expected Based on the *Assumption* That All PGE Are in Nuggets[a]

RM		Au	Ir	Pd	Pt	Ru
CHR-Pt+	detected	1	1	8	2	N
PGE range 50−80 μg/g	calculated	18	15	36	94	23
CHR-Bkg	detected	1	2	N	2	N
PGE range 0.05 μg/g	calculated	0.1	0.1	0.03	0.1	0.1
MASS-1	detected	N	N	N	N	N
PGE range 50 μg/g	calculated	82	71	ND	54	ND
MASS-3	detected	N	N	N	N	N
PGE range 50 μg/g	calculated	ND	64	16	22	64
WMS-1	detected	N	N	2[b]	N	N
PGE range 1−2 μg/g	calculated	0.5	0.3	0.3	1	0.1
WMS-1a	detected	N	N	N	N	N
PGE range 1−2 μg/g	calculated	0.6	0.4	0.5	2	0.2
KPT-1	detected	N	1	2[b]	N	N
PGE range 0.05−0.2 μg/g	calculated	0.2	0.03	0.07	0.2	0.1

[a]Note: N = not detected; ND = not determined. PGE range is the range of concentration of precious metals in the sample. [b]In samples WMS-1 and KPT-1, out of the two Pd nuggets, one was identified in two contiguous pixels but counted as one.

Table 5. Sample Mass Test Portions (SMTP) Having a Precision of 5% and an Assumed Nugget Size of 10 μm

RM	SMTP determined using Moore's[38] third equation	SMTP determined using Poisson distribution	SMTP adjusted for detected nuggets	element used for calculations
CHR-Pt+	0.5 g	0.9 g	0.125 g	Au
CHR-Bkg	80 g	161 g	80 g	Ir
MASS-1	<0.1 g	0.1 g	<0.1 g	Ir
MASS-3	<0.1 g	0.07 g	<0.1 g	Ir
WMS-1	23 g	25 g	<0.1 g	Ru
WMS-1a	16 g	17 g	<0.1 g	Ru
KPT-1	342 g	682 g	342 g	Ir

produce nuggets in most geological environments.Thus, the analyst must also consider other elements that may cause similar heterogeneity; precious metals, however, are often the most prominent. Furthermore, analysts may be required to use still larger test portion masses to ensure that elements can indeed be detected (a conventional DL issue). Taking into account the nuggets actually found in this study (Table 4), these minimum test portion masses should now be reconsidered.

A lower number of detected nuggets when compared to the calculated estimate indicate that a significant fraction of the precious metals held in sulfides or nuggets is too small to be detected with micro-XRF. In these cases, it suggests that these nuggets are not generating heterogeneity at a level that would impact analyses and, as such, can be neglected. If fewer nuggets are found, then the ratio of detected/calculated nugget can be used to reduce the effective concentration. As such, a reduced effective concentration can be used with Moore's equation to reflect more realistically the number of nuggets present.

For MASS-1, MASS-3, and WMS-1a, no nuggets are detected (Table 4) suggesting a very low test portion can be used safely (<0.1 g). For CHR-Pt+, having four times fewer detected nuggets than estimated from calculations, the concentration can be reduced to a fourth of the original estimate to recalculate a new mass test portion (0.125 g, Table 5). For the other RM (CHR-Bkg, WMS-1, and KPT-1), the number of calculated nuggets is below one suggesting that the selected volume should be larger. Nonetheless, the number of nuggets detected (1−2) is small (Table 4), consistent with a random distribution and thus can still be considered to be in agreement with the calculated number. However, as there can not be a higher number of nuggets than what corresponds to the total mass of precious metals, the original calculated test portion mass is considered valid. For sample WMS-1a, a small sample mass test portion can be used without diminishing its representativeness. For samples CHR-Bkg and KPT-1, large sample mass test portions should be used in order to be considered representative. Failure to comply with this necessary use of a larger test portion mass will produce a large analytical variability for these RM.

The minimum effective test portion masses determined using the realistic RM heterogeneity characterizations presented in this study are of such a magnitude that one must conclude that many PGE-bearing samples should only be analyzed by methods that can accommodate a large or a larger mass test portion than what is currently common. Analyses based on a gram to subgram mass will unavoidably be affected by the heterogeneity problems highlighted in this study. Here, we have undertaken the first steps in the development of an empirical approach for quantifying the most important nugget effects due to unresolved heterogeneity even for RM at analytical aliquot scales. It is safe to say that heterogeneity haunts valid and proper analysis at all scales from field sampling to preparation of the aliquot. The only safeguard delivering and guaranteeing the necessary principles with which to counteract heterogeneity at all these scales is the Theory of Sampling (TOS). It should suffice here to refer to the new international standard DS 3077,[36] to Esbensen and Wagner,[5] and to the extensive set of basic references herein.

The critical success factor regarding counteracting the nugget effect will be that both pristine samples (incoming samples from the field intended for analysis) and the RM used for calibration and analytical evaluation are processed in *exactly* the same fashion through all stages of the field-to-analysis pathway. Inasmuch as RM are often expensive, acquisition is often via vials, or satchels, etc. sadly precluding a check of the above stipulation, introducing an in principle uncontrollable uncertainty component in PGE analysis. This study tries to show quantitative light on this important issue, even when RM satchel level heterogeneity plays out a detrimental role, if not properly counteracted (TOS).

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■ CONCLUSIONS

The evolution of laboratory instruments and analytical protocols has led to continuously reduced test portion masses. As a result, increased analytical precision should also be pursued toward lower uncertainty levels. The attendant accuracy issue (representativeness of analytical RM aliquots with respect to the original lot) is a very different matter, however, indeed not an analytical issue per se but rather a matter of being able to reduce the heterogeneity of both pristine samples and RM powder heterogeneity to a level that is fit-for-purpose, subject to the logical requirements that the preparation of all analytical samples and RM must be at all times identical. Representativeness and heterogeneity become especially important interacting factors for trace elements that can crystallize as, or in, discrete phases, such as precious metals. The relevant minimum test portion mass must be determined *empirically* to ensure representativeness of the RM aliquot in order to ensure acceptable analytical accuracy. Determination of minimum test portion mass for RM can be achieved using a heterogeneity mapping method such as micro-XRF or something similar.

Great caution should be exercised with unknown pristine samples, if these can be expected, or suspected, to host precious metals in sufficient concentrations to produce nuggets. Ideally, all such samples should undergo a similar preanalysis heterogeneity testing as described here for RM, which may, or may not, be considered realistic or practical in many routine analytical endeavors. This issue is probably best decided upon from a cost/benefit evaluation of the price one is willing to pay for reliable accuracy of the analytical result with respect to the original lot when considering the entire flow path “from field-to-aliquot”. Because there is no known *general* relationship between the proportions of precious metals held in sulfides, or in nuggets, generalizations are difficult to make unless there is some mass balance or mineralogical characterization available for the specific sample(s) in question. In the absence of information regarding the spatial distribution of precious metals, a geoanalyst will be much better off to assume that all/most precious metals are held in nuggets and undertake the type of appropriate calculations developed here as a first line safety measure. Much practical work remains to map out the microheterogeneity of many more RM; the present is but a first foray into this challenging *terra incognita*.

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Author Contributions

L.P.B. conceived the study, performed the experiments, and wrote part of the manuscript. K.H.E. wrote part of the manuscript introducing the essential Theory of Sampling (TOS). S.-J.B. supervised the project and provided instrumentation and samples. L.P.B. and S.-J.B. provided funding.

Notes

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