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# Rapid Pollutant Identification in Industrial Wastewater using Raman spectroscopy and XRF

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**Abstract:** Given the inherent environmental risks, industrial plants are forced to optimise the efficiency of their on-site treatment processes. Accurate identification of pollutant types and concentrations in wastewater, especially in industrial settings, is often a significant hurdle. In this study, portable Raman spectroscopy and XRF instrumentation were used to analyse industrial wastewater samples from pickling and electropolishing of stainless steel. A three-step methodology for rapid categorisation of the wastewater was developed. Peaks observed in Raman spectra at 900, 990, 1050 and 1380 $cm^{-1}$ enable the type of effluent and its dilution to be distinguished. XRF measurements are then used to determine the approximate elemental composition. The use of portable analytical instruments to estimate contamination levels is crucial to effectively manage the neutralisation of industrial wastewater and respond to unexpected changes in concentrations.

**Keywords**: Raman spectroscopy; on-site identification; industrial wastewater; stainless steel

Industrial wastewater from various sectors, including electroplating and pharmaceuticals, along with landfill leachate, poses significant environmental and health risks due to heavy metal ions and other pollutants. Therefore, it's critical to effectively remove these harmful substances at the industrial plant where they originate. Despite extensive research into treatment technologies and methods, the broader managerial decisions regarding treatment systems are influenced by various factors beyond just technical considerations. Despite the critical need for effective industrial wastewater management, there is limited scientific literature on tools supporting managerial decisions in this area. Modern portable testing equipment, such as Near Infrared Spectroscopy, X-ray Fluorescence (XRF), and Fourier transform infrared (FTIR) spectroscopy, now enables rapid, on-site analysis of contaminants, which is vital for quick decision-making in industrial settings. XRF, once costly and complex, is now widely used in various fields, from metallurgy to environmental assessment, due to its portability, speed, and non-destructive nature for the analysis of elements in different samples. Similarly, recent advancements have transformed Raman spectroscopy into a highly sensitive, portable, and cost-effective analytical tool, enabling real-time analysis of industrial wastewater and various other samples. While both FTIR and Raman spectroscopy are powerful techniques, they offer complementary insights; Raman is more sensitive for liquid samples and tolerates simple conditions, whereas FTIR is generally more robust. The ability of these portable spectroscopes to provide high temporal resolution measurements directly at the industrial process significantly improves monitoring, especially in accident scenarios. These technologies provide crucial support for managing industrial wastewater by allowing for immediate assessment of chemical properties and contamination levels.

This study focused on monitoring industrial wastewater from stainless steel chemical and electrochemical processing, specifically from pickling and electropolishing streams. Accurately identifying contaminant levels in these variable wastewater streams is crucial for effective treatment and neutralization, often requiring quick decision-making due to fluctuating pollutant concentrations. This work demonstrates the use of portable Raman and XRF spectrometers for the preliminary identification of industrial wastewater types, using measurement data from samples of varying composition and dilution. The goal is to establish a novel research and decision-making procedure that serves as an initial step in wastewater stream management for stainless steel processing companies, ultimately leading to more efficient neutralization.

The investigation focused on two primary industrial wastewater streams: pickling wastewater (PWw), containing nitric and hydrofluoric acids with various metal ions including iron, chromium, nickel, copper, among others, and electropolishing wastewater (EPWw), with phosphoric and sulfuric acids and similar metal ions. Researchers tested pure samples of both wastewater types, various mixtures, and individual acids at different dilution factors (1-100), all diluted with tap water to simulate industrial conditions, using Raman spectrometry, XRF, and ICP-OES for analysis. Measurements in this investigation were performed using a portable XRF Vanta C spectrometer from Olympus for elemental analysis (iron, chromium, nickel, copper, phosphorus, sulfur, calcium), the FirstDefender RM Chemical Identification System by Thermo Scientific for Raman spectroscopy, and a Thermo Scientific iCAP 7000 Series ICP-OES apparatus for inductively coupled plasma–optical emission spectroscopy.

The samples tested included 100% electropolishing wastewater (EPWw) and 100% pickling wastewater (PWw), along with mixtures of these two types in various proportions (e.g., 75% PWw + 25% EPWw, 50% PWw + 50% EPWw, and 25% PWw + 75% EPWw), all tested at dilution factors of no more than 100. These mixtures were crucial for simulating real industrial conditions where wastewater often combines outputs from different technological processes.

The procedure for identifying wastewater begins with analyzing the Raman spectrum to detect the presence of sulfuric, orthophosphoric, and nitric acids. Distinct peaks at approximately 900 $cm^{-1}$ (A), 990 $cm^{-1}$ (B), and 1050 $cm^{-1}$ (C) indicate these acids, helping classify the sample as pickling wastewater (PWw), electropolishing wastewater (EPWw), or a mixture. The relative heights of these peaks, such as A > B > C for EPWw or C > A ≥ B for specific mixtures, further characterize the wastewater type and composition. The second step estimates the approximate water content by comparing the height of peak C (at ~1050 $cm^{-1}$) to peak D (at ~1380 $cm^{-1}$ from water). For instance, if peak D is greater than C, the dilution factor is 25 or more, while a less prominent D peak suggests a more concentrated solution with a dilution factor of 2 or less. Finally, XRF spectrometry is used to determine the concentrations of elements like sulfur, potassium, iron, chromium, nickel, and copper. While these methods are still being refined, particularly for highly diluted wastewater, they provide crucial information for managing concentrated industrial wastewater, which presents the biggest environmental challenge.

This research led to a graph designed to help identify and estimate the composition and dilution of industrial wastewater. It demonstrates that portable Raman spectroscopy and XRF spectrometers can provide a preliminary assessment of wastewater from stainless steel pickling and electropolishing. The essence of the research carried out is not to precisely determine the concentrations of the pollutants investigated, but only to estimate them to enable appropriate measures to be taken in the management and treatment of industrial wastewater. Analyzing characteristic peaks in Raman spectra for sulfuric, nitric, and orthophosphoric acids forms the core of a new procedure for identifying wastewater type and its industrial origin. The developed identification graph offers a three-stage procedure: first, identifying the wastewater type (EPWw, PWw, or a mixture); second, determining the proportion of each wastewater type; and third, establishing the wastewater's dilution factor. This rapid identification of contaminants on site can help to effectively neutralise and treat industrial wastewater.

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