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Simultaneous Determination of Cu^{2+}, Co^{2+} and Ni^{2+} by Fiber-Optic Spectroscopy in the Visible and Near-Infrared Range

The simultaneous quantitative determination of dissolved Cu^{2+}, Co^{2+} and Ni^{2+} ions is important in many fields. These include metallurgy, geology, industrial wastewater analysis and the monitoring of biotechnological processes. In many cases, their concentrations need to be measured directly at the sampling site or in-line during an operating process. Characteristic spectral signatures in the visible region allow their measurement using compact spectrometers and fiber-optic probes. Combined with multivariate calibration, this equipment enables the analysis of complex mixtures without prior separation. In the present study, ternary aqueous solutions of copper(II), cobalt(II) and nickel(II) nitrates, prepared according to a diagonal experimental design, were measured using a fiber-optic transflection probe. The resulting spectra were analysed, and a PLS2 multivariate calibration model was developed to determine the concentrations of all three metal ions from a single spectrum of an unknown mixture. Simultaneous determination was achieved over concentration ranges of up to approximately 100 mmol/L, with prediction errors of approximately 0.3-1.2 mmol/L. The proposed approach can be implemented as a compact optical system for rapid field analysis and wastewater monitoring, as well as for in-line process analysis in industrial applications.

Copper, cobalt and nickel are widely used in alloy production, electroplating, battery technologies and other industrial applications. Mining and industrial processing of these metals can generate wastewater containing dissolved metal ions, which must be monitored because elevated concentrations may harm aquatic ecosystems. These elements also serve as trace nutrients in selected biotechnological processes. Reliable determination of Cu^{2+}, Co^{2+} and Ni^{2+} is therefore important for wastewater monitoring and process control.

Although traditional methods such as atomic absorption spectroscopy, inductively coupled plasma techniques, electrochemical analysis and laboratory spectrophotometry can provide high sensitivity and selectivity, they do not always meet the requirements of rapid analysis because they commonly require sampling and sample preparation. For field and process applications, analysis at the sampling site with minimal sample preparation or directly in-line without sampling is therefore desirable.

Visible absorption spectroscopy is well suited to the determination of Cu^{2+}, Co^{2+} and Ni^{2+} because these ions exhibit characteristic absorption bands in the visible region.

Figure 1. Measurement setup with a Transflection fiber-optic probe (art photonics GmbH) with an adjustable optical path length.

The measurements can be performed using compact spectrometers and fiber-optic probes. However, substantial overlap between the absorption bands makes simultaneous determination of the three ions difficult using conventional single-wavelength photometric measurements. Multivariate calibration can extract concentration information from the full spectrum and thus enable quantitative analysis without prior separation.

In this application note, absorbance spectra of ternary aqueous solutions of copper(II), cobalt(II) and nickel(II) nitrates were measured in the visible and short-wave near-infrared regions using a fiber-optic transflection probe (art photonics GmbH, Germany) and a compact slit-type spectrometer. In this application note, the total optical path length was set to 10.0 mm (Fig. 1). Illumination was provided by an AvaLight-DH-S halogen light source (Avantes BV, the Netherlands). A multivariate calibration model was developed and evaluated for the simultaneous determination of all three ions from a single spectrum. The study assessed the feasibility and analytical performance of this approach for field analysis, wastewater monitoring and in-line analysis of industrial and biotechnological processes.

A calibration set of 27 ternary aqueous solutions (25.0 mL each) was prepared from the hydrated metal nitrates $Cu(NO_3)_2{\cdot}3H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ according to a diagonal experimental design (Fig. 2). The reference spectrum was recorded in air without a sample. The resulting spectra are shown in Fig. 3.

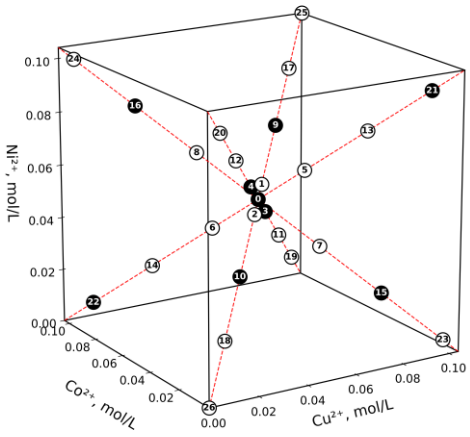

Figure 2. Diagonal experimental design for ternary aqueous mixtures of copper(II), cobalt(II) and nickel(II) nitrates [A. Bogomolov, Anal. Chim. Acta 951 (2017) 46-57]. Open and filled circles represent training and validation samples, respectively; labels indicate sample numbers.

The spectral data shown in Fig. 3 were used to develop calibration models for Cu^{2+}, Co^{2+} and Ni^{2+} concentrations using partial least squares regression for multiple response variables (PLS2). Five latent variables (LVs) were required to obtain accurate and robust calibration models for all three metal ions. Three LVs were associated with variations in metal concentrations. The remaining two LVs may be related to weak spectral effects known to arise from metal-nitrate interactions and salt-induced changes in the water absorption band near 970 nm.

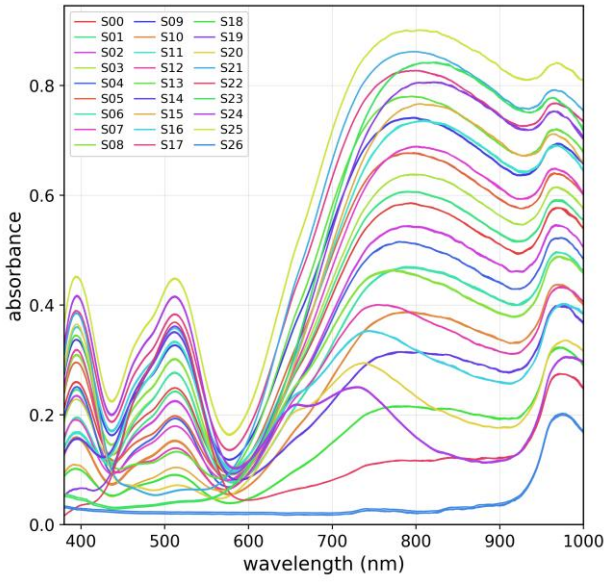

Figure 3. Absorbance spectra of the 27 designed copper(II), cobalt(II) and nickel(II) nitrate solutions. The spectra were smoothed using the Savitzky-Golay algorithm. The three replicate spectra for each sample are plotted in the same colour.

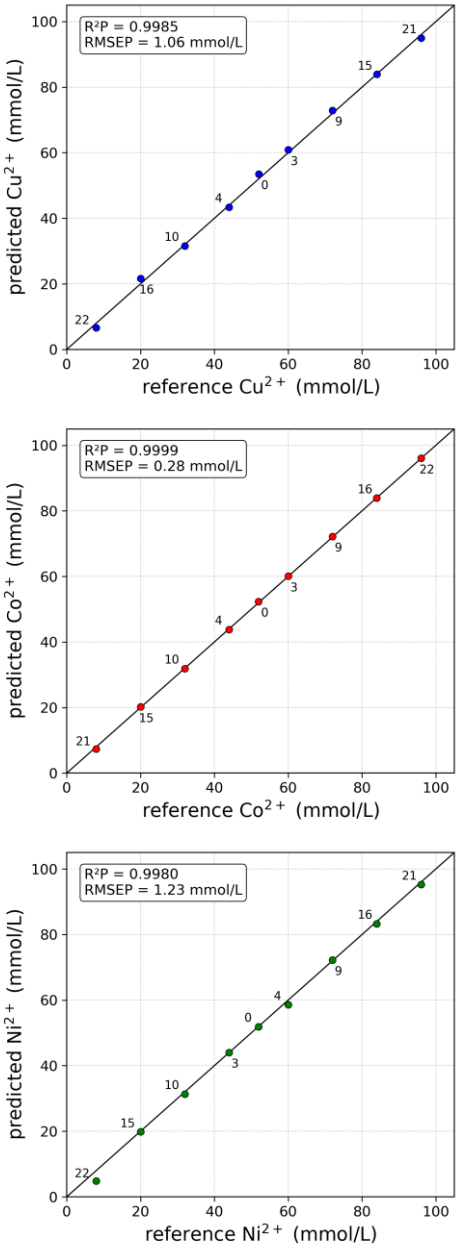

Figure 4. Predicted versus reference concentrations for Cu^{2+} (top), Co^{2+} (middle) and Ni^{2+} (bottom) in the validation set obtained with the five-latent-variable PLS2 model.

The proposed method enables simultaneous determination of copper(II), cobalt(II) and nickel(II) from a single spectrum recorded over the 380-1000 nm range using a compact spectrometer coupled with a fiber-optic probe. The method covers metal concentration ranges up to approximately 0.10 mol/L (0.6% m/v). The obtained results point to the possibility of achieving low detection limits for all three analytes. The broad working range and high prediction accuracy make the method suitable for various practical applications, including rapid field analysis, wastewater monitoring and in-line control of industrial and biotechnological processes.