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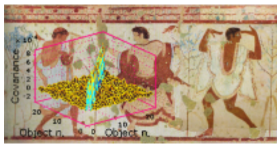

Application of SIMPLS Algorithm for Simultaneous Determination of Co(II), Ni(II) and Cu(II) in Industrial Alloys

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Abstract

Spectrometric multicomponent analysis is a subject of great practical importance in the environmental, clinical, pharmaceutical and cultural heritage areas. The partial least squares modeling based on SIMPLS algorithm was applied for the simultaneous spectrophotometric determination of Co(II), Ni(II) and Cu(II) with ammonium purpurate (murexide) as the complexing agent. The analytical wavelengths of 400 - 490 nm were chosen and the experimental calibration matrix for partial least squares was designed with 21 samples of 0.354 - 5.893, 0.352 - 5.869 and 0.381 - 6.355 µg ml-1 for cobalt, nickel and copper, respectively. A leave one out cross-validation procedure was used for selecting the number of components using PRESS. The method was successfully applied to the simultaneous determination of these metals in five industrial alloys.

Introduction

Cobalt, nickel and copper are environmental pollutant, which have been tested and assessed over the past few years from both the toxicological and the human health viewpoints. While slight quantities of them are essential for normal physiological processes, their excess intake poses an important threat to human health. So, it is necessary to determine their concentrations. Among the most widely used analytical methods are those based on the UV-Vis spectrophotometry techniques. The simultaneous determination of these metal ions is difficult due to the high spectral overlapping observed in the absorbance spectra of their complexes (see Fig. 1). A quantitative spectrophotometry has been greatly improved by the use of a variety of multivariate calibration method; of which the partial least squares (PLS) regression [1-2] is the most widespread, to relate the concentrations of the metal ions to the spectral properties. There are several algorithms for PLS: Nonlinear iterative partial least squares (NIPALS) and SIMPLS algorithm [3]. There is some evidence that SIMPLS algorithm is actually slightly superior to the NIPALS solution, because it maximizes the covariance criterion, which NIPALS does not.

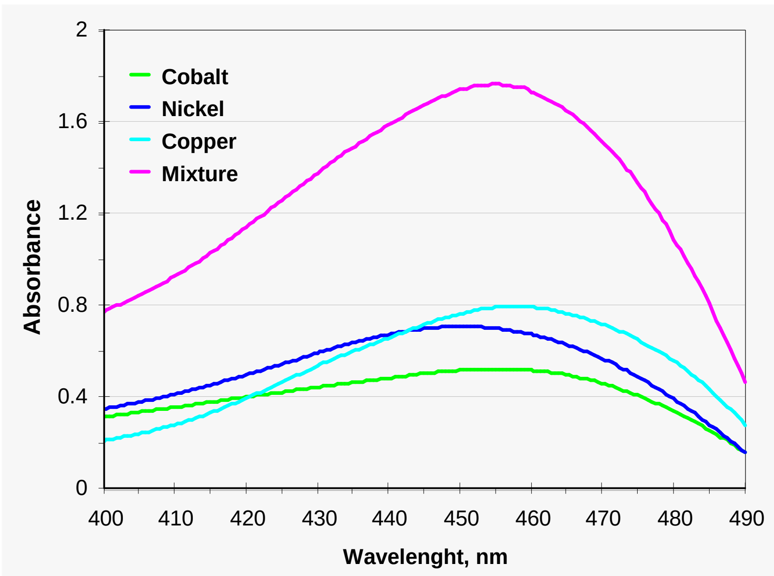

Fig. 1; Absorbance spectra of the cobalt, nickel and copper complexes and their mixture. Concentration of each ion is 2µg.ml^{-1} and the pH is 8.0.

Materials & Methods

All absorbance measurements digitized spectra were collected on a Shimadzu UV2102PC double bean UV-Vis spectrophotometer, using a 10 mm quartz cell. The recorded spectra were digitized with an interval of 0.5 nm between consecutive points. Therefore 181 data points were used to represent a spectrum in the range of 400 - 490nm. The computations were made on a Pentium IV computer. All the programs were written in MATLAB (Mathworks, Version 6.1) by the authors.

2ml buffer solution (pH 8.0) were transferred to 25 ml volumetric flasks followed by the addition of appropriate volumes of Co(II), Ni(II) and Cu(II). Then, 5ml of murexide solution were added to the volume. Each solution was thoroughly mixed and made up to the mark with doubly distilled water, mixed completely. The final concentration of these solutions varied in their respective linear determination ranges 0.354 - 5.893, 0.352 - 5.869 and 0.381 - 6.355 $\mu g\ ml^{-1}$ for cobalt, nickel and copper, respectively. For each measurement, about 2 ml of the above solution was transferred to a spectrophotometric cell and the spectra of all prepared solutions were recorded against of reagent blank sample.

Results

The complexes Co(II), Ni(II) and Cu(II)- murexide have the absorption maximum at λ = 456, 451.5 and 457.5 nm, respectively. The statistical results: Root mean square difference (RMSD), relative error of prediction (REP) and the square of the correlation coefficient (R^2) obtained by applying PLS algorithm to the seven prediction set samples are summarized in Table1.

Tab. 1, Statistical parameters of the test matrix using SIMPLS model

Cation	No. of PLS components	RMSD	R^2	REP (%)
Co	5	0.122	0.995	6.04
Ni	7	0.256	0.997	12.72
Cu	7	0.220	0.989	9.69

The proposed model (PLS) was successfully applied to the simultaneous determination of Co(II), Ni(II) and Cu(II) in five sample alloys. The recoveries obtained by PLS were between 89.89 and 102.22.

Conclusions

The cobalt-nickel-copper mixture is an extremely difficult complex system due to the high spectral overlapping observed in the absorption spectra of their complexes. In such cases, the determination of these metal ions based on complex formation with murexide using PLS was established, with good prediction ability in the synthetic mixtures. Results show that partial least square is an excellent calibration method to the determination of cobalt, nickel and copper together in five industrial alloys.

References

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