# Sample Preparation and Bulk Analytical Methods for PGE

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## Introduction

The geologic setting of primary platinum-group element (PGE) deposits varies from low-grade - large tonnage (Lac des Isles Complex in Canada, Watkinson et al., this volume) to high-grade, narrow "reef" type deposits (Merensky Reef in South Africa, Barnes and Maier; Cawthorne et al., this volume), Stillwater Complex in United States (Zientek et al., this volume), Great Dyke in Zimbabwe (Oberthür, this volume). Nickel-Cu ores (Norilsk-Talnakh in Russia, Kozyrev et al., this volume, Sudbury in Canada, Farrow and Lightfoot, this volume, and Kambalda in West Australia) are also major contributors of PGEs as by-products. The diverse nature of the mineralization results in grades, which vary considerably. New geochemical exploration techniques for PGE have been made viable as a result of the development of new analytical instruments, principally fourth generation ICP/MS technology. Whether it is ore grade assessment, or geochemical surveys of lake-bottom sediments or tree tops, these exploration techniques require accurate and precise analytical data ranging from the sub-ppb to multiple ppm levels.

Field sampling procedures are beyond the scope of this paper; however, proper sampling and sample preparation procedures are of paramount importance prior to considering the method of analysis to be used for the PGE determination. The PGE can occur as discrete mineral phases or in solid solution in mineral phases (Cabri, 1981, 2002; Mitchell and Keays, 1987; Talkington and Watkinson, 1986; Scoates and Eckstrand, 1986. The distribution of PGE can be erratic within samples, particularly if they are present as discrete platinum-group minerals (PGM). This "nugget" effect for PGE is similar to that known to occur commonly for gold, but perhaps not quite as extreme as the PGMs usually are not composed solely of the PGE, whereas, native gold particles would be almost entirely gold or gold-silver alloys. The required sub-sample size that should be chosen for analysis will depend on PGM particle size and the mineralogy of the sample.

There are many methods of analysis available for determining Pt and Pd only. The most common method is the standard lead fire assay using silver as a collector for the Pt and Pd followed by inductively coupled plasma/optical (also commonly known as atomic) emission spectrometry (ICP/OES or ICP/AES), or direct current plasma spectrometry (DCP) for the final analytical finish. A variation on the lead fire assay using gold as a collector is required to determine Rh quantitatively, as Rh forms insoluble alloys in the Ag collector matrix that cannot be dissolved quantitatively. These techniques are rapid, accurate and low cost. For the ultimate in sensitivity, inductively coupled plasma mass spectrometry (ICP/MS) is used for the analytical finish. The ICP/MS method has great application for large-scale lake-bottom sediment surveys (Ontario Geological Survey, 2000), and lithogeochemical surveys looking for depletion and enrichment in magmatic stratigraphy (Hulbert, 2001). The least used analytical finishes for PGE in modern laboratories are atomic absorption spectrometry (AAS) and graphite furnace atomic absorption spectrometry (GFAAS). ICP methods are faster, cheaper, and have fewer elemental interferences.

The nickel sulphide fire assay technique is the most effective for the determination of all PGE plus Au. After collection in the nickel sulphide matrix, the button produced is dissolved in concentrated hydrochloric acid and the residue analyzed by instrumental neutron activation analysis (INAA), or it can be further digested in *aqua regia* and analyzed by ICP/MS. Tellurium coprecipitation may be required to eliminate some interferences, and to ensure that the PGE are not partially dissolved. These procedures are usually slower and more costly than the standard lead fire assay procedure, but they are the only practical methods for quantitative determination of all the PGE plus Au.

Certain matrices, such as water, can be analyzed directly by ICP/MS; however, at natural levels, (<1 nanogram/litre), the PGEs are unlikely to be detected. In addition, adsorption on to the polyethylene containers is a distinct possibility, despite acidification to pH 2. This effect has been described previously for Au by Hall et al. (1986) and probably also occurs with the PGE. Pre-concentration by a factor of 10 would probably be required to establish background levels for PGE in water.

Plant ash can also be analyzed directly by ICP/MS (Dunn et al., 2001) for Pt and Pd providing appropriate analytical cor-

rections are applied. An advantage of this technique is that only 0.25 g to 0.5 g of ash is required for digestion. This represents a very much larger volume of dried vegetation. For example, a 1% ash yield (ash yield is defined as ash weight/dry weight x 100%) would require 50 g of dry vegetation to give 0.5 g of ash. Typically, it is only convenient to collect and ash 50 g to 100 g of vegetation as this represents a relatively large sample volume. In addition, geologists and geochemists may request a 60 plus multi-element package of elements (including Cu, Ni, Cr, Co, As, Sb, Se, Te, Bi) which can be determined at the same time as the Pt and Pd by ICP/MS. Vegetation ash has also been analyzed by Pb fire assay collection (Dunn, 1986; Dunn et al., 1989). This technique has potential blank problems, it requires 1 g or more of ash, and provides data only for Pt, Pd, and Au, making this a much less attractive option.

Selective extractions are growing rapidly in their use for mineral exploration. These analytical procedures attack specific mineral phases such as amorphous manganese (Enzyme Leach℠), amorphous Mn and Fe oxides, and weakly bound ions (PGETerrasol℠), and weakly bound ions (MMI™). These can be analyzed for all of the PGE (Enzyme Leach℠ and PGE Terrasol℠) (Hill and Clark, 2001) or for Pt and Pd (MMI™). Generally, these techniques extract only small amounts of interfering elements, but inter-element corrections must still be applied.

For certain rock matrices, it is possible to analyze rocks and soils for PGE by *aqua regia* digestion of a large sample with subsequent analysis by ICP/MS. However, some PGE phases occur as minerals and alloys, which are not dissolved with acids. Detection limits are relatively high (fraction of ppm, i.e., 0.2 ppm for Pd) for some PGE due to corrections which must be applied for interfering elements. Extractions into MIBK or DIBK may be used to reduce this type of interference, but this technique is not recommended for the most reliable PGE results.

Analysis of PGE by gravimetry, DC arc/spark emission, and spectrophotometry have been made redundant by modern technology and are not discussed further.

There are a number of laboratories which proclaim to have "special proprietary processes for PGE." Most of these laboratories use either *aqua regia* digestion and analysis by AAS, ICP/OES or DCP with or without some type of "special fire assay" (iron, nickel, copper, and tin have been noted). Analyses performed in this manner are unreliable at best and will usually report multi-ounce/ton results due to measuring interferences caused by elements such as Fe, Ni, Cu, Sn, and possibly others.

## Sampling

Pitard (1989) notes that "preparation is a sequence of non-selective observations such as transfer, crushing, grinding, pulverizing, drying, mixing, etc., carried out on a batch of matter in order to bring it under a convenient form for the next processing stage, which can be another sampling stage or the ultimate analysis. Preparation shall not be confused with sampling, which is the selection process itself." Any of the preparation steps listed can lead to substantial error if not applied properly. Hellman (1999), AusIMM-AIG (1999), Bloom and Titaro (1997), and Brooks (2001) have described a number of these preparation failures.

Geological materials collected for analysis should be representative of the material being sampled. Theoretically, the size of sample should depend on the particle size distribution of the PGE-bearing phases, and consideration should be given to the deposit geology. There are many PGE-bearing phases, that include arsenides, bismuthides, selenides, tellurides, sulphides, native metals, and alloys, and the PGE may be present in solid solution in various sulphide minerals. Cabri (1993, 2002) describes more fully the mineralogical possibilities, which exceed 100 PGM and over 20 PGE-bearing mineral species, several of which are common sulphides. Determination of PGE mineralogy is complex and there are few skilled mineralogists in this field. Determination of the PGM particle size, and hence required sample size (François-Bongarçon, 1998), is not a trivial task and usually it is performed after a deposit of some consequence has been outlined.

Commonly, the appropriate size of sample is determined by trial and error through an iterative process of sampling and analysis until an appropriate sized sample is determined. Initially, samples collected depend on the proposed genetic model for the mineralization. For example, chromite seams are sampled one way, whereas, sulphide mineralization, (or establishing background levels in rock) are sampled differently. Further discussion of field sampling is beyond the scope of this paper. Suffice it to say that a minimum requirement for determining sampling variance should be to take replicate samples in the field. This will give an estimate of how much variance is caused by field sampling, and permits adjustment of the sampling program to an acceptable level.

Sampling remains the largest source of error for PGE exploration programs. The use of chip sampling and composite sampling may provide the best representivity of the sample. "High grading" of chromite seams or Cu-Ni mineralization should be avoided in order to obtain reliable estimates of grade. Brooks (2001) provides many examples of how sampling errors have resulted in a number of exploration and mining development projects to be severely compromised. Consistency in the selected sampling procedure used for any given project is keynote.

## Sample Preparation

Once rock samples arrive in the laboratory, they must be prepared accordingly for analysis. A jaw crusher finely crushes the entire sample on the primary crush. Secondary cone crushers are no longer widely used. A TM Rhino™ crusher or rolls crusher is widely used in many commercial laboratories for the primary crush and will crush to 80% -2 mm (-8 mesh) if properly maintained. Typically, rotary or riffle splitters are used to produce a representative sample, which can then be pulverized to 95% -75 µm (-200 mesh) (some labs use 95% - 105 µm or -150 mesh). Usually, a 100 g to 1 kg split can be pulverized depending on the mills available in the laboratory. For most samples it is best to pulverize using sealed bowl pulverizers [ring and puck type (sometimes called swing mills), or "flying saucer"

type mills such as those produced by Labtechnics]. Ring and puck mills usually provide the finest pulp.

Pulps from ring mills, which pulverize 100 g to 200 g, are dumped onto a "cloth" or sheet and the "pour to fill" process is used. This technique does not cause segregation problems.

Brooks (2001), recommends caution when using "flying saucer" type pulverizers; he showed an example of up to 35% difference taken from samples prepared using this type of pulverizer from samples from the Bendigo gold deposit in Australia. He theorized that minerals with high specific gravity such as Au or the PGM segregate and settle to the bottom of the bowl. This can particularly be a problem if the sample is pulverized for too long a time period. Common practice when using bowls pulverizing 2.5 kg or more is to take a scoop of pulverized material out of the bowl, usually near the top of the pile, and discard the remaining material. It is virtually impossible to dump the powder out of the bowl due to its weight and Brooks' warning must be carefully considered when using this sample preparation protocol. A solution to determine if there is a problem may be to take several splits as pulp replicates from the top, sides and bottom of the pulverized sample when it is still in the original bowl and evaluate the variance.

Brooks (2001) also notes:

*"— errors of the order of 30% to 40% of the true values of gold, uranium, copper, and platinum to name a few, are readily introduced by such practices as unfaithful halving of core, incorrect feeding of sample crushers, incorrect feeding of splitters, such as Jones riffle splitters — or even using incorrectly designed equipment. Soft, high value minerals such as native gold, electrum and molybdenite readily contaminate sample preparation equipment, while dense minerals such as gold, electrum, uraninite and the platinum group metals —" tend to separate from comminuted host rocks because the latter have specific gravities that are of the order of a quarter to an eighth of the heavy minerals of interest.*

He goes further to recommend against using contra-rotating disc pulverizers, which will segregate minerals based on density. The situation may be further aggravated by improper mat rolling with improper sub-sampling. The heavy minerals segregate on the mat surface, and have an overlying layer of the lower grade pulp.

Use of "wash dirt" or cleaner sand to clean process equipment between samples is suggested to avoid cross contamination. Contamination from sample comminution equipment also can occur. For an example, in the late 1990s, it was found that pulverizing bowls of the "flying saucer" type were made from steel coming from scrap iron originally used for ball mills from a gold mine. Gold contamination of more than 10 000 samples occurred before the problem was found. Clearly when new equipment or supplies are used, appropriate process blanks must be run to identify these problems and correct them before using new process equipment or supplies.

## Quality Control

After the pulp has been prepared, randomly selected pulp duplicates or even replicates should be chosen for replicate analyses. Routinely, at least 1 in 20 samples should be replicated. More frequent replicates should be chosen if the analytical method chosen requires this. An additional control is to take preparation duplicates which are splits of the -10 mesh reject material which can be sub-sampled by mechanical splitting and then separately pulverized. If sufficient preparation and pulp duplicates are chosen for analyses, variance can be computed from each of these steps to determine if the sample preparation steps are adequate. If variance exceeds expectations, modifications to the procedure are advisable. In extreme "nugget effect" cases, a metallic screen analysis may be advised. In a metallic screen analysis a large sample is pulverized and completely screened at say -150 mesh. All the coarse mineralization (native gold, metallic PGM), which may have been flattened on pulverizing is screened out and assayed separately. This removes the coarse nuggets, which can cause homogeneity problems and ensures all coarse particles are assayed from the whole sample. The -150 mesh (in duplicate) material is analyzed separately. The assays are recombined based on the original distribution of the oversize and undersize material and a combined assay is arrived at.

It is important that rock samples be finely ground to achieve, for example, 95% that will pass through a -200 mesh (-74 μm), particularly when chromite is present. If rock samples are not finely ground chromite grains may not be completely melted during fire assay procedures.

Many geologists elect to sieve their soils or sediments to -80 mesh (-177 μm). This is the absolute coarsest particle size required for a fire assay. This coarse particle size, however, may result in poor PGE recovery and/or reproducibility. Use of a -150 mesh (-105 μm) sieve size ensures more complete dissolution of grains in the fire assay process. Depending on what information the geologist wants to obtain (e.g., chemical versus mechanical dispersion) the appropriate sample preparation procedure can be chosen. This may require a two-stage preparation program including sieving and pulverizing.

Strict sample preparation procedures should be followed since they probably represent (outside of field sampling), the largest component of the total analytical error. Preparation blanks, preparation duplicates and sample replicates should be routinely reported with analytical data. This is becoming mandatory with the International Standards Organization accreditation to ISO/IEC Guide 25 or its new replacement ISO 17025 and accreditation to CAN-P-1579, the Standard for Mineral Analysis Laboratories developed by the Standards Council of Canada (SCC).

## Reference Materials and Validation of Results

An analytical laboratory normally assumes that blanks and control standards are included with sample submissions so that further validation of laboratory analytical results can be assessed. It appears, however, that this does not always happen in routine sample submissions to commercial laboratories, partly because there is a scarcity of International Certified Reference Materials for PGE. Most, with the exception

**Table 1. Some of the more widely used analytical certified reference materials for PGE**

| Standard | Source | Pt (ppb) | Pd (ppb) | Rh (ppb) | Ir (ppb) | Os (ppb) | Ru (ppb) | Au (ppb) |
|---|---|---|---|---|---|---|---|---|
| SARM-7 | MINTEK (Merensky Reef) | 3740 | 1540 | 240 | 74 | 63 | 430 | 310 |
| PTC-1A | CANMET (sulphide concentrate) | 2720 | 4480 | 330 | 110* | — | 210* | 1310 |
| PTM-1A | CANMET (Ni-Cu matte) | 7310 | 10 010 | 920* | 350* | — | 700* | 3300 |
| PTA-1 | CANMET (platiniferous black sand) | 3050 | — | — | — | — | — | — |
| SU-1A | CANMET (Ni-Cu-Co ore) | 410 | 370 | — | — | — | — | 200 |
| UMT-1 | CANMET (ultramafic ore tailings) | 129 | 106 | 9.5 | 8.8 | 8.0* | 10.9 | 48 |
| WGB-1 | CANMET (gabbro rock) | 6.1 | 13.9 | 0.32 | 0.33 | — | 0.3 | 2.9 |
| WMG-1 | CANMET (mineralized gabbro) | 731 | 382 | 26 | 46 | 24* | 35 | 110 |
| WMS-1 | CANMET (massive sulphide) | 1741 | 1185 | 225 | 235 | 119* | 99 | 279 |
| WPR-1 | CANMET (altered peridotite) | 285 | 235 | 13.4 | 13.5 | 13* | 22 | 42 |
| TDB-1 | CANMET (diabase) | 5.8 | 22.4 | 0.7* | 0.15* | — | 0.3* | 6.3 |

*values are recommended, only, or are for informational purposes.

of SARM-7, are sold in volumes of 100 g to 400 g (Table 1), and use of 30 g to 50 g aliquots for fire assay quickly consumes these standards. Custom standards of lower cost and higher volume can also be made from a variety of source materials to match exploration needs. Typically, the selected materials selected can be prepared and homogenized then submitted for "round robin" testing to arrive at consensus values. Standard preparation can be performed by a number of government facilities (e.g., CANMET and Ontario Geoscience Laboratories) and/or by commercial laboratories, or sample preparation equipment manufacturers (e.g., Rocklabs). Matrices of standards should be similar to the material being submitted for analysis otherwise the procedures will not be adequately tested; i.e., PGE chromite standards should be used for chromite PGE prospects and sulphide standards for sulphide projects. Also, a range of standards covering a range of values should be used, rather than a single standard. Some variability should be expected due to natural variation which is documented by the entity supplying the standard reference material.

CANMET (Canada Centre for Mineral and Energy Technology), as part of PTP-MAL (Proficiency Testing Program for Mineral Analysis Laboratories), provides proficiency testing of laboratories for Pt and Pd. These proficiency tests for Pt and Pd occur twice per year and are known to the participating laboratories. In the last PTP-MAL test of 2000, 45 laboratories worldwide participated, but only 25 participated for Pt and Pd. As general good practice, a recent report by the Toronto Stock Exchange and Ontario Securities Commission (1999) recommends a representative selection, usually 5% to 10%, of pulps and rejects should be sent to another laboratory to confirm analytical results and to ensure that a laboratory does not have bias in results. This cannot be overly stressed as many laboratories may have difficulty with PGE analyses.

## Lead Fire Assay Collection

Since antiquity, the method of choice for gold analysis has been fire assay. The first recorded use of the fire assay technique was that of Erker, assayer to the Holy Roman Empire and fire assay probably even predates that time. The classical lead fire assay, which uses silver as a collector, collects Pt and Pd as well as Au, if the sample is fluxed properly. The principle behind this technique is that the sample is mixed with a flux which lowers the melting point of the geological sample material, forming a totally molten liquid at 1000°C to 1100°C. Usually the fusion time is 45 to 60 minutes. The flux is usually composed of litharge (PbO), soda ash ($Na_2CO_3$), sodium borate (borax, $Na_2B_4O_7$), silica and household flour (added as a reductant) to which Ag has been added as a collector (usually in solution for highest purity). Details on the lead fire assay procedure are available in Bugbee (1940), Steele et al. (1970), Moloughney and Faye (1976), Beamish and Van Loon (1977), Haffty et al. (1977), Moloughney (1986), and Hoffman et al. (1998). The Au, Pt, Pd, and Ag are highly soluble and compatible with lead which has been reduced from PbO by the carbon present and is not compatible with the boro-silicate slag. As the lead droplets in the molten mixture settle to the bottom of the crucible, due to the high specific gravity of lead, the Au, Pt, Pd, and Ag are normally scavenged effectively from the melt by the lead. The flux must be of the appropriate viscosity to allow the PbO to be reduced to the Pb droplets and come into intimate contact with the sample material before it has a chance to settle under gravity to the bottom of the crucible. If a flux is too fluid, settling occurs too rapidly; if the flux is too viscous it results in Pb shot (molten Pb droplets) to be present in the slag and this may cause some retention of PGE and Au in the slag.

The crucible melt is poured into a mold which allows the lead to sink to the bottom; the slag, which contains most of the silicates as well as most unwanted elements (e.g., Fe, Cu, Ni, V) to solidify on top of the lead button. This straightforward procedure concentrates Pt, Pd, and Au from a large sample and achieves separation from the interfering matrix for the subsequent instrumental procedures.

Variations in flux composition are required for different sample types. If the sample has not been properly fluxed there are telltale signs (button size not correct, flux has etched the crucible, flux boiled over, lead shot present in slag, slag too viscous, etc.) The experienced fire assayer can usually identify these signs and adjust the flux accordingly. Analytical recovery

Table 2. **Fire assay modifications required for Pt, Pd, Au analysis***

| | Problem | Fire Assay Modification Required |
|---|---|---|
| Chromite | Very refractory, reductant, may result in low Pt, Pd recovery. May cause litharge to emulsify. | Grind finely, add extra borax, increase flux/sample ratio by reducing sample size; or add additional auxiliary flux. |
| Cu, Ni | Contaminates Pb button, results in low Pt, Pd recovery, may form Cu, Ni matte or droplets which will scavenge PGE, Cu in slag may hold Au, Pt, Pd. | Extra litharge (PbO), increase flux/sample ratio, possibly pre-leach samples with HCl. |
| MgO | Viscous slag. May cause litharge to emulsify. | Extra borax, increase flux/sample ratio. |
| Sulphide | Contamination of Pb. May cause sulphide droplets in slag or a sulphide matte to form which will scavenge PGE. | Potassium nitrate (niter) added as an oxidizer and extra litharge (PbO), increase flux/sample ratio, pre-roast samples to get rid of most sulfur. |
| Se, Te | Wets cupel. Au and Pt, Pd may be absorbed into cupel. | Look for tell-tale color rings in cupel. Scorification of sample required. |

*Haffty et al. (1997).

will suffer if this is not done properly. Assembly line procedures, with up to seven fusion pourings at one time, may not allow the fire assayer to properly view the viscosity of each poured fusion and should be avoided unless total PGE recovery is not a requirement or you are dealing with same sample material. Unknown mineral/matrix samples from prospects or differing sources should be custom-fluxed to produce the best analytical results.

The lead button, weighing 25 g to 30 g, contains the Au, Pt, Pd, and Ag. For the subsequent procedures, the lead must be eliminated in a process called cupellation by placing the lead button into a cupel made of bone ash or magnesia and heating to 900°C to 960°C. The lead is primarily absorbed (95% +) into the cupel leaving a 3 mg to 5 mg Ag bead (prill or doré) containing the Au, Pt, and Pd as well as some, but not all, of the Rh and Ir. The expertise of the fire assayer is required to determine temperatures of fusion and cupellation and rates of heating based on the composition of the sample. PGE and gold may be associated with Se or Te which at levels of 10's of ppm can wet the surface of the cupel and cause the PGE and Au to be substantially lost to the cupel by absorption. There are usually tell-tale signs that this has occurred with distinctive color rings showing on the cupel. Occasionally, additional steps (e.g., scorification) are required to treat impure Pb buttons containing Te or Se, otherwise, low recoveries will occur.

At this point, the Au, Pt, and Pd have been effectively separated from the interferrents. Van Wyk and Dixon (1983) determined that unless a reducing atmosphere in the crucible is maintained, and the ratio of PbO to reducing agent is 9 to 12, recoveries of Pt, Pd are low. Their recovery results on SARM-7 (Merensky Reef) and UG-2 (upper chromitite, Bushveld Complex) increased by 5% and 16% respectively by changing the ratio to the 9 to 12 target. Diamantatos (1977, 1986), and Haffty et al. (1977) also describe other potential interfering elements such as Cr, Cu, Ni, and S. Although the separation technique is fairly simple, more skill is required than for a simple gold analysis. The mode of occurrence of the PGE is usually in association with high chromite, MgO, Cu, and Ni minerals, selenides, tellurides and/or sulphides. This requires adjustments to the flux as described in Table 2, because one fire assay flux does not fit all types of samples.

The Ag doré bead method presents a major problem for Rh and Ir analysis. Rhodium and Ir may not be dissolved completely in the bead as it may have formed insoluble alloys. A solution to this problem is to use Au as a collector instead of Ag.

Generally, it is very useful to provide the laboratory with sample descriptions so that the samples can be fluxed properly the first time, particularly if the amount of sample material available is at a premium. Although the lead fire assay fusion is reducing, it is more commonly regarded as an oxidizing fire assay as a result of the cupellation stage, where the lead button is oxidized. This results in complete loss of Os as the volatile and potentially lethal (if in a high enough concentration) osmium tetraoxide. Table 3 shows a comparison of detection limits for Au, Pt, and Pd from the price lists of a number of commercial laboratories. These detection limits will vary with sample size used, dilution and type of instrument. Table 4 shows results for Au, Pt, and Pd on chromite (18.5% $Cr_2O_3$) submitted to a commercial laboratory without indicating the nature of material. When improperly fluxed the results shown as "orig" were obtained. The sample was then properly fluxed with the results labeled repeat obtained.

## Analytical Finishes for the Lead Fire Assay Collection

There are three main instrumental techniques used to analyze the resulting *aqua regia* solution produced from the dissolution of the doré bead: atomic absorption spectrometry (AAS), ICP/OES, and ICP/MS. AAS has the poorest sensitivity (unless a graphite furnace is used) for Pt and Pd, and the most inter-element interferences; ICP/OES has intermediate sensitivity; and ICP/MS has the best sensitivity. ICP/MS also has the highest capital cost and skill requirements, and AAS the lowest.

AAS and graphite furnace atomic absorption spectrometry (GFAAS) have been described by Scnepfe and Grimaldi (1969), Fryer and Kerrich (1978), Aruscavage et al. (1984) and Kontas et al. (1986). Their procedure involves (parting) dissolving the Ag doré bead in $HNO_3$ acid and then dissolving the gold flake containing Pt, Pd with *aqua regia*. The AAS technique does not have the required detection limits for low level Pt, Pd determinations. GFAAS is better, but the technique is relatively slow and shows no advantages over ICP/OES or ICP/MS determinations. GFAAS also has a relatively small linear dynamic range (i.e., the range of concentrations over which instrument response is linear) requiring more frequent dilution.

**Table 3. Comparison of the detection limits for Pt, Pd, Rh, and Au on Ag and Au doré beads from the lead fire assay fusion (all ppb)**

| | Pd | Pt | Rh | Au** |
|---|---|---|---|---|
| **FA-AAS** | 10 | 50 | — | 5 |
| **FA-GFAAS** | 0.5 | 1 | — | 2 |
| **FA-ICP** | 4 | 5 | 5* | 2 |
| **FA-DCP** | 1 | 10 | | 2 |
| **FA-ICP/MS** | 0.1 | 0.1 | 0.5* | 2 |

*determined on Au doré bead.

**Au detection limit is due to fire assay reagent blank limitations and can vary considerably depending on the laboratory, source of reagents and contamination levels.

Note: Detection limits vary with analytical instrument, laboratory, method, etc. The above compilation was made using a number of commercial laboratories published price lists.

Other less common methods of analysis involving the Pb fire assay collection include radiochemical separations of Pt and Pd after irradiating the sample in a nuclear reactor. The sample then undergoes the Pb fire assay silver cupellation and the resultant Ag bead is measured by INAA. This method has been described by Turkstra et al. (1970), and Rowe and Simon (1971). Caughlin (1989) has described a method for the analysis of the doré bead by atomic fluorescence spectroscopy.

ICP/OES or DCP/OES (DCP is mostly obsolete) are much faster than AAS or GFAAS and have a much better sensitivity for Pt than the AAS. Wemyss and Scott (1978), Watson et al. (1983) and Date et al. (1987), have described the analysis of the PGE by ICP/OES analysis. With this technique (rapid and virtually interference free) the doré bead, usually from a 30 g fire assay charge, is dissolved in *aqua regia* and diluted for analysis. Dilution amounts vary with the laboratory and will cause detection limits to vary with the laboratory as well. The solution is then aspirated into an argon plasma at 8000° Kelvin. The emission spectra are measured and quantified.

Analytical finishes also include ICP/MS. Gregoire (1988) described this technique using a third generation ICP/MS coupled to a graphite furnace. Current ICP/MS technology is an order of magnitude more sensitive, negating the need for a graphite furnace. With this technique, the sample solution is also aspirated into an argon plasma at about 8000° Kelvin. The elements in solution are ionized and are introduced into a mass spectrometer kept under high vacuum. The masses of the elements are measured and quantified by the detector associated with the mass spectrometer. Typically, it is possible to obtain detection limits of <0.1 ppb for Pt and Pd using fire assay preconcentration provided the flux contains very low Pt and Pd. The detection limit is defined as the blank plus three times the standard deviation of the blank from at least nine prepared blanks as defined by the International Standards Organization, in CAN-P-1579 (Standards Council of Canada, 1997).

There are two types of ICP/MS instruments, those that use quadropole mass spectrometers and those that use a magnetic sector mass spectrometer, usually referred to as a high resolution-ICP/MS or HR-ICP/MS. The HR-ICP/MS is approximately one order of magnitude more sensitive than the quadropole ICP/MS and, theoretically, it could analyze Pt and Pd to 10 ppt in rocks, soils, and sediments if low enough blanks are achievable.

**Table 4. Comparison of chromite in triplicate analyzed by inadequate fluxing of sample**

| | Pt (ppb) | | Pd (ppb) | | Au (ppb) | |
|---|---|---|---|---|---|---|
| | Orig | Repeat | Orig | Repeat | Orig | Repeat |
| **CR-1** | 25 | 110 | 131 | 720 | 9 | 42 |
| **CR-2** | 32 | 130 | 177 | 715 | 10 | 37 |
| **CR-3** | 14 | 135 | 86 | 760 | 5 | 46 |

The columns with ORIG were the original poorly fluxed Pb fire assay-ICP results. Samples with repeat were repeated with modification of flux for high chromite. Sample contained 18.5% $Cr_2O_3$.

Natural background in rocks, soils, and sediments are typically below 3 ppb for Pt and Pd in most geological materials. ICP/MS provides the only real means of quantifying Pt and Pd at this level. It is only with the advent of ICP/MS that it has become possible to measure background levels in most surficial materials including lake-bottom sediments (Ontario Geological Survey, 2000), stream sediments, soils, and rocks.

## Nickel Sulphide Fire Assay

The nickel sulphide fire assay technique was first described by Robert et al. (1971). Robert and Van Wyk (1975) described the effects of various matrix elements on the nickel sulphide fire assay. Robert et al. (1971) described modification to the technique for high chromite materials. This technique was adapted by Hoffman et al. (1978) to determine all the PGE and gold at low ppb to sub-ppb levels by INAA using a 50 g sample.

The nickel sulphide fire assay involves mixing the sample with flux, which is a combination of sodium carbonate (soda ash — $Na_2CO_3$), sodium borate (borax — $Na_2B_4O_7$), nickel powder, sulphur and silica. To ensure a low blank, only Ni produced by the carbonyl process should be used. With the carbonyl process, the Ni is vaporized and reprecipitated leaving the PGE substantially behind resulting in an exceptionally low blank. There is still some minor variability from batch to batch of Ni powder, but only Ru has been found by the authors to be a potential problem. Nickel produced by other processes usually has much higher levels of PGE. Unless the sample material to be analyzed is unmineralized, the Ni, Cu, Cr, and S content should be determined in advance in order to properly flux the sample. For a 50 g sample, 16 g of Ni, 10 g of S, 10 g of $SiO_2$, 60 g of borax and 30 g of soda ash should be present for the fusion to quantitatively collect the PGE and allow the dissolution of the resulting Ni sulphide button in hot concentrated HCl acid. The sample itself can contribute part of the collector. For example, a sample assaying 5% Ni and 20% S would only require 13.5 g of Ni [16 g – (.05 x 50 g] and 0 grams of S added [10 g – (50 g x 0.20)]. In the event that there is more than 20% S present, the sample size must be reduced accordingly for a maximum of 10 g of S. Usually, $SiO_2$ is contributed by the sample; however, for sulphide-rich material, $SiO_2$ must be added so that at least 10 g are present. Excess S will prevent the Ni sulphide button from fully dissolving. The Ni sulphide button, with excess S, will oxidize and disintegrate rapidly (1 to 2 days).

Table 5. Comparison of PGE and Au detection limits by INAA and ICP/MS using a nickel sulphide fire assay

| | Os (ppb) | Ir (ppb) | Ru (ppb) | Rh (ppb) | Pt (ppb) | Pd (ppb) | Au (ppb) |
|---|---|---|---|---|---|---|---|
| INAA Finish | 2 | 0.1 | 5 | 0.1 | 5 | 2 | 0.5 |
| ICP/MS Finish | volatilized | 1 | 1 | 1 | 0.5 | 0.5 | 1 |

Note: Detection limits were determined at Activation Laboratories Ltd. ICP/MS used was a PE/SCIEX Elan 6000.

The flux and sample are fired in fireclay crucibles at 1000°C to 1100°C for 90 minutes. The nickel and sulphur combine to form nickel sulphide droplets, which scavenge the entire PGE family and Au from the molten flux as they settle to the bottom of the crucible in a similar manner to that previously described for the lead collection. The molten material is poured into a fire assay mold and the nickel sulphide button forms at the base of the mold with the borosilicate slag on top. The button is pulverized and dissolved in 400 ml of hot concentrated HCl acid in a covered beaker on a hot plate. The solution is allowed to cool as soon as the fine bubbling stops, indicating dissolution has been completed. The fine black residue of insoluble sulphides formed at the bottom of the beaker contains the PGE and Au (Robert et al., 1971 and Hoffman et al., 1978). It is important that the solution remain saturated in sulphur during the dissolution (this will be the case if the button, which should weigh 21 g to 27 g, is dissolved in 400 ml of acid). If an excess of acid is added, Au then Pd then Pt will begin to go into solution in that order and may be lost. This may occur also if the solution is left to boil once the sample has dissolved. Laboratories that perform this method and report high Au loss are also probably preferentially losing Pd and Pt, in that order, due to overboiling or S undersaturation. The solution and trace of residue is filtered under a vacuum using a 47 mm 0.45 µm filter. The filtrate is washed to remove the traces of Ni and HCl using deionized water. The residue can then be irradiated for INAA as described by Hoffman et al. (1978) or be further dissolved in *aqua regia* and analyzed by ICP/MS. A comparison of relative detection limits of the methods is shown in Table 5. This fire assay procedure is reducing in nature and does not volatilize Os for the INAA procedure. For the ICP/MS procedure, the residue must be further dissolved in *aqua regia* which creates volatile losses of Os (Robert et al., 1971).

Several modifications to the procedure have been attempted by various researchers to account for matrix problems. Robert and Van Wyk (1975) and Robert et al. (1977) described a modification of the procedure for high-chromite-bearing samples. The soda ash and borax content to sample ratio (flux/sample) was doubled and a higher dissolution temperature was used. Our own experiments confirm a much better recovery of PGE from chromite using this modification. Borthwick and Naldrett (1984) substituted lithium tetraborate for borax for high-chromite samples. Our own experiments, using their modification, resulted in almost complete loss of Ru with a marginal, if any, improvement in Pd and Pt over the higher flux/sample ratio method. Diamantatos (1977) found that recovery of Au, and sometimes Pt, could be low compared to the Pb fire assay. Hoffman et al. (1978), using radiochemical tracers, determined there could be Au losses of up to 9% by this method with losses occurring primarily in the dissolution step. If the dissolution was arrested as soon as the ground nickel sulphide button dissolved, there were virtually no losses for any PGE with gold losses in the order of 2% to 3%. Shazali et al. (1987) determined that if tellurium were added in the dissolution step, losses would be minimized (tellurium co-precipitation method).

Parry (1980) described a downsized NiS collection modification to do radiochemical separation and then INAA. Recoveries with this technique were inadequate. Stockman (1983) described a rapid radiochemical separation for the PGE based on tellurium co-precipitation as a means of separating the PGE from the sample matrix. This method uses a small sample size due to the radiation hazard of the irradiated material. Brügmann et al. (1987) also developed a radiochemical separation method for the PGE using NiS as a collector, which was an improvement over the method of Parry (1980).

Several problems are encountered with the nickel sulphide fire assay technique. High levels of Zn, generally over 5%, affect the fire assay resulting in no formation of a nickel sulphide button. Copper levels of over a few percent cause the button to not dissolve completely as copper sulphides are also partially insoluble in HCl. High levels (>0.5%) of As and Se also create a large amount of residue. A repeat fusion of the residue or reduction of sample size may improve the quality of the residue. The tellurium co-precipitation method can be used to help avoid losses of PGE. Once the PGE sulphide residue has been collected on filter paper, Hoffman et al. (1978) have described a method for the INAA analysis; however, high levels of Au will cause an elevated detection limit for Pt as a result of the Compton edge background causing a spectral interference on Pt-199 at 158 KeV. High levels of Cu and As also cause an elevation in detection limits for Pd due to an increase in background. The half-lives of the other PGE are such that they are unaffected by Au, Cu, and As. Detection limits (Table 5) for Rh and Ir generally are better by INAA than by ICP/MS, whereas, detection limits for Pt, Pd, and Ru are better by ICP/MS. Os can only be determined reliably by INAA unless a very labor-intensive distillation technique is used. Doherty (1999), in a test of the nickel sulphide and Pb fire assay collection methods for PGE using commercial laboratories, concluded that the NiS collection and INAA "provided reasonably accurate results with few exceptions." The lead collection fire assay PGE results and gold blanks came out rather poorly in her test.

The main disadvantages of the NiS technique are the high cost, corrosive nature of fire assay dissolution and the large amount of chemical waste which must be disposed of. It appears that, in general, NiS provides superior collection of PGE from difficult matrices (chromite, nickel- and copper-bearing sulphides, and some lateritized materials).

**Table 6. PGE analysis by Ni sulphide fire assay, Pb fire assay, and direct instrumental ICP/MS**

| Mass Used (amu) | Interfering Elements | | |
|---|---|---|---|
| | Ni-S collection ICP/MS | Pb collection ICP/MS | Instrumental ICP/MS |
| Ru-96 | Fe, Se, Ni | Not collected quantitatively* | Fe, Se, Br, Mo, Zr |
| Ru-99 | Co | Not collected quantitatively* | Co, Cu |
| Ru-100 | Ni | Not collected quantitatively* | Ni, Mo, Sr |
| Ru-101 | Ni | Not collected quantitatively* | Rb, Ni |
| Rh-103 | Cu | Not collected quantitatively* | Cu, Zn, Rb, Sr |
| Pd-105 | Cu | None | Y, Cu |
| Pd-106 | None | None | Zr, Zn, Cd, Sr |
| Pd-108 | None | None | Zn, Zr, Mo, Cd |
| Os-188 | Partial volatilization | Volatized | Yb |
| Os-189 | Partial volatilization | Volatized | Yb |
| Os-190 | Partial volatilization | Volatized | Yb |
| Ir-191 | None | Poor collection | Lu |
| Ir-193 | None | Poor collection | Hf |
| Pt-194 | None | None | Hf |
| Pt-195 | None | None | Hf |
| Pt-196 | None | None | Hf |
| Au-197 | None | None | Ta |

* not collected quantitatively unless Au, rather than Ag, is added as a collector.

**Table 7. Detection limits for PGE and Au by ICP/MS on water (ppt) (ng/ml)**

| | Os (µg/L) | Ir (µg/L) | Ru (µg/L) | Rh (µg/L) | Pt (µg/L) | Pd (µg/L) | Au (µg/L) |
|---|---|---|---|---|---|---|---|
| Water | 2 | 2 | 10 | 20 | 3 | 4 | 2 |

Note: Detection limits were obtained at Activation Laboratories Ltd. using a PE/SCIEX ELAN 6100 ICP/MS.

## Analysis of the PGE and Au Instrumentally by ICP/MS

The determination of the PGE and gold can be accomplished on certain types of samples without a fire assay preconcentration prior to analysis by ICP/MS. Typically, an *aqua regia* digestion is utilized; however, certain minerals and alloys of the PGE will not be solubilized, such as native iridium and Ir-Os alloys (formerly known as "osmiridium"). Hall and Bonham-Carter (1988) describe some of the problems with this digestion for PGE.

Table 6 shows various masses used for ICP/MS determinations for the PGE as well as the potential interferences for which corrections must be made. Detection limits vary for the PGE determination depending on the composition of the matrix and the degree of the solubilization of the interferants.

Certain selective extractions used for geochemistry such as Enzyme Leach℠, PGETerrasol Leach℠, and MMI™, which rely on dissolution of certain mineral phases, can have PGE (or Pt, Pd) and Au determined relatively simply as these procedures leave most of the interferants behind in the undissolved portion of the matrix. Similarly, it is possible to measure PGE and Au in water to the limits indicated in Table 7. In addition to the PGE, the ICP/MS method can obtain data for approximately 60 other elements simultaneously.

Vegetation presents a unique opportunity to conduct large-scale regional or detailed surveys rapidly using helicopter supported programs involving tree-top sampling. This type of sampling can also be conducted in the winter months when snow covers the ground and on species which protrude out of the canopy in jungle terrain. This provides a unique method to explore in poorly accessed terrain. Dunn et al. (2001) have indicated that 30 to 60 tree-top samples can be collected per hour, depending on conditions. For his boreal forest surveys, Dunn snaps off the tops from trees that protrude higher than others above the canopy. The species selected for an individual survey should be the same. Samples of tree tops are dried to allow the needles (coniferous species) to be separated and discarded. The twig material (about 60 g to 80 g) is then ashed at 475°C under controlled conditions. The use of outer bark of black spruce trees and other tissues of common trees and shrubs are described in Dunn (1986). Ash (0.25 g to 0.5 g) is digested in *aqua regia* and analyzed by ICP/MS to the detection limits shown in Table 8. In addition to Pt, Pd, and Au, a suite of 60+ other elements can be determined simultaneously. Prior to the development of ICP/MS, Dunn et al. (1989) noted that the only way to obtain the required data was to ash the vegetation, conduct a fire assay of the ash and determine Au, Pt, and Pd by ICP/OES. Detection limits by fire assay would not be better than by ICP/MS unless a large amount of ash (e.g., 2 g, requiring a large volume of fresh tissue) were used which would be impractical. Furthermore, fire assay does not provide data on the other 61 elements obtained by ICP/MS, yet the cost is about the same.

## "Special Proprietary Processes" for PGE Analysis

There have been many claims of developed "special proprietary processes" for the determination of platinum-group elements and gold. Most of these special techniques require black sands (magnetite and/or hematite) or other iron, copper or

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Table 8. Detection limits for PGE and Au by ICP/MS for some selective extractions and ashed vegetation

| | Os (ppb) | Ir (ppb) | Ru (ppb) | Rh (ppb) | Pt (ppb) | Pd (ppb) | Au (ppb) |
|---|---|---|---|---|---|---|---|
| PGE Terrasol℠ | 0.1 | 10 | 0.2 | 5 | 0.1 | 1 | 0.1 |
| Enhanced Enzyme Leach℠ | 0.5 | — | 0.5 | — | 0.5 | 0.5 | 0.005 |
| Ashed Vegetation | — | — | — | — | 2 | 3 | 2 |

Note: Detection Limits were obtained at Activation Laboratories Ltd. using a PE/SCIEX ELAN 6100 ICP/MS.

Table 9. Wavelengths used for ICP/OES or DCP/OES and interferences found

| Element | Wavelength* | Interferants** |
|---|---|---|
| Au | 242.795 | Fe, Ni |
| Pd | 340.458 | Fe, Ni |
| Pt | 214.423 | Fe |
| Ir | 224.268 | Ni, Cu, V, Fe |
| Os | 228.230 | Al, Ca, Cr, Cu, Fe |
| Rh | 233.47 | Ni, Fe |

*Example of wavelengths quoted as best by a number of equipment manufacturers.

**Interferants are usually so high in geological materials they can't be corrected adequately.

Table 10. Apparent platinum group element and Au content calculated for interferences

| | Au (oz/ton) | Pt (oz/ton) | Pd (oz/ton) | Rh (oz/ton) | Ir (oz/ton) |
|---|---|---|---|---|---|
| Ingot 50% Fe 50% Ni | 0.93 | 6.3 | 5.03 | 1477 | 38 |
| U.S. 5¢ coin | <0.003 | 11.5 | 5.63 | 520 | 5314 |

Note: An iron-nickel ingot of approximately 50% iron and 50% nickel with trace amounts of copper with no platinum group elements will show apparent concentrations of platinum group elements and gold as shown in interference values. A U.S. 5¢ coin will also show apparent PGE when not corrected for interferences.

nickel rich starting material in which to generate the multi-ounce/ton platinum-group element and gold values.

Some of these techniques begin with a Ni (not NiS) fire assay or Sn fire assay (Moloughney, 1986) procedure. The Ni fire assay procedure is done at a high temperature of 1540°C to melt the sample and results in a FeNi ingot. Iron and Ni, Cu, V, Mn, and other elements contributed by the sample, depending on its composition, are collected by the FeNi molten material which settles to the bottom of the fire assay crucible. Most of these "special" techniques involve subsequent dissolution of the Fe, Ni ± Cu, V, Mn, etc., bar with *aqua regia* and analysis by ICP/OES or DCP emission spectroscopy without any type of separation. Table 9 lists a variety of wavelengths used by some of these practioners and the interferences encountered. It is impossible to measure gold and the PGE in this sample matrix without separation of the interfering elements, regardless of their claims. Table 10 shows the magnitude of error for the PGE for a 50% Fe, 50% Ni sample and by analyzing a U.S. 5-cent coin, and subsequent analysis by ICP/OES without separation. All of the apparent PGE values reported are due to interference.

The practioners of these questionable PGE and gold analysis frequently have many variations of the above processes, some of which include cooking in crock pots to placing on a "magnetizer" overnight before starting the process. Almost all refer to the PGE wavelengths listed by the equipment manufacturer as verification of their results. It appears that all are measuring interferences. Many of these practioners purport to have multibillion-dollar deposits of contained PGE and Au, which to date have not been verified by accepted analytical methods described in this paper.

It is imperative when testing by these "proprietary" procedures that a high iron blank be put through the entire process as well as a certified reference material of known PGE content. These control materials should be inserted blindly within sample submissions when testing these procedures. In a recent court appearance, one of these "proprietary" practioners claimed that of 20 000 samples analyzed over the last ten years from multiple properties of what has been described as "desert dirt," at least 25% returned multiple ounces/ton of Au and the PGE. This included dirt from a street corner in Tucson and someone's front yard. Actual PGE concentrate standards from the mine in the Stillwater Complex did not return the expected Pt and Pd values.

We have not found any validity to any of these multi-ounce Au and PGE claims when the geology is not suitable and the emission spectroscopy techniques are used without separation from interferants prior to analyses.

## Conclusions

PGE occur in many ways as discrete minerals, alloy phases, and may also be in solid solution in other minerals. Proper field sampling and sample preparation techniques are required to produce representative PGE values. The use of pulp duplicates, preparation duplicates, blanks, and control reference materials are standard quality control requirements necessary in order to evaluate the validity of PGE results. Control standards should be matrix-matched whenever possible, otherwise, one is comparing apples and oranges since recoveries will not necessarily be the same for different matrices. PGE analysis is typically more complex than Au or base metal assays and it is recommended that laboratories to be used should have passed proficiency-testing programs for PGE. Comparison of PGE results by other laboratories is suggested for 5% to 10% of samples from pulps and rejects. Systematic validation of results from different ore types, if using the lead fire assay collection, is suggested by using the NiS as a collector to verify collection recoveries.

The Pb fire assay using Ag as a collector is used for the bulk of the PGE and Au analysis. Gold is substituted as a collector when Rh must be determined. ICP/OES and ICP/MS are typically used for the analytical finish on the fire assay beads. ICP/MS provides the lowest detection limits for the final analytical determination. The nature of occurrence of the PGE with chromite and copper and nickel sulphides requires that the samples be properly fluxed to avoid low recoveries.

The NiS fire assay provides the only means of collecting all of the PGE. The INAA (for all PGE) or ICP/MS (all PGE except Os) provides the final determinative step. For problem samples or best possible detection limits, a combination of NiS fire assay with INAA and ICP/MS finishes will do the best job. Occasionally, use of the Pb collection ICP/MS can augment the analysis.

New exploration methods using selective extractions on soil for the PGE are becoming more widely used as a result of advances in analytical technology. Similarly, the use of lake-bottom sediments, vegetation surveys, stream sediments, and lithostratigraphic whole rock PGE analysis promises to revolutionize the way PGE exploration is carried out.

The claim of special or "proprietary" assay techniques and the resulting report of multi-ounce PGE should be verified through a due diligence process using blanks containing interferants and reference materials from certified sources.

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