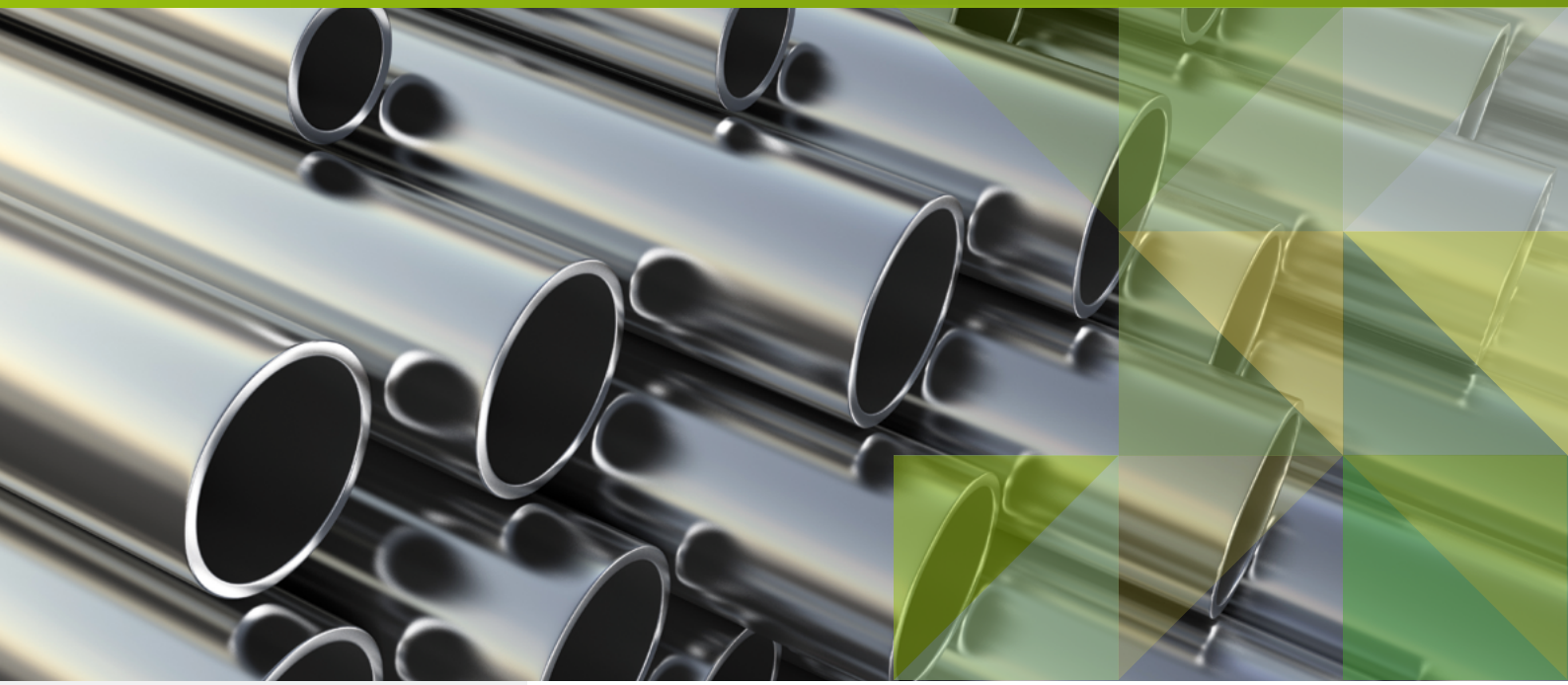

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How to maintain the best pickling results with metal pickling process?

Mineral acid and pickle liquor measurements done fast with Timegated® Raman technology

Conventional acid quantifications, including titrimetric and potentiometric techniques, can be time consuming and they often require sample preparation procedures and the use of reagents. Vibrational spectroscopy techniques like IR or Raman on the other hand usually require minimal amounts of sample preparation and they are often easier to apply for on-line measurements. Online acid quantification can be especially important for industrial processes like metal pickling. Metal pickling is a process where a corrosive pickling liquor removes impurities from a metal surface. The pickle liquor acid contents and any potential changes in the acid concentrations have to be known in order to achieve the best pickling results. A continuous analysis method would enable a faster adjustment of pickle liquor composition during a pickling process run.

Raman spectroscopy is an established process analytical technology tool which, unlike most IR spectroscopy methods, is well suited for working with aqueous solutions. Raman spectroscopy does not only produce elemental information but instead it provides information about the molecular structure of the analytes. Sulfuric acid and nitric acid quantifications for example are based on studying the sulphate and nitrate species vibrational Raman spectra.

Timegated Raman is most often used for samples with high levels of interfering photoluminescence emission. Timegating can also be practical in process conditions. It removes background emission (e.g. room lighting) and thermal emission interference. It also enables measurements through polymer windows or cuvettes by rejecting the fluorescence produced by the polymer material. This can be especially useful for samples which contain substances (e.g. hydrofluoric acid) that corrode glass and other window materials.

Acid quantification using timegated Raman was studied with pickle liquor samples from stainless steel pickling processes. The samples contained mainly 11-89 g/L HNO_3, 20-160 g/L H_2SO_4 and 5-57 g/L HF. Because the samples contained hydrofluoric acid, the undiluted samples were measured through disposable polymer cuvettes. The spectra acquisition time was about 3 minutes per sample. Mineral acid spectra in aqueous solutions are presented in figure 1.

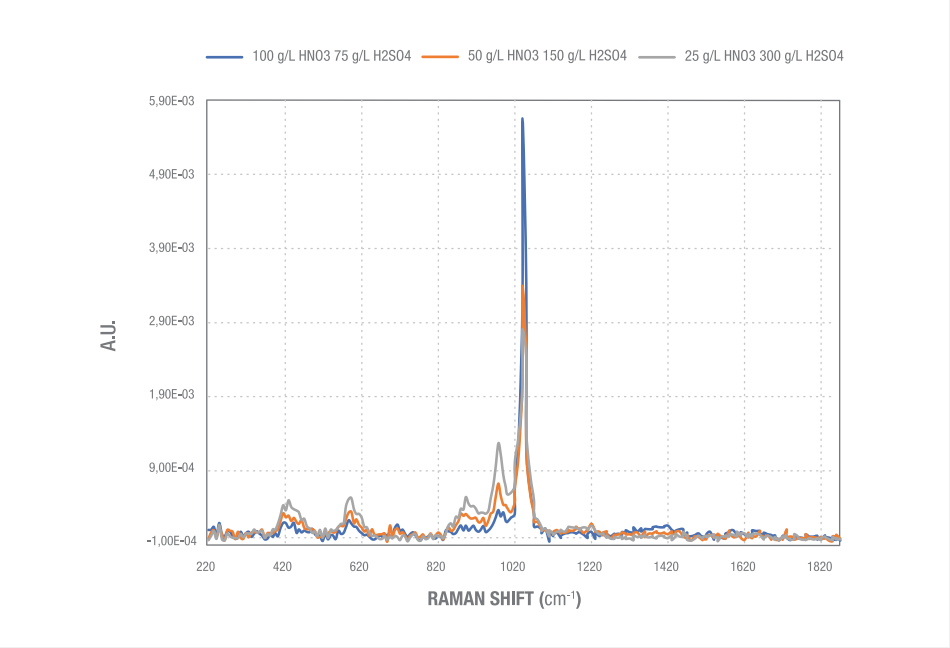

Figure 1:
Nitric and sulfuric acid Raman spectra in aqueous samples.

Multivariate calibration methods are widely used with vibrational spectroscopy techniques. These methods can help resolve some ambiguities resulting from partial overlapping of signals or otherwise complex spectra which are difficult to analyse using conventional univariate methods.

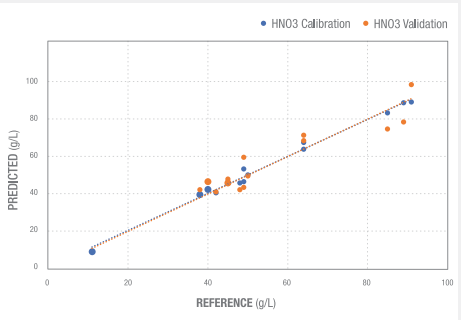

Figure 2:
HNO_3 PLSR calibration and cross validation plots.

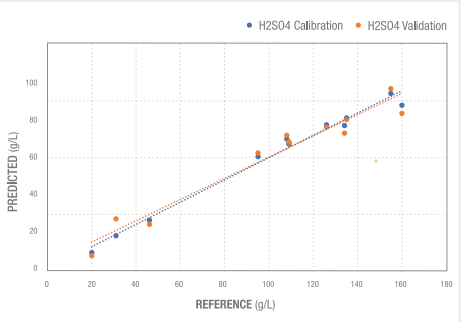

Figure 3:
H_2SO_4 PLSR calibration and cross validation plots.

A PLSR (Partial Least Squares Regression) model was applied for HNO_3 and H_2SO_4 quantification using Unscrambler 10.4.1 software (CAMO Software AS, Norway). Reference acid concentration values were used for the model construction. The reference acid concentrations were determined using NaOH titration for total acid concentration, nephelometry for sulfuric acid and a nitrate selective electrode for nitric acid concentration. 15 pickle liquor samples were available with reference nitric acid concentration values and 12 samples with reference sulfuric acid concentration values.

A full leave one out cross validation (LOOCV) was used for the PLSR model validation. Root mean square error values, R-squared values of cross validation and calibration plots (figures 2 and 3), explained variance and residual variance were used for model evaluation.

Usually a larger measurement data pool is used for a multivariate calibration model. However, this smaller scale study shows the potential of using timegated Raman spectroscopy for nitric and sulfuric acid quantification and the results are promising especially considering the very limited sample pool. Timegated Raman spectroscopy is suitable for on-line measurements and it can be coupled with other on-line measurement techniques for flexible data acquisition and process control.

Figure 4:
The pickling process removes impurities from metal surfaces.

Summary

Timegated® Raman spectroscopy is suitable for on-line measurements for nitric and sulphuric acid quantification. It has many advantages compared to conventional acid quantification methods, such as:

01

Timegated Raman is a fast technique for acid quantification and it can be applied for on-line measurements

02

Only minimal sample preparation is required

03

Timegating increases measurement reliability by minimizing background interference including photoluminescence, room lighting and thermal emission interference

04

Raman spectroscopy is well suited for working with aqueous solutions

For more in-depth details please see:
Heilala B.; Mäkinen A.; Nissinen I.; Nissinen J.; Mäkynen A.; Perämäki P.; Microchem. J., **2018**, 137, 324

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