

# Field analysis of low ppb gold using pXRF and new detectORE technology

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## SUMMARY

The ability to easily analyse for Au in the field at meaningfully-low levels for mineral exploration has not been achievable until now. Portable X-Ray Fluorescence (pXRF) has been a game changer for explorers when it was first introduced about a decade ago. However, whereas pXRF can analyse for metals such as Cu, Zn, As and Fe at concentration levels relevant to mineral exploration, it can only effectively analyse for Au above 10 ppm and only then when interfering elements are in low concentrations. Here, new patent-pending detectORE technology is presented that can detect Au using a pXRF at five orders of magnitude lower. The method has been tested against certified reference materials and whilst not a “total” Au method like fire assay or neutron activation analysis, it provides the mineral explorer with crucial analytical results in the field; geochemical exploration relies on comparative rather than total Au results. Having data available during the execution of a soil sampling or drilling program allows the geologist to make critical decisions on where to collect next “on-the-fly”. For example, changing the drilling plan to define the extent of the mineralisation in a first pass campaign. Currently, mineral explorers may have to wait weeks or months before the results of the Au analysis are returned from the analytical laboratory, and by this time drilling is over, possibly for another year. Medium to small exploration companies can ill afford to wait that long where reporting of positive results is important to their success.

**Key words:** pXRF, gold exploration, adaptive sampling, soil analysis, drill cutting analysis,

## INTRODUCTION

Geochemical data have been generated in the field for a range of elements, such as Cu, Zn, Pb, Fe, Mn and Ni, but analysis of Au has generally not been practical. It has been long recognised that the ability to analyse elements in the field outside of the traditional laboratory is advantageous for a number of reasons depending on the application: (1) Determining a pollutant in the field may reduce the impact on ecosystems by determining the point source sooner so that timely remedial action can be implemented (Rouillon and Taylor, 2016). (2) Analysing geological samples in the field such as soils and drill cuttings may lead to the discovery of mineral deposits faster. Geochemical data from drilling or soil sampling programs can alter the programs themselves and lead to additional samples being taken and analysed, a technique known as adaptive or interactive sampling. Considerable savings are made if more targeted sampling is conducted and the number of samples that have to be laboratory analysed is reduced or eliminated altogether. (3) Recognition and understanding of geochemical processes greatly benefits from the ability to analyse multiple samples *in situ* and directly e.g. accumulation of minerals in soil horizons (Turner et al, 2017).

Fast and reliable geochemical data outside of the laboratory has become a reality with the advent of the field portable X-ray fluorescence spectrometer (pXRF). The pXRF has enabled geochemists from several disciplines to analyse a range of elements in a variety of media at accuracy levels comparable with laboratory data. Analysing samples quickly and at low cost by pXRF has permitted geochemists to increase sample density leading to a greater understanding of the distribution of elements and more detailed geochemical maps in a given setting. Large geochemical surveys for mineral exploration have now been undertaken using pXRF alone (C. Drown, pers. comm.) and real time drilling targets have been established during a single sampling program. Not only are costs reduced through savings in transportation, sample preparation, sample analyses, reducing number of field campaigns but also value has been generated by evaluating and reporting data to company boards and the stock exchange in a timely manner.

Interactive or adaptive sampling has been practised by Au prospectors for millennia in order to optimize their exploration time and resources. Physical techniques include panning, loaming, puddling, dry blowing, and more recently, metal detecting which can give semi-quantitative information on the presence or absence of coarse particulate Au or nuggets in a particular area. Microscopic Au has been analysed in the field too usually involving chemical techniques and include colorimetry (Stanton, 1966), electrochemistry (Lintern et al., 1992), chromatography (Farewell and Kagel, 1987) and traditional laboratory methods (converted to field use) such as atomic absorption spectroscopy. Procedures associated with these methods may involve weighing of chemicals, heating of digest solutions, use of solvents, and transportation of gases so their use is generally undesirable in the field and they have not been adopted for commercial field applications; detection limits may also be too high to be practical.

Gold by pXRF has been used extensively by jewellers to provide instantaneous analysis of items such as rings, bracelets and necklaces, but the application to other industries such as mineral exploration and mineral processing has rarely been done. This is because two intractable problems arise with the direct analysis of Au in mineral exploration samples by pXRF: high detection limit and interferences from other elements. Typically, Au concentrations by pXRF must be present at multi-ppm levels before it can be detected whereas

most exploration samples are in the ppb range. Furthermore, elements commonly associated with Au mineralisation such as W and As have excitation energies similar to Au and are present at orders of magnitude higher concentration, masking the Au peak.

DetectORE is a new process, consumable and software application used with a commercially available pXRF that analyses Au in the field; the invention is patent pending. Laboratory solutions indicate that the detection limit for Au is <0.2 ppb. The data from the analyses of over 130 different certified reference materials containing Au ranging from a few to several thousands of ppb will demonstrate the broad concentration range of the method and its accuracy. Three geochemical soil surveys for Au conducted in the field are described and demonstrate the ruggedness of the method. Hundreds of drill cutting samples from several exploration companies have been analysed and the results from these will demonstrate the effectiveness of the method for different sample matrices and potential shortcomings. These samples contain elements that normally would interfere with Au analysis by conventional pXRF.

## METHOD AND RESULTS

The analysis of Au in mineral exploration samples by detectORE and pXRF is first achieved through a digestion, a concentration and an exclusion step to remove interfering elements. Direct Au analysis by pXRF is not possible for routine exploration samples. A number of digest methods may be used but the data that follow have been obtained using a room temperature alkali digest solution. Room temperature alkali digests of exploration samples are fast, routine, and well characterised by analytical laboratories and have been carried out for many decades and include the BLEG (bulk leach extractable Au) method. All samples have been analysed using an off-the-shelf Olympus DELTA pXRF instrument unless stated otherwise. In the detectORE method, the geological sample is weighed into a plastic bottle containing proprietary chemicals and a proprietary collector device. Water is added to the bottle. The digestion of sample, exclusion of interferences and concentration of Au on a collector device is done over a period of twenty four hours. The Au that is leached and collected from the sample during this period is representative and related to the total amount of Au that can be recovered from the sample. The collector device used during the digest excludes interfering elements that may have been digested at the same time. At the end of the digest the bottle is cleaned and may be reused. The collector device is analysed by the pXRF and the concentration of Au is processed and calculated from the raw data output from the pXRF instrument using the detectORE software application. Proprietary detectORE standards are used to calibrate the pXRF so that the Au concentration in the final sample may be measured. The method is simple, robust and fit-for purpose. .

Calibration curves of single analysis of the collector devices with adsorbed Au from nominal standard solutions are shown in Figure 1. The results are linear ( $y=1.2x +0.3$ ) over the concentration range from 1 ppb to 100 ppb. Precision is excellent over the higher concentrations range (Figure 2, 250 for 1000 ppb) but lowers with decreasing Au concentration. At 5 ppb the standard error of the mean is ~2 ppb (relative standard deviation is ~10%) but at 1 ppb the error increases (35% RSD). Analyses have been undertaken on standard solutions <1 ppb using the new Olympus VANTA pXRF, which appears to offer increased precision and resolution for Au (Figure 2).

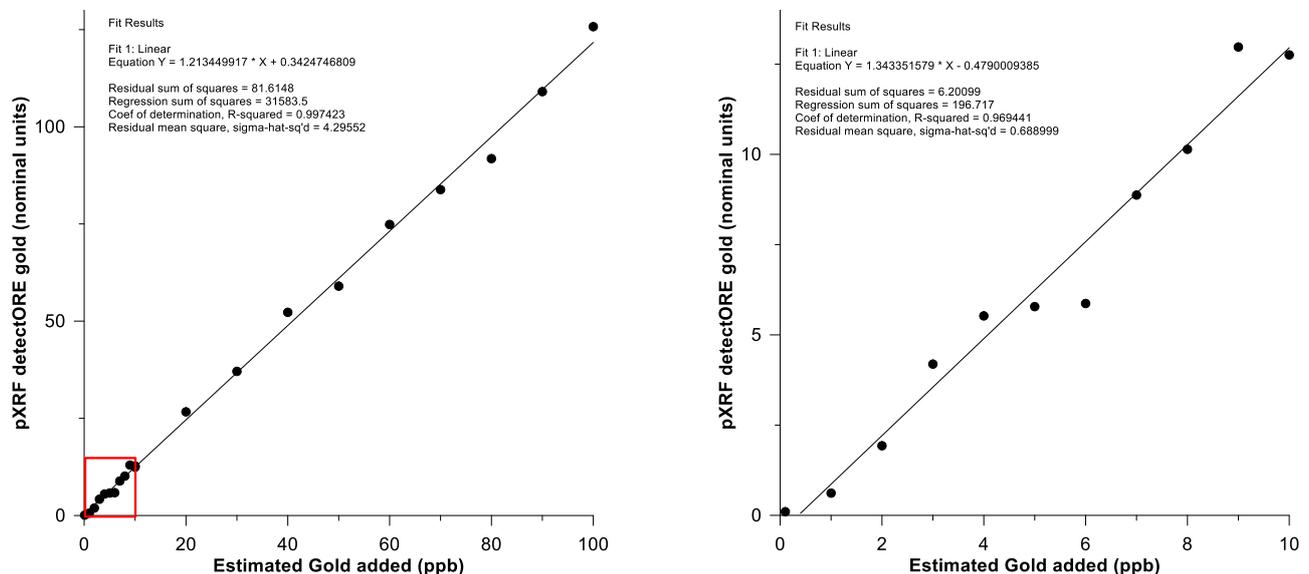


Figure 1: Calibration curves for Au on the collector device through a range of concentrations from <1 to 100 ppb. The red boxed area (left hand side, LHS) is amplified on the RHS for clarity at the lower concentrations.

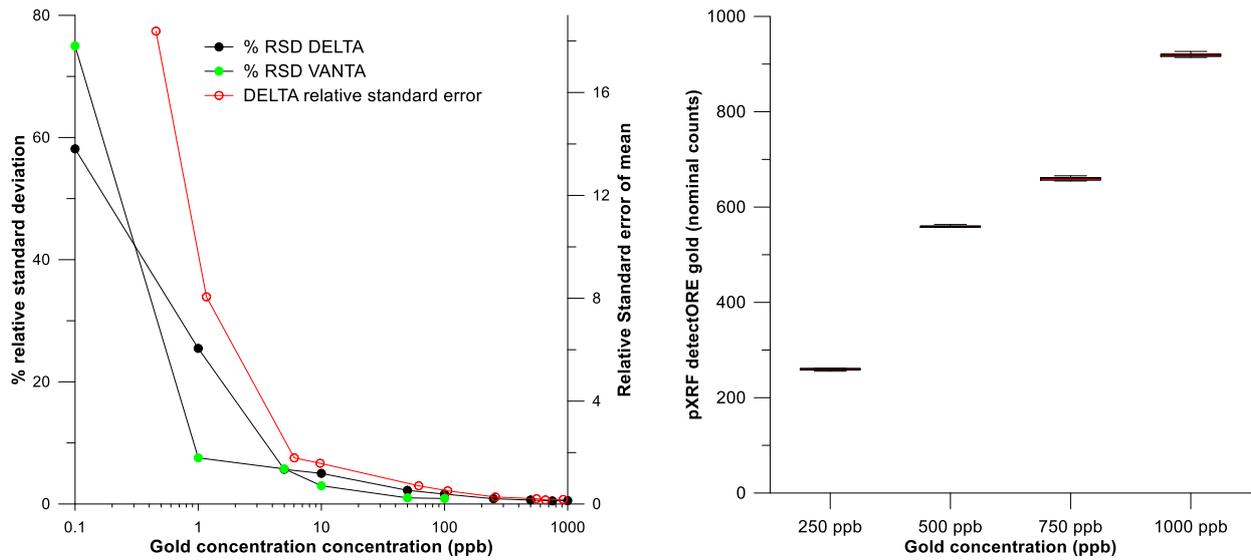


Figure 2: LHS DetectORE repeats (10) of standards with nominal Au concentrations from 0.1 to 1000 ppb Au. The % relative standard deviation (RSD) for the DELTA instrument deteriorates (>25 %) below 5 ppb but is <10 % RSD above 5 ppb and decreases with increasing concentration. VANTA instrument precision is superior. Precision for both instruments is excellent for concentrations above 100 ppb (RHS, 10 repeats).

A selection of geological commercially available certified reference materials (CRMs) were analysed that had Au concentrations ranging from ~2 ppb to ~10000 ppb (Figure 3). These were single pXRF analyses performed on a single digestion of the CRM. Increased accuracy would be expected from multiple analyses of the same CRM by pXRF. Plotting the data from the analyses gives an  $r^2$  of 0.85 for 1000 to 10000 ppb,  $r^2$  of 0.97 for 2 – 1000 ppb and  $r^2$  of 0.9 for all data combined.

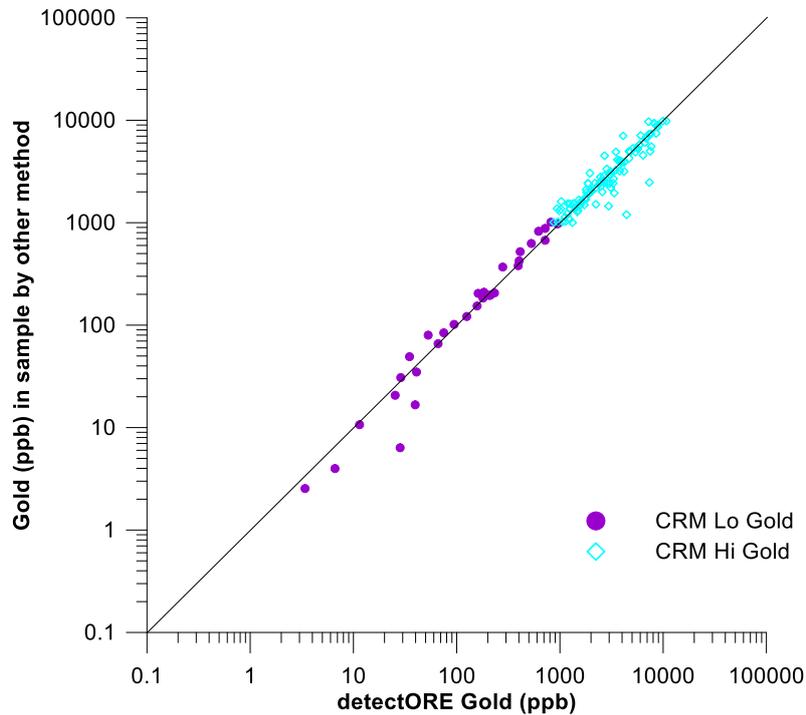


Figure 3: Comparison of Au results obtained with detectORE and other methods (fire assay and aqua regia, ICPMS). CRMs with > 1 ppm Au are shown with blue symbols and those < 1 ppm are shown in purple.

Approximately 250 samples from three exploration companies working in WA, Queensland and South Australia have been analysed and data compared with the detectORE method. Samples from pulps were analysed by the detectORE method and compared with results obtained from laboratory aqua regia or fire assay (Figure 4). As with the CRMs, these were single pXRF analyses performed on a single digestion of the sample. Many samples from Pilot 1 averaged >50% combined sulphide and chalcopyrite with one sample recording >7% Cu and report lower Au by detectORE; these samples probably contain refractory Au. Pilot 2 samples compared well

between the two methods over 100 ppb concentration (as reported by detectORE method). Samples from Pilot 3 were well below 10 ppb Au and were not accurately reported by detectORE. However, greater accuracy is expected when the samples are re-analysed with the VANTA instrument (see LHS Figure 2).

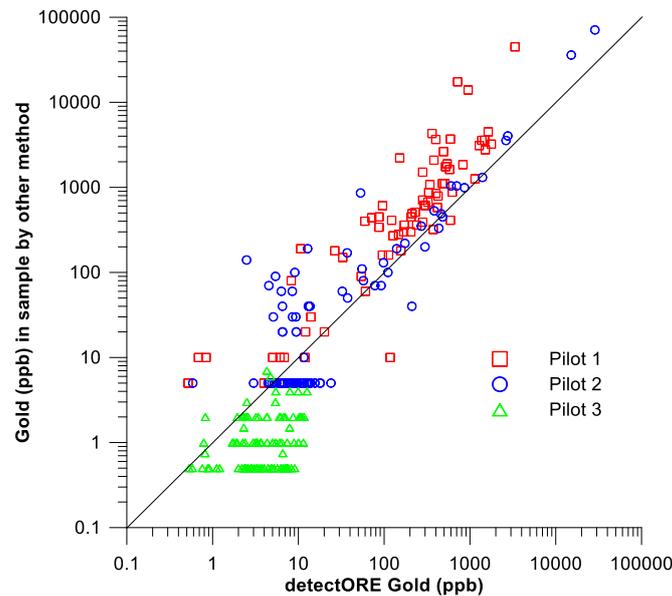


Figure 4: Comparison of detectORE method vs other methods (aqua regia or fire assay with ICPMS finish) for three sets of pilot samples from around Australia.

Samples were analysed in the field for Au from three sites at Holleton (one site shown in Figure 4). Results showed excellent agreement with samples previously collected from the same area. Earlier bulk samples were taken at different depths (0.15-1.5 m), pulverised and analysed by fire assay, whereas samples for detectORE were taken from near the surface (0-0.4 m) and were merely sieved (to 2 mm). The detectORE method was able to reproduce the same anomalies using near surface soil rather than deeper samples taken with an auger (Figure 5) at this site. The results from detectORE confirm that the mineral exploration does not require total Au data for the determination of geochemical anomalies worthy of follow-up.

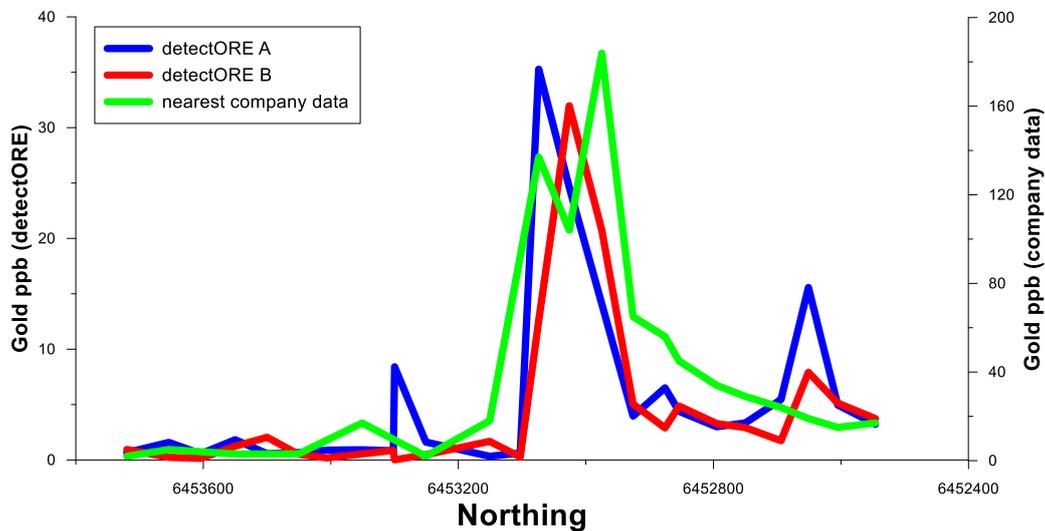


Figure 5: Gold results from Site 1 traverse at Holleton (Western Australia). The detectORE A and detectORE B results are duplicate soil samples (0-0.3 m). The “nearest company data” are for samples taken several months previous from the same site but from deeper in the profile (0-1.5 m depth) and analysed for Au using fire assay. Therefore, although the data are not strictly comparable and differ in magnitude (detectORE red and blue, left axis; company, green, right axis), there is similar contrast between anomaly and background and the anomalous area around 6453000N was achieved in the field with detectORE.

### CONCLUSIONS

The new detectORE is innovative technology offering a simple, field, practical method for mineral explorers with fast, robust, precise, accurate and interference-free Au analysis. DetectORE has been laboratory tested with encouraging results versus a variety of samples

including CRMs, drill cuttings and soil samples; it has also been tested in the field at three sites. The method analyses “free” Au not encapsulated within minerals like quartz and is well-suited for mineral exploration which relies on contrasting data (background vs anomaly) rather than total analyses. DetectORE facilitates interactive or adaptive sampling for Au allowing mineral explorers to get more value from their sampling programs. Undertaking analyses in the field removes other problems that develop in times of increased economic activity. For example, as commercial analytical laboratories become overwhelmed with samples, they experience increasing pressure to maintain an adequate service and consequently their reputation may be compromised, as is that of the exploration companies they serve, by a reduction in quality of the results. DetectORE will reduce exploration costs and companies using it may be seen favourably by investors.

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## REFERENCES

- Farwell, S.O. and Kagel, C.T., 1987. A non-instrumental qualitative test for free gold in geological samples. *Applied Geochemistry*, 2, 227-229.
- Lintern, M.J., Mann, A.W. and Longman, G.D., 1992. Field analysis of gold by cyanide digestion and anodic stripping voltammetry. *Journal of Geochemical Exploration*, 43, 233-248.
- Rouillon, M. and Taylor, M.P., 2016. Can field portable X-ray fluorescence (pXRF) produce high quality data for application in environmental contamination research? *Environmental Pollution*, 214, 255-264.
- Stanton, R.E., 1966. *Rapid Methods of Trace Analysis for Geochemical Applications*. Edward Arnold, London, 96 pp.
- Turner, A., Poon, H., Taylor, A. and Brown, M.T., 2017. In situ determination of trace elements in *Fucus* spp. by field-portable-XRF. *Science of the Total Environment*, 593, 227-235.