5. Statistical comparison of methods used to measure uranium and thorium

5.1 Introduction

For this study, three different methods were used to measure the U and Th content of gold tailings sampled from the New Machavie TDF north of Stilfontein. These methods were down-hole natural gamma spectrometry, natural gamma spectrometry of samples and ICP-MS analyses of samples. It is important to compare the results of these different methods as each has both strengths and limitations.

Down-hole natural gamma spectrometry requires specialized field equipment and training in order to be used effectively but is by far the least expensive method and consumes the least amount of time. Natural gamma sample assay requires lead shielding to remove background radiation as a source of error, as well as constant intervals of calibration and measurements of shift. Samples also need to be prepared prior to assaying (dried, weighed, sealed with an air tight seal and left for radon equilibrium to be achieved). Sample assaying also requires long counting intervals to improve counting statistics and thus accuracy of measurements, thereby making laboratory assaying of samples the most time consuming methods. ICP-MS analyses require highly specialized equipment and personnel who are trained in using this method. This makes ICP-MS the most expensive method but also the most accurate since radionuclides are measured directly, which is not the case with natural gamma spectrometry. For this reason ICP-MS was used as a reference to measure the accuracy of the other two methods.

5.2 Objectives and motivation

The objective of this section is to statistically evaluate the best method for the quantification of natural gamma radiation of a gold TDF and to calibrate the raw data to radionuclide concentration (ppm).

This section is of importance to any further study and possible consultations regarding the quantification of radionuclides within gold TDFs as the results should be applicable as long as the instrumentation is the same. This may save costs, improve modelling detail as more data can be gathered, and provide a better information base from which decisions regarding re-mining of TDFs can be made.

5.3 Methodology

As explained by McKillup & Dyar (2010), the normality of data sets determines the statistical soundness of the data. Thus the normality of each data set was checked before continuing with further analyses. Histograms of each element and each method used were drawn to check the normality of the data (Figure 5.1). Once normality was confirmed, scatter plots were drawn to compare the relationships between different variables. If relationships were found, correlation coefficients were calculated to quantify the linear relation between the variables, and regression analyses were done to quantify the variability as well as the predictability of different variables.

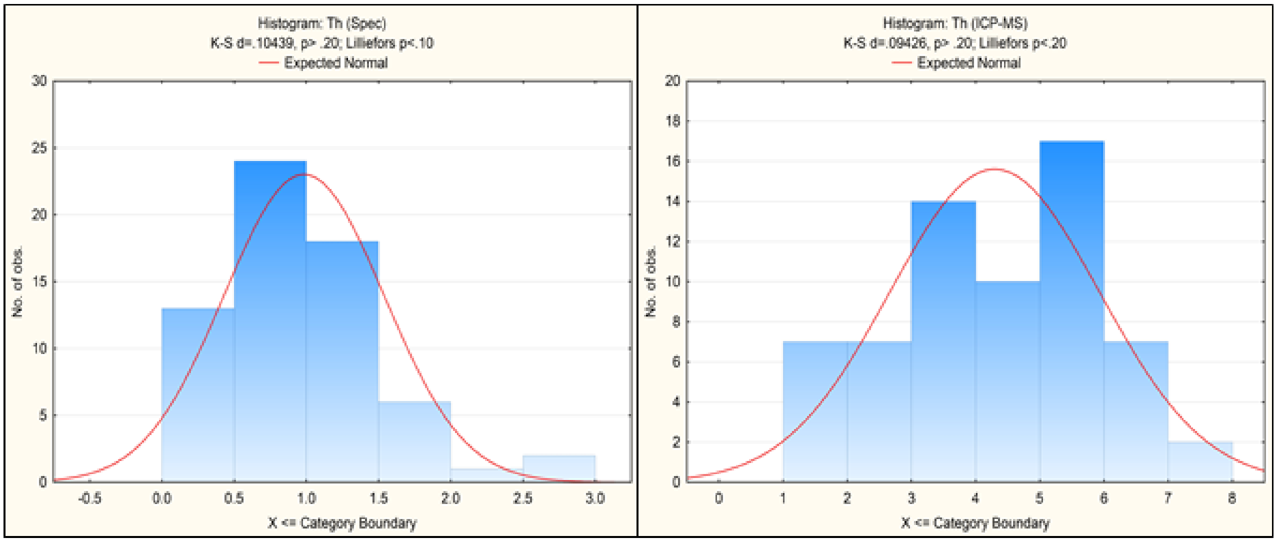

Figure 5.1: Histogram of Th as measured by laboratory natural gamma spectrometry and ICP-MS

5.4 Results and discussion of statistical analyses

5.4.1 Uranium

Figure 5.2 shows the scatterplot of U as measured with ICP-MS and laboratory natural gamma spectrometry of samples.

A correlation coefficient (r) of 0.80345 indicates a well-defined linear relationship between both measurements. The coefficient of determination (r^2) for these measurements is 0.673705 with a standard error of 0.70142. In this case the higher variation can either be attributed to analytical error or to environmental factors. Analytical errors for laboratory natural gamma spectrometry may include the homogeneity of the sample, calibration errors, detector drift, changes in background radiation levels, sample positioning. Disequilibrium is an environmental factor that may produce errors in measurement. In order to prevent these errors from occurring, various methods were used to correct for this possibility as described in the Methodology chapter (Section 4.4). Since the degree of disequilibrium between U and the daughter elements that were gamma active (and measured using natural gamma spectrometry) was not corrected for in this graph, the major contributor to the variance is disequilibrium. ICP-MS is a direct measurement of U, thus the variance can be used to describe the degree of disequilibrium between U and its daughter products in gold tailings.

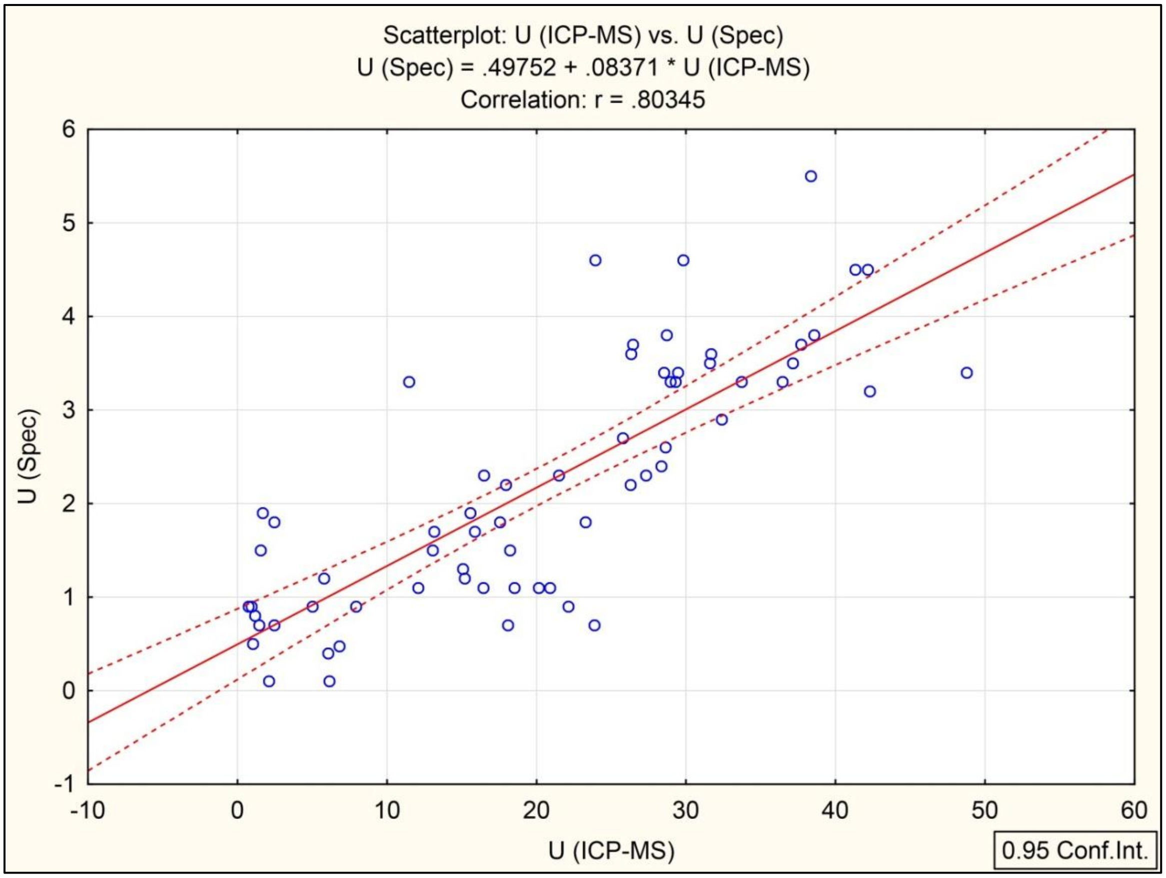

Figure 5.2: U, ICP-MS vs laboratory natural gamma spectrometry

Although the variance between ICP-MS and laboratory natural gamma spectrometry is higher than expected, the regression equation can still be used (due to the high linear correlation) to calibrate the spectrometric data. A known concentration of U (from ICP-MS) can be related back to the count rate as described by IAEA (2003), IAEA (1993) and Richards (1981) as the matrix equation for converting count rates to concentration (ppm).

Figure 5.3 indicates the linear relationship between down-hole natural gamma spectrometry and the ICP-MS concentration. In this case the r is slightly better at 0.81256 compared to the laboratory spectrometry results which can be ascribed to the variance caused by sample size. Spectrometry assumes that an infinite sample is measured, as is the case in field measurements, but this is not the case when measuring samples. This is corrected for by removing background effects (using lead shielding), and calibrating for mass and position of samples (IAEA, 2003., Van Rensburg, 2011). Down-hole natural gamma spectrometry relies on a probe lowered down a hole at a certain rate which then records counts at certain time intervals. This rate (user-defined) gives readings between 2 and 4 cm intervals meaning that in order to compare samples to down-hole probing results, an average of readings were used for each 10 cm depth interval of the samples. In this case the r^2 is 0.66022087 which can also be ascribed to the disequilibrium between U and its daughter products. The down-hole count rate can also be converted to concentration through the matrix equation mentioned above.

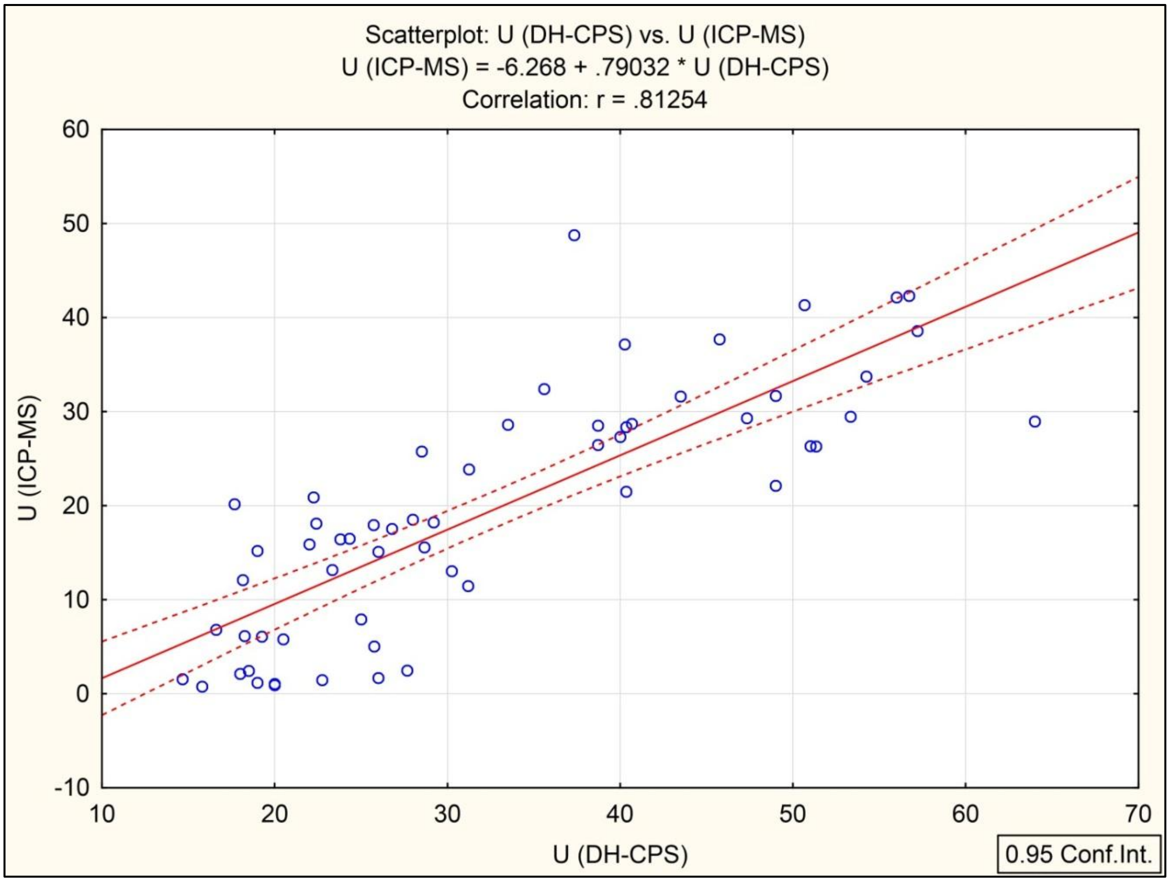

Figure 5.3: U, ICP-MS vs down-hole spectrometry

5.4.2 Thorium

As seen in Figure 5.4, Th as measured with a laboratory natural gamma spectrometry has a very weak relationship with ICP-MS results and accordingly a very high variance. In this case the high variance cannot be ascribed to disequilibrium only, but also to the detector limitations. As count rates decrease with very low concentrations, the error margin of the detector increases due to decreased statistical representation of counts. The result of this lower counting statistic is increased variation between measured values and actual concentration. Adding to this error margin is the fact that samples has significantly lower count rates than field measurements since only small portions are removed and tested.

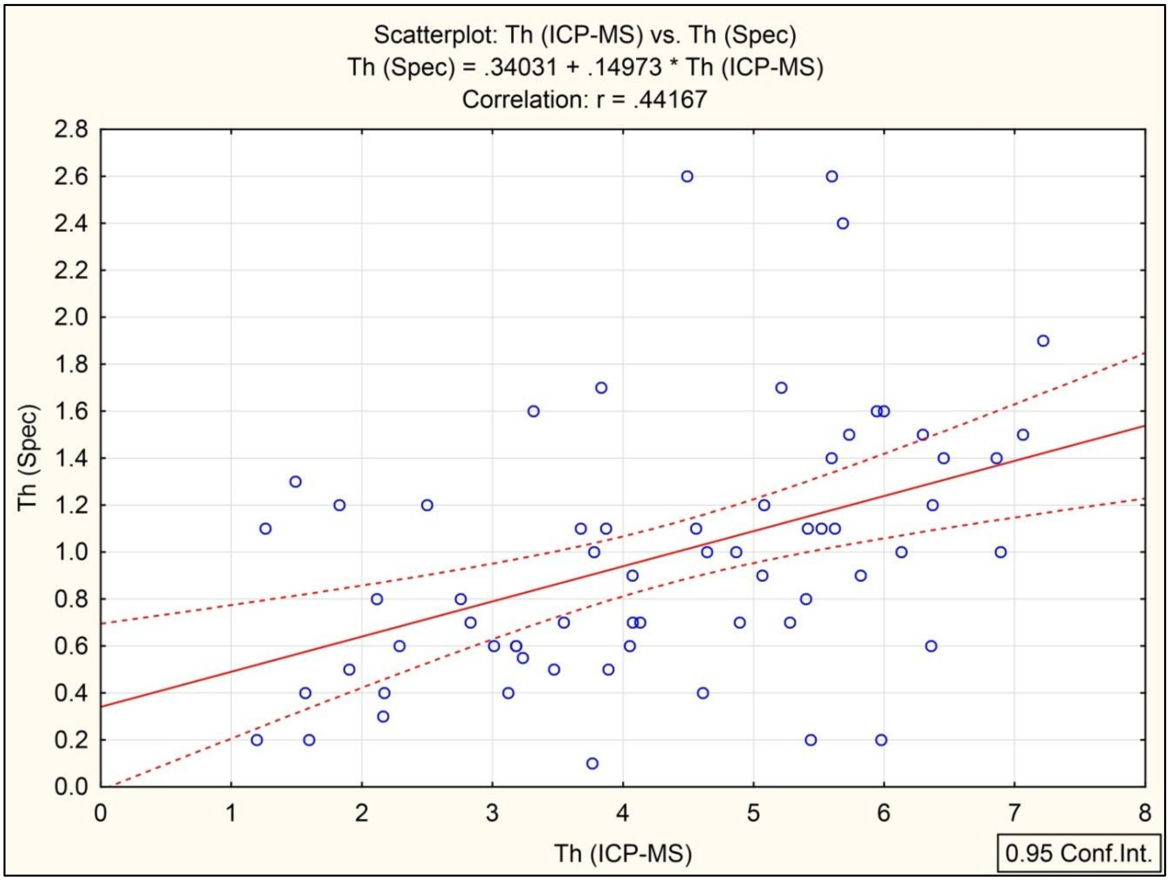

Figure 5.4: Th, ICP-MS vs laboratory natural gamma spectrometry

Figure 5.5 indicates how counting statistics vary between samples and field measurements at low concentrations. A strong linear relationship can be seen between down-hole Th measurements and ICP-MS results. This improved relationship is observed because an infinite sample was measured with enough counting statistics to represent the concentration compared to the finite volume of a sample. The down-hole count rate can also be converted to concentration through the matrix equation mentioned above.

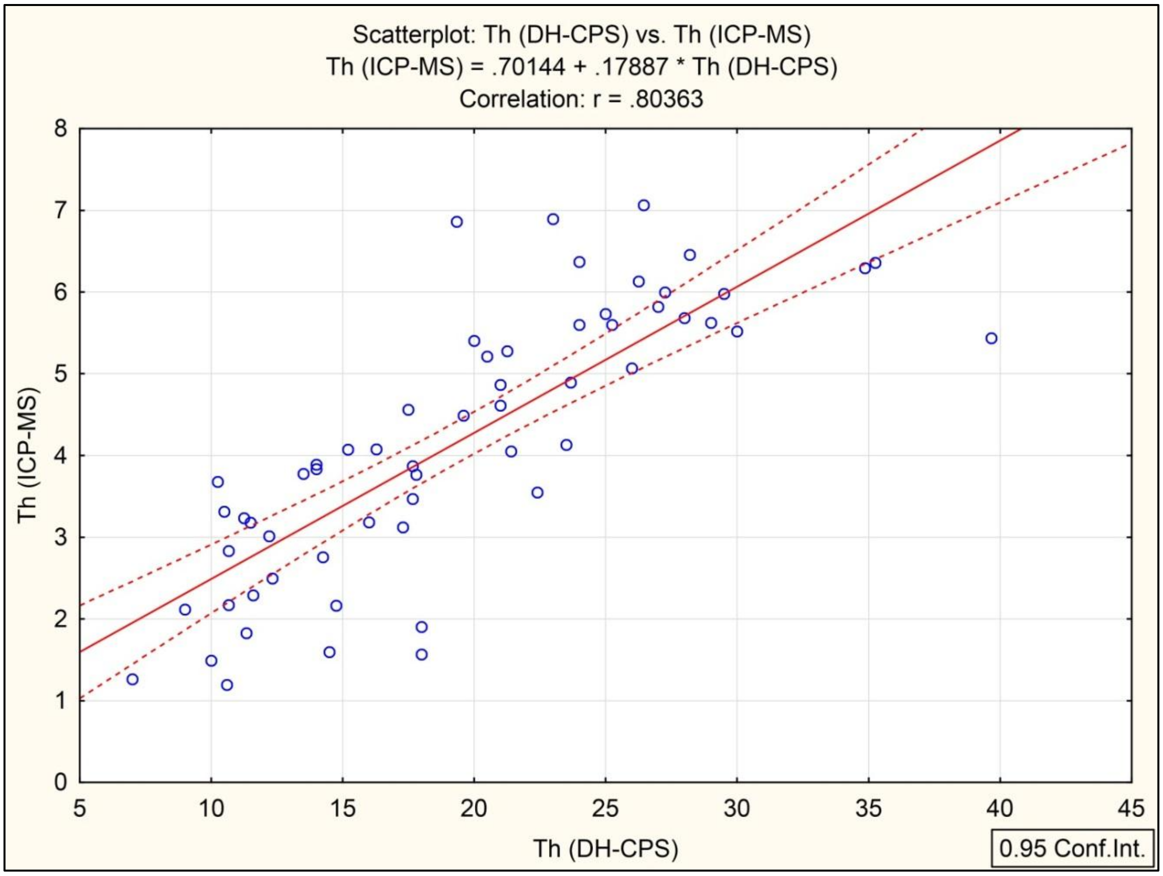

Figure 5.5: Th, ICP-MS vs down-hole spectrometry

5.5 Conclusion

Statistically, down-hole spectrometry performed slightly better than laboratory natural gamma spectrometry which may be due to the size of samples compared to the infinite sample as measured in the field. Very low Th concentrations along with sample size showed that laboratory natural gamma spectrometry was not able to quantify Th content accurately. A possible solution would be to increase the period over which an assay is measured thus increasing the counting statistics, or to use a larger detector crystal which would measure lower concentrations more accurately. However, Th is not actively pursued as an ore element in South African gold tailings, thus the Th content is not as important for resource estimation. Both methods accurately estimated the U content and can be used in conjunction with some sampling and ICP-MS analyses to quantify the U resources in gold tailings. Some ICP-MS analyses will be necessary in order to quantify the degree of disequilibrium. Economically speaking, laboratory natural gamma spectrometry performed better since initial costs only include capital expenditure on instruments and lead shielding, whilst the actual measurements is fairly simple and does not need professionally trained operators to perform. Down-hole probing has both capital expenditure as well as professional field technicians, which should be accounted for. The speed and accuracy of data acquisition for down-hole spectrometry far exceeds the other methods. Laboratory natural gamma spectrometry is extremely time consuming compared to down-hole probing and samples need to be taken at accurate depths to be meaningful.

Down-hole probing can be considered the best method to quantify radionuclide concentration in gold TDFs. The calibration of natural gamma data will be most accurate using this method as well. As an alternative to the matrix method for calibrating cps to concentration, the linear regression equation can be used to calibrate cps, although this is only possible if variance is low enough.