



Evaluation of time-gated Raman spectroscopy for the determination of nitric, sulfuric and hydrofluoric acid concentrations in pickle liquor



Bryan Heilala^{a,c}, Ari Mäkinen^a, Ilkka Nissinen^b, Jan Nissinen^b, Anssi Mäkynen^a, Paavo Perämäki^{c,*}

^a Optoelectronics and Measurement Techniques, University of Oulu, P.O. Box 8000, 90014 Oulu, Finland

^b Circuits and systems, University of Oulu, P.O. Box 8000, 90014 Oulu, Finland

^c Research Unit of Sustainable Chemistry, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland

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ABSTRACT

The focus of this study was to assess the feasibility of time-gated Raman spectroscopy for stainless steel pickle liquor acid quantification. Pickle liquor is used for dissolving metal surface impurities during the pickling process. The pickle liquor samples consisted mainly of 11–89 g/L HNO₃, 20–160 g/L H₂SO₄, 5–57 g/L HF and stainless steel residue. Raman peaks correlating with the different acids were identified in both aqueous and pickle liquor solutions. The linearity between Raman scattering intensity and acid concentration was studied. Multivariate PLSR calibration for pickle liquor HNO₃, H₂SO₄ and HF quantification was also investigated. Time-gated Raman spectroscopy was found to be a promising technique for pickle liquor HNO₃ and H₂SO₄ quantification.

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1. Introduction

In the field of metal industry, various surface treatments often require that rust and other surface impurities are removed. During the pickling process some of the metal surface dissolves in the corrosive pickling liquor removing the surface impurities in the process [1,2]. Pickle liquors can be divided into two groups: Liquors used in galvanizing plants and liquors used in stainless steel rolling mills. Galvanizing plant pickling liquors usually consist primarily of hydrochloric acid and metal ions. The pickle liquors in steel rolling mills are usually more complex acid mixtures and they contain primarily hydrofluoric and nitric or sulfuric acid and metal ions [1]. Pickle liquor samples used in this study also contained sulfuric acid in addition to hydrofluoric and nitric acid.

Acid contents of pickle liquors have to be known in order to achieve the best pickling results. Methods used for pickling bath acid concentration measurements include acid-base titrations for total and free acid concentration determination and the use of fluoride selective electrode for hydrofluoric acid concentration determination [2,3]. Also multi-sensor techniques have been developed that make use of combined analysis methods including ion selective electrode, ultrasonic speed, conductivity, density and refraction index measurements [4,5].

This study was aimed at assessing the suitability of Raman spectroscopy for one-step acid analysis of stainless steel pickling bath process liquors. The method could be used to save on acid consumption and to reduce chemical metal surface wear. Raman spectroscopy is a convenient analysis technique that requires minimal sample preparation and enables on-line measurements. Raman spectroscopy is also suited for analysis of aqueous samples unlike many techniques based on IR spectroscopy. The currently used pickle liquor analysis methods are quite time consuming. Developing a continuous analysis method would provide valuable information about the pickling bath composition in shorter time intervals and it would also enable faster adjustment of pickle liquor composition.

Measurements in this study were done using a time-gated Raman spectrometer. Fluorescence emission from the sample solution has a longer delay compared with Raman scattering, which is almost instantaneous. A time-gated Raman apparatus exploits this time difference and is capable of fluorescence rejection. Time-gated Raman techniques are usually used for samples with disruptive levels of fluorescence. In this study, the analyzed sample solutions exhibited a low amount of fluorescence except for fluorescence originating from the plastic cuvettes. However, time gating usually keeps the spectra background quite low and makes the measurements less susceptible to stray light and cosmic rays, which in turn reduces the need for preprocessing of the spectral data. Earlier research focusing on quantification of three different pickling bath mineral acids using time-gated Raman spectroscopy has not been published to the best of the authors knowledge.

* Corresponding author.

E-mail address: paavo.peramaki@oulu.fi (P. Perämäki).

2. Experimental

2.1. Reagents

The following analysis grade acids (Merck Millipore) were used in this study: 65% HNO₃, 95–97% H₂SO₄, and 40% HF. The water used for sample preparation and cuvette rinsing was purified with a Merck Millipore Elix system.

2.2. Sample solution and reference measurements

The pickle liquor samples used in this study consisted of 11–89 g/L HNO₃, 20–160 g/L H₂SO₄, 5–57 g/L HF, and 6–59 g/L iron. Because the pickle liquors were used for stainless steel pickling, they probably contained several other metals in addition to iron.

At the stainless steel factory where the pickle liquor samples were received from, the total acid concentrations were determined with NaOH titration and SO₄²⁻ concentrations were measured using nephelometry with a BaSO₄ precipitate. Fluoride and nitrate concentrations were measured using ion selective electrodes. The pickle liquor acid concentrations are calculated using the measurement results of the aforementioned analysis methods. In this study, these measurement results were used as reference results. The quality control measurements for these reference analysis techniques are conducted using aqueous acid samples without the actual pickle liquor sample matrix. The QC measurements of a time period of about 18 months (n = 70) had a standard deviation of 0.85 g/L for HNO₃ (31.5 g/L concentration), 2.8 g/L for H₂SO₄ (98.0 g/L concentration) and 0.49 g/L for HF (10 g/L concentration).

2.3. Instrumentation

Raman measurements were done with a time-gated experimental Raman spectrometer equipped with a single photon avalanche diode (SPAD) detector [6–8]. An experimental 532 nm pulsed laser was used for sample illumination. The pulsed micro-chip laser was based on a semiconductor saturable absorber mirror (SESAM) having a pulse width (full width at half maximum) and energy of approximately 150 ps and 0.2 μJ, respectively.

Before the determinations utilizing multivariate data analysis in calibration, the Raman spectrometer was upgraded with a new laser that enabled shorter measurement times. It was verified that no spectra drift or changes caused by sample heating were present while using the more powerful laser. The new Teem Photonics 532 nm laser had a repetition rate of 360 kHz, Δλ of <0.11 nm, pulse width (FWHM) of 160 ps and pulse energy of 1 μJ resulting to approximately 300 mW of average power.

Initial measurements without HF were done using glass cuvettes and the later measurements with samples containing HF were done using disposable plastic BRAND UV cuvettes (BRAND GMBH + CO KG; Wertheim, Germany). The plastic cuvettes produced several Raman peaks but they were removed using blank correction. Data collection time was about 5 min per sample with the first laser and about 3 min with the Teem Photonics laser. Data processing, peak fitting and peak area integration were done using an in-house script in the MATLAB R2016b software environment (The MathWorks, Massachusetts). Unscrambler 10.4.1 software package (CAMO Software AS, Norway) was used for multivariate data analysis.

3. Results and discussion

3.1. Spectra

Peaks due to HNO₃ and H₂SO₄ were first identified from aqueous solutions with various acid concentrations (Fig. 1). The identified peaks were at the 1100–300 cm⁻¹ wavenumber region. Sulfuric acid

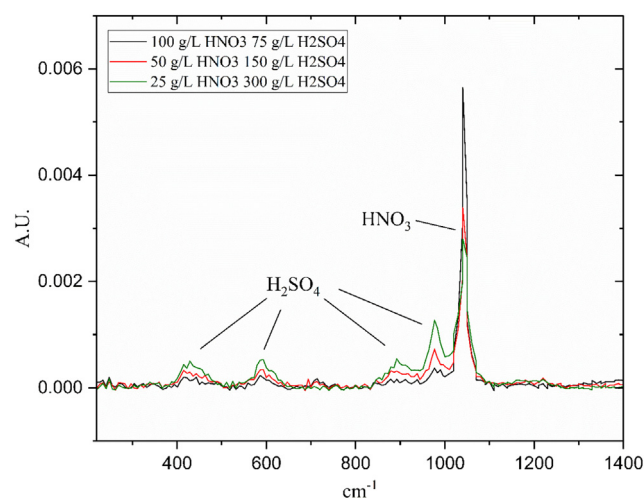


Fig. 1. Raman peaks due to aqueous solutions of H₂SO₄ (75, 150 and 300 g/L) and HNO₃ (100, 50 and 25 g/L).

produced several peaks (977, 892, 592 and 429 cm⁻¹). The peaks at 429 and 592 cm⁻¹ can probably be assigned to bisulfate ion, 892 cm⁻¹ peak to HSO₄⁻ symmetric stretch (ν_1) and 977 cm⁻¹ to SO₄²⁻ bend (ν_2) [9,10]. Nitric acid produced one identified peak (1042 cm⁻¹). This peak corresponds to nitrate ion symmetric stretch band [11]. These findings are in agreement with previous reports [9–12].

Linear dependence between the intensity of Raman scattering and concentration was observed for both HNO₃ and H₂SO₄. Although the responses seemed linear even when analyzing solutions containing both HNO₃ and H₂SO₄, sulfuric acid produces some Raman scattering (HSO₄⁻ (ν_3) and (ν_4) modes) at the HNO₃ 1042 cm⁻¹ wavenumber region [9,10,12,13]. Hence a multivariate model might be a more suitable data analysis method in part because of this (discussed more in depth later).

Any Raman peaks correlating with sample HF concentration were not observed with the time-gated Raman spectrometer used. In addition to the 1870–220 cm⁻¹ wavenumber range, the 3520–1870 cm⁻¹ range was also scanned to check for any relevant Raman peaks. No usable peaks due to HF were detected in aqueous samples even when measuring samples with high HF concentrations of 110–225 g/L. However, Raman signals due to HF have been reported earlier although with a different Raman apparatus and laser wavelength [11].

An earlier paper [14] suggests that Raman peaks due to HF might be difficult to observe in a sample matrix containing sulfuric acid. Sulfuric acid might react with hydrofluoric acid producing fluorosulfonic acid dampening the HF Raman peaks. The researchers were able to correlate fluorosulfonic acid peaks (1082 and 810 cm⁻¹) with HF concentrations. In this study however, no quantifiable peaks due to HFSO₃ were observed. Neither were any changes observed in H₂SO₄ peaks with varying HF concentrations.

The features of the spectra originating from pickle liquor samples (Figs. 2 and 3) were not significantly different from the aqueous solution spectra. The pickle liquor matrix produced some additional noise and a minor peak between the 592 and 429 cm⁻¹ sulfuric acid peaks. No shifts in HNO₃ or H₂SO₄ peak positions were observed. However, high iron concentrations may affect sulfate band positions [13].

Even though the pickle liquor pH was quite low, a dark blue precipitate was observed at the bottom of the cuvettes when the pickle solution was kept in the cuvettes for several days. Precipitation could affect the measurements and it would probably be desirable to analyze the samples shortly after sampling. This was not, however, possible during this study.

The measured Raman peak intensities were lower in pickle liquor spectra compared with aqueous sample spectra. The pickle liquor

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