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Multicomponent Analysis by Flow Injection Using a Partial Least-squares Calibration Method. Simultaneous Spectrophotometric Determination of Iron, Cobalt and Nickel at Sub-ppm Levels

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A partial least-squares multivariate calibration method for the analysis of binary and ternary mixtures of Fe, Co and Ni, based on their reaction with 2,2′-dipyridyl ketone picolinoylhydrazone in a flow injection manifold was developed. The parameters controlling the behaviour of the system were investigated. For individual determinations, molar absorptivities of 6.64 × 10^3 (Fe, 367 nm), 3.89 × 10^3 (Co, 410 nm) and 5.17 × 10^3 l mol^{-1} cm^{-1} (Ni, 385 nm), were obtained, the limits of detection being 1.062, 1.489 and 0.685 μmol l^{-1}, for Fe, Co and Ni, respectively. The optimized method was applied to the analysis of two samples with complex matrices (a washing solution used in an automotive factory and a waste acidic mine effluent).

Keywords: *Iron, cobalt and nickel simultaneous determination; picolinoylhydrazones; flow injection; spectrophotometry; partial least squares*

Introduction

Iron, cobalt and nickel are metals which appear together in many real samples, both natural and artificial. In most instances, the characterization of these samples includes the determination of the metal ions present in them. The simultaneous determination of iron, cobalt and nickel has been studied in different samples and by using very different techniques. Thus, X-ray fluorescence studies were performed by Morris,[1] who determined microgram amounts of Fe, Co and Ni, among other metals, in sea-water after their preconcentration by solvent extraction with ammonium tetramethylene dithiocarbamate and isobutyl methyl ketone, and by Lau and Ho,[2] who reported limits of detection in the μg l^{-1} range after preconcentration as piperazine-1,4-bis(dithiocarbamate) complexes. Atomic fluorescence spectrometry has been also used after atomization using a microwave-induced plasma.[3] Several workers have employed electrochemical techniques for the simultaneous determination of Fe, Co and Ni, *e.g.*, polarography,[4] square-wave voltammetry[5] and alternating current voltammetry[6] have been successfully applied to copper alloys, food and polymer materials, respectively.

Another group of techniques that have frequently been used for the simultaneous determination of Fe, Co and Ni are the chromatographic methods. Although some gas chromatographic applications have been reported,[7] most use liquid chromatography. Xie *et al.*[8] studied the simultaneous determination of trace amounts of Fe, Co and Ni (besides Cu, Zn and Pb) in human hair by ion chromatography and reversed-phase HPLC has been applied, for instance, by Miura and Tokunaga,[9] who used 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol for chelating metal ions, and by Doležal and Sommer,[10] who formed metal chelates of 4-(2-pyridylazo)resorcinol and 4-(2-thiazolylazo)resorcinol. Also important but less frequently used are methods based on neutron activation analysis[11] and atomic absorption spectrometry.[12,13]

Finally, the methods most frequently employed for the simultaneous determination of Fe, Co and Ni are spectrophotometric. Thus, the first approach was carried out in 1966 by Pueschel *et al.*,[14] who developed a tedious process based on the spectrophotometric response of the metallic complexes formed with 1-(2-pyridylazo)-2-naphthol. This method was later applied to natural waters.[15] Various other spectrophotometric reagents have been used for the simultaneous determination of these metals. For example, hexamethylphosphoramide forms coloured complexes in the presence of SCN^-,[16] 2[-di-(2-pyridyl)methylidenehydrazino]pyridimide[17] is used at pH 9 and in aqueous ethanolic medium, 2,2′-dipyridyl ketone 2-quinolylhydrazone[18] at pH 9 and in aqueous ethanolic medium, EDTA[19] for macro amounts of metals and multicomponent analyses and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[20] at both pH 4.7 and 9 and with partial least-squares (PLS) calculations. Recently, a preliminary study with 2,2′-dipyridyl ketone picolinoylhydrazone (dPKPH) in acetate medium, and using an algorithm based on dual transformation of ordinary least-squares regression, has been carried out.[21]

All the above work involved batch methodology. This paper reports the on-line simultaneous spectrophotometric determination of iron, cobalt and nickel with dPKPH using flow injection (FI). For overcoming the drawback of spectral interferences, calculation of the metal concentrations was performed by using a multivariate calibration approach. With this aim, a PLS algorithm was employed.

Experimental

Reagents and Solutions

Commercial stock standard solutions of Fe, Co and Ni were purchased from Merck (Darmstadt, Germany). Ascorbic acid (analytical-reagent grade) was obtained from Panreac (Barcelona, Spain). All other reagents were of analytical-reagent grade and purchased from Merck. All solutions were prepared with doubly distilled water. The spectrophotometric reagent dPKPH was synthesized as described elsewhere.[22]

A stock standard solution of ascorbic acid (5% m/v) was prepared by dissolving 1.25 g of ascorbic acid in water in a 25 ml calibrated flask.

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For the preparation of the FI reagent, dPKPH (final concentration 0.02% m/v) was dissolved in ethanol (final concentration 2.5% v/v) and added to an acetate buffer solution previously prepared by dissolving the appropriate amount of sodium acetate in acetic acid solution (final concentration 0.02 mol l^{-1}) and then adjusting the pH to 4.9. Finally, the required volume of the ascorbic acid stock standard solution (up to a final concentration of 0.05% m/v) was added to ensure the presence of iron in its divalent form, and the reagent solution was diluted to the desired volume.

Apparatus

The FI manifold is shown schematically in Fig. 1. A Minipuls 2 four-path peristaltic pump (Gilson, Villiers-le-Bel, France), equipped with Tygon tubing, was used to manipulate the flows of reagent and sample solutions. The set-up consisted of a six-port sample injection valve with a Model 5041 sample loop (Rheodyne, Cotati, CA, USA), a Lambda 11 UV/VIS spectrophotometer (Perkin-Elmer, Überlingen, Germany) and an 80 μl quartz flow cell with a 10 mm pathlength (Hellma, Mullheim, Germany). Transport lines and reaction coils were made using 0.8 mm id PTFE tubing. Connections were made of polypropylene (Omnifit, Cambridge, UK).

Acidity was measured with a Model 2001 pH meter (Crison, Alella, Spain) and a Model 52-02 combined glass–Ag/AgCl electrode (Crison).

Procedure

To ensure the highest spectrophotometric signal for each sample injection, optimization of the FI manifold was performed by varying the reaction coil length (30–330 cm), sample volume (30–230 μl) and flow rate (0.25–1.5 ml min^{-1}). Once these parameters had been optimized, individual calibration plots for Fe, Co and Ni were measured from six standard solutions each within the concentration range 0.1–1 μg ml^{-1}.

The PLS-1 algorithm included in the package developed by Blanco *et al.*[23] was used to process the data for the simultaneous determination of Fe, Co and Ni. To simplify the process, the calibration set was prepared by following a two-level factorial design, 0.1 μg ml^{-1} being the low-level concentration and 1 μg ml^{-1} the high-level concentration. Prior to PLS processing, each calibration solution was injected six successive times to measure the absorbance of the developed complexes at six selected wavelengths (367, 375, 385, 400, 410 and 430 nm). The calibration model was obtained by cross-validation and the number of factors was chosen as the lowest yielding a prediction error statistically not different from the minimum prediction error.[24] The calibration model was then validated with eight synthetic samples containing Fe, Co and Ni in different ratios within the studied range.

For studying interferences, the influence of several ions was tested, including those that most frequently accompany Fe, Co and Ni in real samples. We studied the effect of the interfering ions, at different concentrations, on the absorbance of a solution containing 1 μg ml^{-1} of each analyte. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample of >5%. This increment of absorbance was evaluated at three wavelengths, 367, 385 and 410 nm (corresponding to the maximum absorption of Fe, Ni and Co complexes, respectively), to establish the different effects of the interfering ions on each analyte.

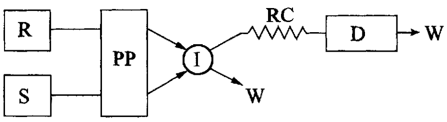

Fig. 1 Flow injection manifold. R, Reagent solution; S, sample solution; PP, peristaltic pump; I, injection valve; RC, reaction coil; D, detector and W, waste.

Finally, the proposed method was applied to the determination of Fe, Co and Ni in two different real samples with complex matrices. A washing solution used in an automotive factory was directly analysed after filtration through a 0.45 μm pore-size filter. The other sample was a waste acidic mine effluent, previously subjected to three successive selective separation processes for recovering iron, copper and aluminium by precipitation, solvent extraction and ion exchange, respectively.

Results and Discussion

Optimization of FI Conditions

The parameters influencing the reaction of a solution of 1 μg ml^{-1} of nickel with dPKPH contained in the FI reagent were investigated. The flow rate of the reagent solution was varied from 0.25 to 1.5 ml min^{-1} for three different sample volumes, 30, 136 and 230 μl. The results obtained are shown in Fig. 2 The optimum values chosen were 1 ml min^{-1} and 136 μl of sample because of the good ratio between the detector response and reagent and sample consumption and because the best repeatability was attained. At this flow rate, a sampling frequency of 50-70 samples h^{-1} can be achieved.

The influence of the reaction coil was investigated within the range 30–330 cm. An increase in the length of the reaction coil increased both the precision of the analysis and the linear range of the calibration curves, but the sensitivity decreased. An optimum length of 130 cm of 0.8 mm id tubing was chosen.

Individual Determination

Individual calibration curves were constructed with six points, each obtained by three parallel injections, as absorbance *versus* metal concentration in the range 0.1–1 μg ml^{-1}, and evaluated by linear regression.

The molar absorptivities were 6.64×10^3 (Fe, 367 nm), 3.89×10^3 (Co, 410 nm) and 5.17×10^3 l mol^{-1} cm^{-1} (Ni, 385 nm). The intercepts on the ordinate were negligible in all three cases. Limits of detection, calculated as LOD = 3 s_0/slope, where s_0 is the standard deviation of the intercept on the ordinate were Fe 1.062 μmol l^{-1} (0.059 μg ml^{-1}), Co 1.489 μmol l^{-1} (0.088 μg ml^{-1}) and Ni 0.685 μmol l^{-1} (0.049 μg ml^{-1}).

Simultaneous Determination

Fig. 3 shows the absorption spectra for the individual metal complexes and a mixture. As can be seen, strong spectral

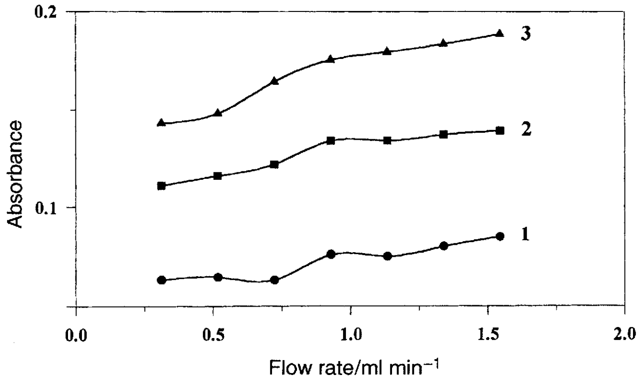

Fig. 2 Dependence of absorbance at 385 nm on flow rate for Ni(II)–dPKPH complex. Sample volume: injected: 1, 30; 2, 136 and 3, 230 μl.

overlap prevents the direct simultaneous determination of all three metal ions. Therefore, a PLS multivariate calibration approach was used. PLS procedures are designated to be full-spectrum computational methods; however, they have also shown their usefulness when using a reduced number of wavelengths.[25,26] For preparing the calibration matrix, a two-level exponential design, with metal concentrations of 0.1 μg ml^{-1} (low level) and 1 μg ml^{-1} (high level), was used. In a previous study, an optimization process for the selection of wavelengths was carried out.[21] It was found that 6–8 wavelengths resolved the ternary system adequately. In this work, to obtain good agreement between accuracy and rapidity of analysis, six wavelengths were chosen. Thus, the increment of the absorbance of each calibration solution was evaluated at six different wavelengths, three of them corresponding to the maximum of the absorption of the complexes; the other three were chosen in the spectral zone where the reagent shows very little absorption, and with the maximum absorptivity differences. Under these conditions, and measuring each solution at least four times, the calibration model was obtained. The calibration model was validated with an eight solution set containing Fe, Co and Ni in different proportions between 0.2 and 0.9 μg ml^{-1}. The results obtained are given in Table 1. To choose the number of factors to be used, the validation set was tested for both three and four factors. In both cases the results were satisfactory, the relative average errors being under 5.4% in all cases. As can be seen, when analysing synthetic samples, a very small difference was observed for three and four factors. Nevertheless, to analyse real samples the use of four factors was necessary because of the complexity of the matrix effect.

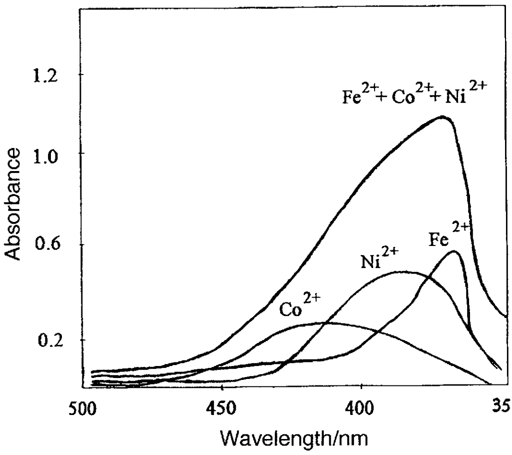

Fig. 3 Absorption spectra of M^{II}–dPKPH solutions. Curves for 1 μg ml^{-1} Co^{II}, 1 μg ml^{-1} Ni^{II}, 1 μg ml^{-1} Fe^{II} and 1 μg ml^{-1} Co^{II} + 1 μg ml^{-1} Ni^{II} + 1 μg ml^{-1} Fe^{II}.

Table 1 Results obtained in the validation of the calibration model for three and four factors

				Found/μg ml^{-1}					
	Added/μg ml^{-1}			Three factors			Four factors		
Sample	Fe	Co	Ni	Fe	Co	Ni	Fe	Co	Ni
1	0.8	0.6	0.9	0.77	0.62	0.93	0.78	0.63	0.93
2	0.7	0.2	0.5	0.70	0.21	0.52	0.70	0.21	0.52
3	0.2	0.2	0.8	0.22	0.21	0.78	0.22	0.22	0.78
4	0.4	0.7	0.2	0.40	0.72	0.20	0.38	0.70	0.21
5	0.8	—	0.3	0.83	−0.02	0.30	0.84	−0.02	0.30
6	0.3	0.5	—	0.31	0.52	−0.00	0.32	0.52	−0.00
7	—	0.6	0.8	0.06	0.58	0.78	0.03	0.57	0.79
8	0.4	—	—	0.43	−0.05	−0.01	0.43	−0.04	−0.01

Among the interfering ions tested, CH_3COO^-, Br^-, $CO_3{}^{2-}$, CN^-, F^-, I^-, $NO_3{}^-$, $NO_2{}^-$, $C_2O_4{}^{2-}$, $PO_4{}^{3-}$, $SO_4{}^{2-}$, Al^{3+}, Ba^{2+}, Be^{2+}, Bi^{3+}, Ca^{2+}, Li^+, Mg^{2+} and Sr^{2+} did not interfere at concentrations 1000 times higher than those of the analytes, Mn^{2+}, Pb^{2+} and the rare earth elements were found not to interfere at a concentration of 100 μg ml^{-1} and S^{2-}, Au^{3+}, Cr^{3+} and Ti^{4+} caused no interference up to a concentration of 10 μg ml^{-1}. The strongest interferences occurred with $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$, $MnO_4{}^-$, Sn^{2+}, Hg^{2+}, Zn^{2+} and Cu^{2+}, which interfered at concentrations 10 times higher than those of the analytes. At these concentrations, Cd^{2+} was found to interfere only in the determination of iron. However, most of these interferences can be easily overcome. Thus, reduction of $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$ and $MnO_4{}^-$ can be achieved by adding H_2O_2. Other interfering ions can be masked with the appropriate reagent. As an example, the simultaneous determination of 1 μg ml^{-1} of Fe^{2+}, Co^{2+} and Ni^{2+} can be achieved in the presence of up to 50 μg ml^{-1} of Sn^{2+} or 20 μg ml^{-1} of Cd^{2+} by masking them with citrate.

Application

The proposed calibration method was applied to the determination of Fe, Co and Ni in two real samples. As described above, the first sample was a washing solution used in an automotive factory. First, the presence of 0.761 μg ml^{-1} of Fe was determined by AAS. By using the proposed method, 0.738 μg ml^{-1} of Fe was obtained, the relative average error being −3.02%. In both instances, the absence of Co and Ni was verified. The second sample was a mine effluent with known concentrations (measured by ICP-AES) of 3.40, 38.4 and 572.5 μg ml^{-1} of Fe, Co and Ni, respectively. The values found with the proposed method were 3.76, 38.6 and 553.6 μg ml^{-1}, the relative average errors being 10.53, 0.52 and −3.30%, for Fe, Co and Ni, respectively. Hence the results obtained with the proposed method are in good agreement with the known values, even with a strong matrix effect.

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