High Precision Determination of Major Components Using ICP-OES and the Bracketing Technique

Introduction

Typically, ICP-OES is used for the determination of minor and trace elements. If main components need to be determined, a strong focus is placed on the precision of the measurement. Particularly in the research of modern materials, a very precise analysis is increasingly required because the stoichiometric composition. In the jewelry industry, an exact analysis has been a requirement for a long time. The precious metals content is the main factor for their monetary value. Therefore, it needs to be most accurately determined when trading precious metals or precious metal products.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) can be used perfectly for the precise determination of major compounds. A special technique for high-precision measurements has been developed by the precious metals industry for the determination of the composition of jewelry alloys. This bracketing technique is described in the ISO standards 11494 [1] and 11495 [2]. The bracketing principle can also be used for the analysis of other major compounds in general, where high precision and accuracy is required, **such as P & K in Fertilizers!** The following report describes the basic approach of analyzing major compounds according to ISO 11495, as well as the implementation of the bracketing technique using the ICP Analyzer Pro software.

Analysis of major compounds using bracketing

Bracketing is described in ISO 11494 [1] and 11495 [2] as the analysis of standards and samples in an alternating sequence. The bracketing method achieves very high precision and accuracy and thus is used for the determination of the stoichiometric composition of materials and for the analysis any compound which requires highest analysis accuracy. The calibration solutions are prepared from single element standard solutions or, according to ISO 11495, by using different amounts of pure materials, which are exactly weighed and digested. The same amount of an internal standard solution is added to each calibration standard and sample. The metal contents of the sample solutions are determined empirically using an ICP-OES instrument and comparison of the spectral emission intensities of the analyte with the analyte intensities of calibration standards. Before applying the bracketing method, an analysis using an external calibration is helpful to find the right concentration for the low and high bracketing standard. The calibration function is created by measuring the prepared calibration standards and plotting the measured intensities of the selected analyte emission lines of the standards against the respective concentrations. Measuring the analyte intensities for the sample, a "preliminary" element concentration can be calculated. This measurement is used as a pre-analysis in order to identify the two nearest standards, which bracket the sample. Figure 1 shows an example of a calibration curve, together with a sample result. The two standards next to the sample are marked as "Low Standard" and "High Standard". These calibration standards are used in the second analysis step for the exact determination of the element concentration.

While the determination of concentrations using external calibration functions established with several standards is a sufficiently accurate method for many applications, it balances out the errors of the standards used as well as nonlinearities and drift over time. However, even when small, this has a negative effect on the accuracy of the analysis. In order to eliminate these errors and to achieve high precision and accuracy for the determination of major compounds, the bracketing method is used.

The principle of a bracketing method is the alternating measurement of one sample and two standards. First, the low standard is measured, then the sample and the high standard. These three measurements can be counted as one bracketing cycle. After this, the sample is measured again followed by the second measurement of the low standard, which finishes the second bracketing cycle. The sequence is typically continued until five bracketing cycles are completed. Figure 2 displays the bracketing sequence graphically.

In addition to bracketing, also the internal standard technique is applied. Here, the analyte intensity values are ratioed with the intensities of an internal standard, an element added to all standards and samples at a constant concentration. The idea is that variations, e.g. from the pump, the sample introduction, nebulization and sample transport but also flicker noise out of the plasma affecting the emission intensities, affect the analyte and the internal standard in the same way. The ratio of the two eliminates those variations, improving short- and long-term precision. When selecting an element to be used as internal standard, it is important to verify that it is not already contained in the sample at varying concentrations and that its emission lines do not show a similar behavior as the analyte lines. This is often the case for lines of the same type (atomic and ionic lines), for lines which are in the same wavelength range or for lines where the excitation energy or the sum of ionization and excitation energy have similar values. Typically, elements with a low abundance in nature and not too many emission lines in the spectrum are selected. Yttrium and Scandium are among the elements most commonly used.

The analyte concentration of each sample measurement is established using the corresponding low and high standard measurement of each bracketing cycle as a calibration function. This function is defined by the corrected intensity ratio of each measurement and the exact amount of analyte inside the standards. Using this method, highest accuracy can be achieved if also the exact amount of the internal standard solution that is added to all solutions is known. Finally, the analyte content of the sample can be calculated using the mean concentration value of all sample measurements and the sample weight.

Figure 1: Example of a calibration function

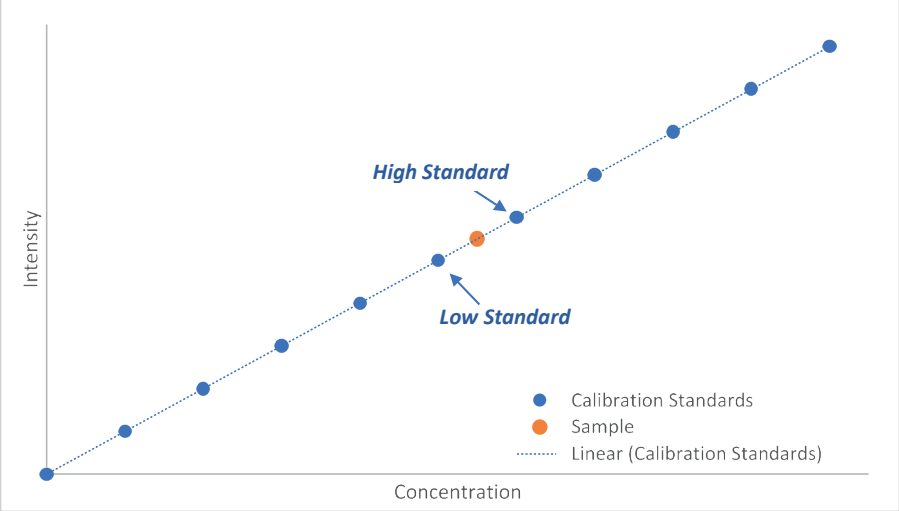
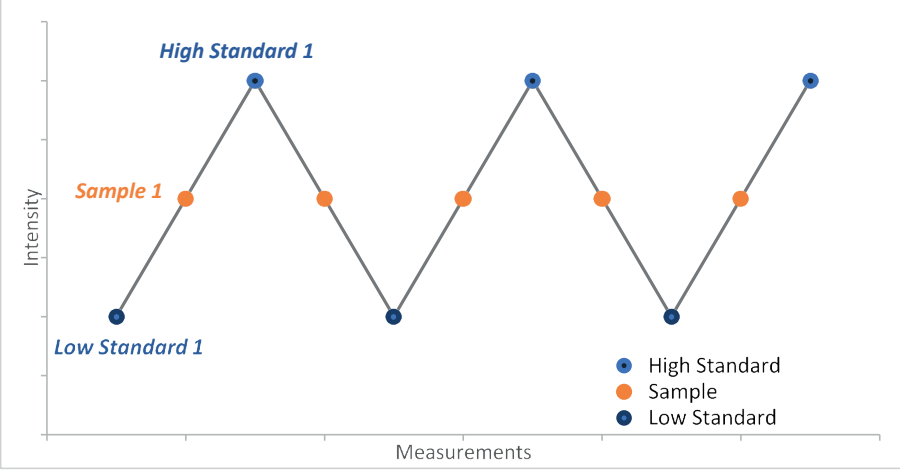


Figure2: Bracketing sequence with five bracketing cycles



Bracketing using the ICP Analyzer Pro software

The analysis of major compounds with the bracketing method can easily be performed with the ICP Analyzer Pro software through the bracketing plugin, which activates all necessary settings and calculations.

First, an analytical method needs to be created. Method development is a simple step by step process (Figure 3). For example, the analyte and internal standard lines need to be selected, the plasma parameters have to be set, the standards need to be defined, and evaluation parameters have to be set. Due to a version concept, all method changes are fully traceable and can be reviewed inside the version history.

For the bracketing calculation, there is additionally the possibility to define the purity of the standard material. **A known material should be used for the preparation of the calibration standards, the certified purity of this material should be inserted (for P & K in fertilizers, a Magruder reference material should be used)! For this example we will use pure palladium reference material as a substitute to demonstrate the technique.** It is also possible to use single or multi-element standard solutions for the preparation of the standards.

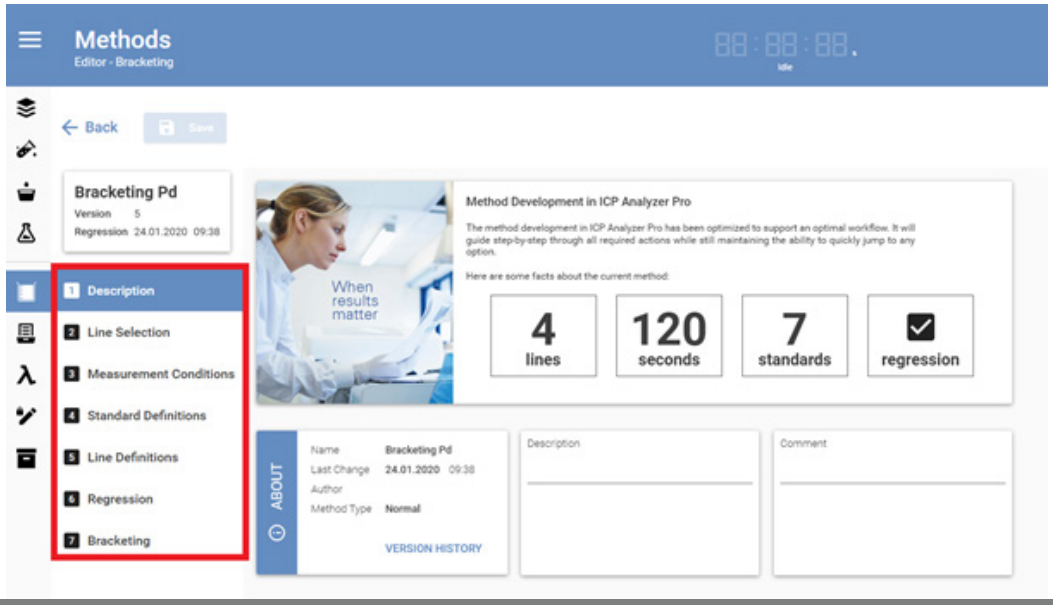


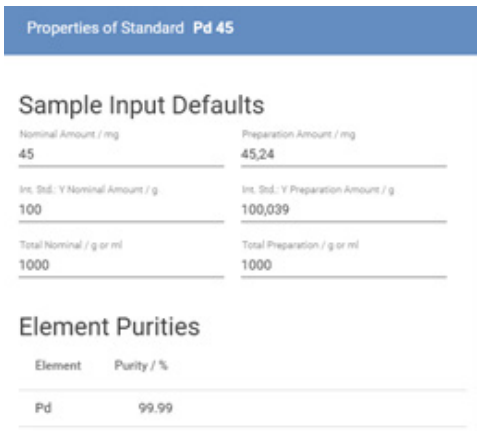
Figure 3: Method development in ICP Analyzer Pro software

Also, the nominal amounts of the weighted standard material, internal standard solution and the total volume or weight can be predefined in the method.

The measurement of the standards concludes the method setup. The measurements can be performed automatically using an autosampler and the software's sequence module. Figure 5 shows the dialog for the definition of the calibration standards. In this example, seven standards were defined in the method and are visible in the top left corner of the dialog. Since the standards are slightly different with every preparation, to correct the concentrations a nominal to actual comparison is used for the sample amount, the total volume or weight and the amount of the internal standard. The inputs for the selected standard are entered. After the positions of the standards are defined, the sequence for the automatic measurement of the standards can be started.

The resulting calibration function is displayed in the method development's regression view, as shown in figure 6 for one analytical line. The effect of the nominal to actual comparison is displayed in the area highlighted in red. The "certified" concentrations (Cert.

Figure 4: Definition of bracketing standards



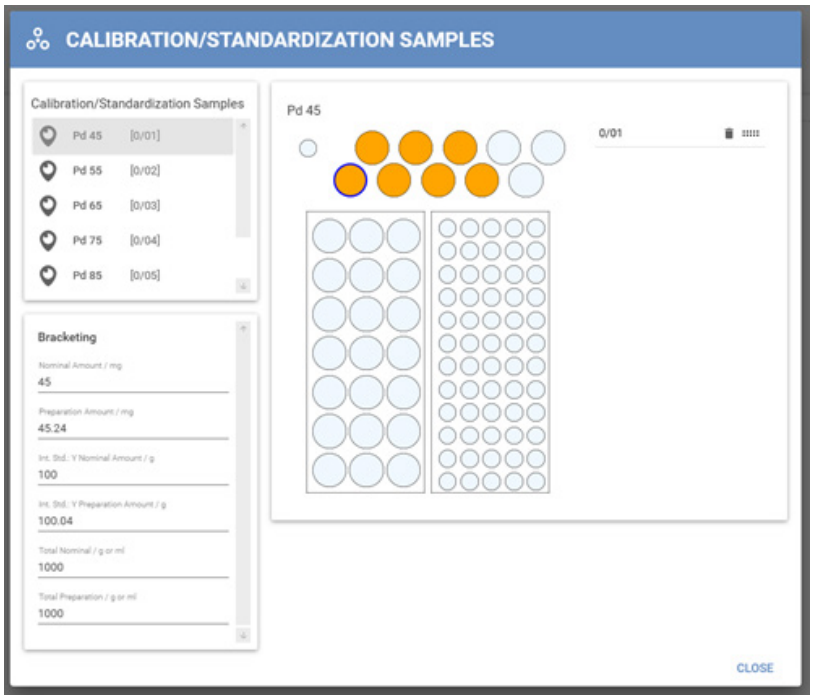


Figure 5: Definition of the sample positions and inputs for each calibration standard

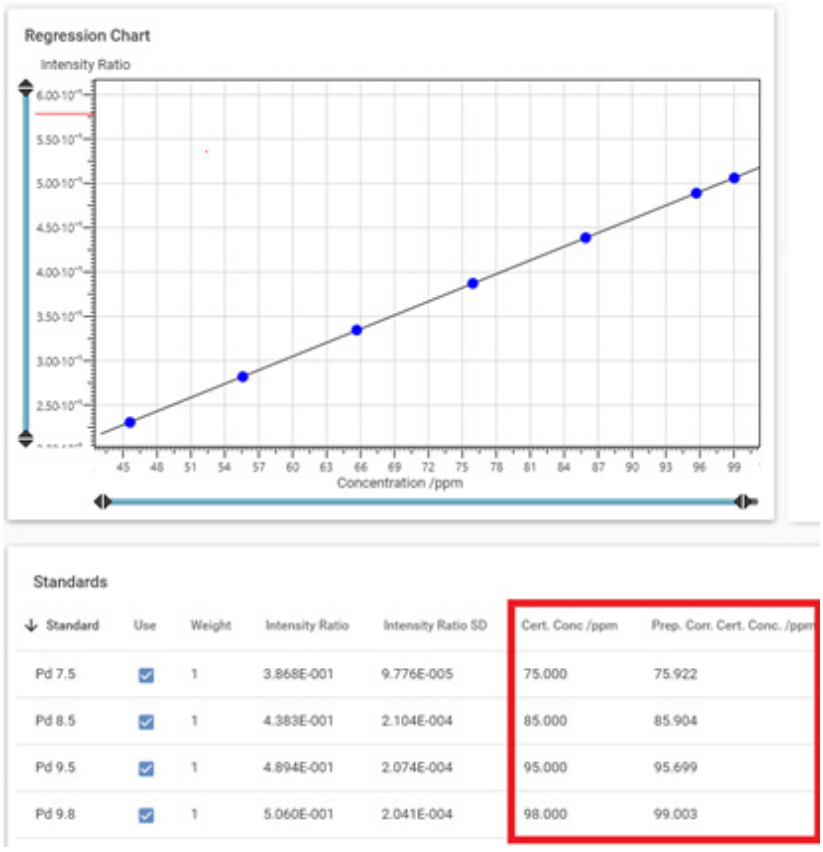


Figure 6: Example of a calibration function with the corrected standard concentrations calculated using actual preparation amounts

Conc) were used for the definition of the standards. Since the actual preparation amounts deviate from the nominal amounts, the standard concentrations were corrected to preparation-corrected certified concentrations (Prep. Corr. Cert. Conc).

Now, the samples can be analyzed. In case the sample concentrations are completely unknown, preliminary concentrations for the selection of the bracketing standards can be obtained by “normal” analysis of the samples using the established calibration functions.

Figure 7 shows the sequence view of the ICP Analyzer Pro software with a bracketing setup and two bracketing samples. Like in method development, the user is guided through the setup process step by step. New samples can simply be added by typing in the list, the use of a multi-add function or the addition via the clipboard. Events like calibration, rinse and control sample measurements can be added by drag and drop; logic functions like automatic repetition and failure actions are included. After the addition of a bracketing sample into the sequence list and the input of the required information — the sample weight, the total amount of the digested sample and the nominal and preparation amount for the internal standard — the bracketing cycle configuration can be defined.

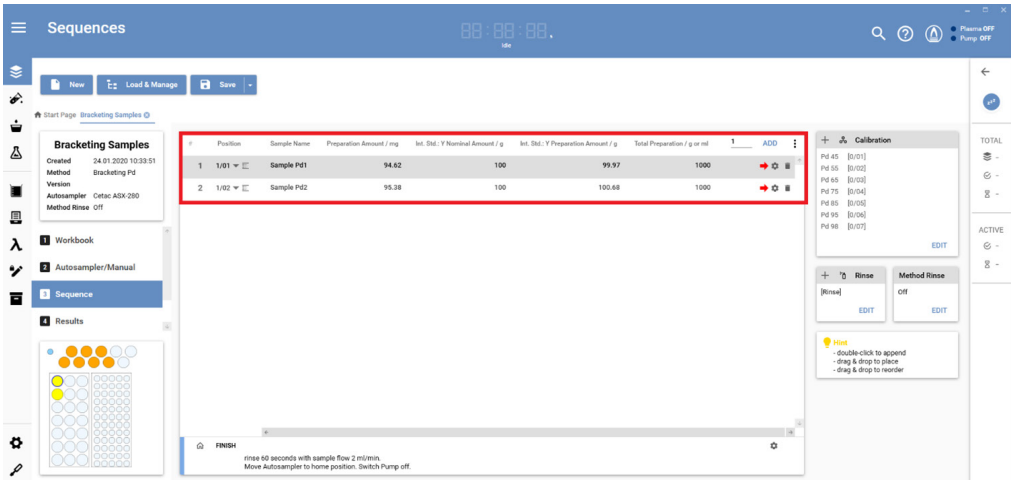


Figure 7: Sequence view of the ICP Analyzer Pro software with a bracketing setup

The ⚙ icon starts the setup (figure 8). In this dialog, the number of bracketing cycles and the two standards can be chosen. The CREATE button automatically creates the bracketing sequence. The sequence can be reviewed, edited when needed and the definition easily be copied to other samples. After the sequence measurement was started, the measurement progress as well as the final results are directly displayed in the sequence view of the software.

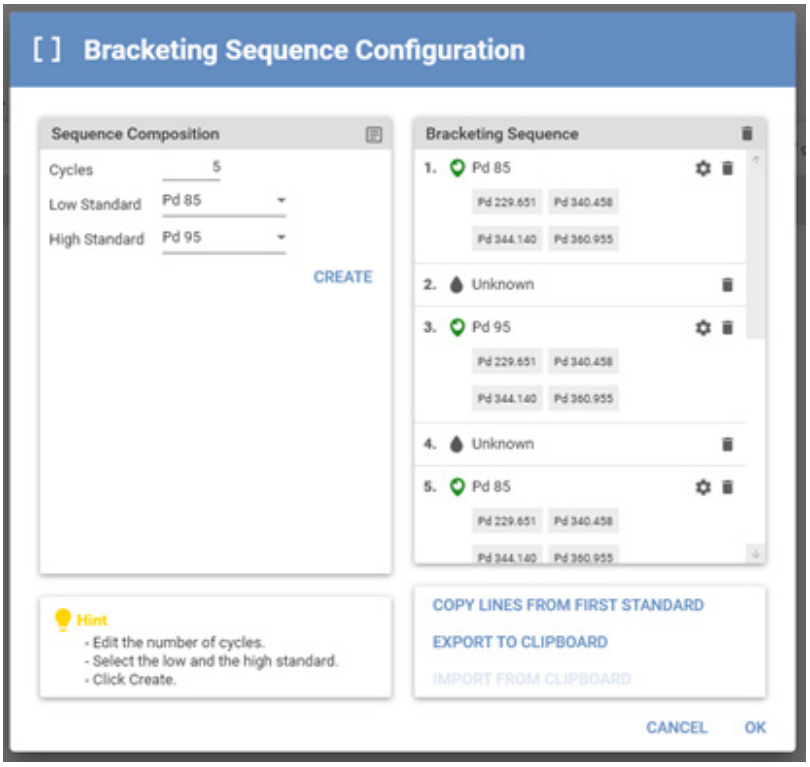


Figure 8: Configuration of a bracketing sequence

Thanks to a powerful recalculation tool, ICP Analyzer Pro also offers the recalculation of bracketing samples. If final results require changes, they can be loaded into the recalculation tool. Figure 9 shows the recalculation view for bracketing results with two samples loaded. Selecting a sample from the left-hand sided list, the details of this bracketing sample are displayed.

The view is divided into four areas. The red-marked area shows the results from the individual bracketing cycles as well as the mean, reported value. In this example, five bracketing cycles were performed. To easily review the results, the solution concentration is provided as the "raw" value in addition.

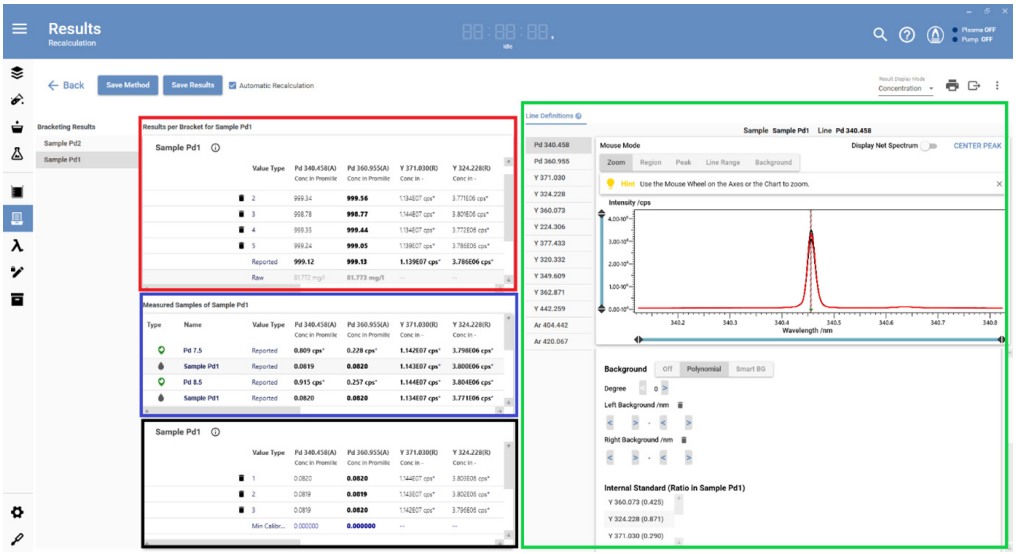


Figure 9: Recalculation view of bracketing results

The blue-marked area is the recalculation view which displays all results from the bracketing sequence as mean values in intensity units. By selecting one of the standards or samples, the details of this measurement are shown in the black-marked area. In this view, the single replicates, mean values and RSD values are shown.

The right, green marked side of the recalculation view enables the editing of different parameters, e.g. the correction of line parameters like the peak position, the assignment of internal standard lines, changes of the sample inputs or even the sample name. After any change, the software directly recalculates all results based on the change made, with the effect simultaneously visible in the left sided result tables.

When all necessary changes are completed, the results can be saved. Saving creates a new version of the results. The previous, original version of the result is still accessible through the calculation history (figure 10). Here, all result calculations can be reviewed and the changes between the different calculations be visualized, which provides perfect traceability.

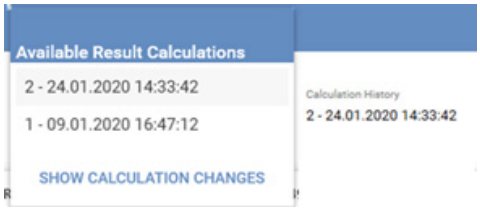


Figure 10: Calculation history of sample measurements

Accuracy and precision of Bracketing

As an example for the accuracy and precision of a bracketing method, the determination of palladium in palladium jewelry alloys according to the ISO standard 11495 [2] is shown. Two palladium samples, and a duplicate of the second sample, were analyzed using the bracketing method. Table 1 displays the reported concentrations of the original samples together with the corresponding relative standard deviation (RSD). The results show a perfect precision and a good repeatability of the duplicate determination.

The relative standard deviation (RSD) of the standard and sample measurements should be lower than the required mean value of 0.2% [ISO11495]. As shown in table 2, the measured RSD values for all measurements of a bracketing sequence, consisting of five bracketing cycles, are far below this required limit for all measured bracketing samples. **It is this benefit that the bracketing technique can improve the High Precision measurement of P & K in fertilizers, reducing the mechanical and matrix errors associated with preparation and ICP analysis of feeds and fertilizers.**

Table 1: Sample Results of two bracketing samples including one duplicate sample

	Sample Pd 1	Sample Pd 2-1	Sample Pd 2-2
Concentration [‰]	999.12	997.05	997.07
RSD	0.027%	0.018%	0.044%

Table 2: Relative standard deviation (RSD) of all sample analysis from a bracketing sequence, consisting of five bracketing cycles

	Sample Pd 1 RSD [%]	Sample Pd 2-1 RSD [%]	Sample Pd 2-2 RSD [%]
Analysis	0.067	0.073	0.062
Analysis	0.045	0.081	0.063
Analysis	0.099	0.055	0.084
Analysis	0.037	0.072	0.073
Analysis	0.066	0.097	0.061

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