

---

**THE DETERMINATION OF Cu, Ni, AND Co USING 2-(2-PYRIDYLAZO)-1-NAPHTHOL-4-SULFONIC ACID BY MULTICOMPONENT FLOW INJECTION ANALYSIS (MC-FIA)**

Petr DOLEŽEL and Vlastimil KUBÁŇ

*Department of Analytical Chemistry, J. E. Purkyně University, 611 37 Brno*Received October 5th, 1987  
Accepted November 19th, 1987

---

2-(2-Pyridylazo)-1-naphthol-4-sulfonic acid (IPAN4S) was used to develop a method for the simultaneous spectrophotometric determination of Cu(II), Ni(II), and Co(III) by reverse flow injection analysis (FIA) using a multichannel UV-VIS detector with a diode array. The method can be used to determine the individual ions in the range 5–50  $\mu\text{mol dm}^{-3}$  Ni(II) or Cu(II) and 5–60  $\mu\text{mol dm}^{-3}$  Co(III) in binary and ternary mixtures at ratios of 1 : 1 to 1 : 10 with a maximal relative deviation of units of per cent for the major components and tens of per cent for the minor components. The precision and accuracy of the determination are the same or slightly worse than for stationary measurements with half to one fifth the sensitivity. Measurement of the absorption spectra for the maximum analytical signal in digital form for  $c(\text{IPAN4S}) = 0.12 \text{ mmol} \cdot \text{dm}^{-3}$ ,  $c(\text{NaIO}_4) = 1.2 \text{ mmol dm}^{-3}$  in 0.2M acetate buffer medium at pH 5.00 permits rapid determination (15 s per sample) of all the components using a simple program for multicomponent analysis in "overdetermined" systems.

---

The use of a multichannel fast-scanning UV-VIS detector with a diode array for multicomponent analysis using FIA under dynamic conditions seems very promising. A number of compounds can be determined on the basis of their characteristic absorption or of the characteristic absorption of their reaction products, formed by the individual components of the analyzed mixture with a suitable analytical reagent or mixture of analytical reagents<sup>1-3</sup>.

This work describes the use of reverse flow injection analysis for the simultaneous determination of several components using a multichannel UV-VIS detector with a diode array. The indirect determination of Cu(II), Co(III), and Ni(II) using 2-(2-pyridylazo)-1-naphthol-4-sulfonic acid (IPAN4S) was elected as an example. The results of the r-FIA determination are compared with the results for multicomponent analysis using the classical stationary arrangement.

## EXPERIMENTAL

### Chemicals and Instruments

2-(2-Pyridylazo)-1-naphthol-4-sulfonic acid was reprecipitated from solution in 0.2M-NaOH using a 6M-HCl solution, washed with 10% (v/v) ethanol, dried at 60°C and equilibrated in the air<sup>4</sup>. The stock solution with  $c(\text{1PAN4S}) = 0.5 \text{ mmol dm}^{-3}$  was prepared by dissolving a weighed amount of chromatographically pure substance with purity of 93.5% in dimethylformamide (3 cm<sup>3</sup>) and diluted with water after complete dissolution, to yield the required volume.

The stock solutions of Cu(II), Co(II), and Ni(II) were prepared by dissolving weighed amounts of the nitrate of the given ion of p.a. purity (Lachema, Brno, Czechoslovakia) in 1M-HNO<sub>3</sub>. The final metal concentrations ( $10.1 \text{ mmol dm}^{-3}$  Ni(II),  $12.3 \text{ mmol dm}^{-3}$  Co(II), and  $10.0 \text{ mmol dm}^{-3}$  Cu(II)) were determined by chelatometric titration. Working solutions were prepared by diluting the stock solutions with water to yield a final concentration of nitric acid of  $10 \text{ mmol dm}^{-3}$ .

The other chemicals used were the commercial substances (Lachema, Brno, Czechoslovakia) of p.a. purity. Solutions were prepared using doubly distilled water from a Bi-18 all-quartz apparatus (Heraeus Quarzschmelze, Hanau, F.R.G.).

All the measurements were carried out on equipment that has been described previously<sup>2</sup>. The solutions of samples and the carrier liquid in the FIA equipment were transported in teflon capillaries with an inner diameter of 0.6 mm (Chemplast, Wayne, U.S.A.) with an overall length between the injection point and the detection site of  $L = 42 \text{ cm}$ . The carrier liquid was a solution of the individual metal ions or their mixture in  $1 \cdot 10^{-3} \text{ M}$  or  $1 \cdot 10^{-2} \text{ M-HNO}_3$ , to which a suitable volume of a solution of the mixed reagent with a concentration of  $c(\text{1PAN4S}) = 0.12 \text{ mmol dm}^{-3}$ ,  $c(\text{NaIO}_4) = 1.2 \text{ mmol dm}^{-3}$ , and acetate buffer ( $c(\text{Ac}^-) = 0.2 \text{ mol dm}^{-3}$ ) with pH 5.0 (where not stated otherwise).

The concentrations of the individual components of the reaction mixture were calculated using a simple program for multicomponent analysis<sup>2,5</sup>. The accuracy and precision of the determination of the concentrations of all the components was verified under stationary and dynamic conditions of the FIA analyzer using model mixtures of Cu(II), Ni(II), and Co(III) in all the possible binary and ternary combinations and at various concentration ratios of the individual components in the range 1 : 1 to 1 : 10. The criteria employed were the relative deviation values<sup>2</sup>,  $\Delta A(\%)$  and  $\Delta c(\%)$  and the Youden graphic method<sup>6</sup>.

## RESULTS AND DISCUSSION

The NiL chelate is formed in the pH interval 1–7.5 in an aqueous solution with  $c(\text{1PAN4S}) = 32 \text{ } \mu\text{mol dm}^{-3}$  and a concentration excess of Ni(II),  $c_{\text{M}}/c_{\text{L}} \geq 25$  at an ionic strength of  $I = 0.10$  (HNO<sub>3</sub> + NaOH). This chelate has characteristic absorption maxima at 535 and 567 nm. In a concentration excess of 1PAN4S ( $c_{\text{L}}/c_{\text{M}} = 30\text{--}270$ ) at pH < 3.7, the NiL(LH)<sup>-</sup> chelate is formed in solution and is characterized by slightly shifted absorption maxima at 538 and 569 nm. A broad isosbestic point lies at 489–492 nm. At lower concentration excesses of both components and at pH < 1.7, the NiL and NiL(LH)<sup>-</sup> chelates are gradually formed<sup>4</sup>.

The absorption spectra of aqueous solutions with  $c(\text{Cu(II)}) = 10.0 \text{ } \mu\text{mol dm}^{-3}$  and variable concentration  $c(\text{1PAN4S}) = 7.2\text{--}175 \text{ } \mu\text{mol dm}^{-3}$  measured at constant acidity pH = 0.74 or pH < 4.0 confirm<sup>4</sup> the formation of the two chelates CuL

and  $\text{CuL}_2^{2-}$  with absorption maxima at 380 and 558 or 552 and 580 nm, respectively. The isosbestic point lies at 508 nm.

In the presence of 1PAN4S and other N-heterocyclic azodyes, Co(II) is readily oxidized<sup>7,8</sup> to Co(III) and forms the kinetically very stable chelate  $\text{CoL}_2^{2-}$ , which, at pH 2.9 in the presence of  $c(\text{NaIO}_4) = 0.3 \text{ mmol dm}^{-3}$  and  $c(1\text{PAN4S}) = 0.12 \text{ mmol dm}^{-3}$ , is characterized by absorption maxima at 585 and 630 nm. The isosbestic point lies at 515 nm. The reaction rate increases in the presence of oxidizing agents and on an increase in the pH of the solution. The chelate is formed quantitatively within 5 min. (see ref.<sup>8</sup>). It is kinetically very stable and is not decomposed either by masking agents or strong mineral acids. The optical parameters of the chelate are not affected by a concentration of  $c(\text{EDTA}) = 0.12 \text{ mmol dm}^{-3}$ .

The absorbance pH curves for aqueous solutions of Ni(II), Cu(II), and Co(III) with concentrations of metal of c.  $6 \mu\text{mol dm}^{-3}$  in the presence of 1PAN4S ( $60 \mu\text{mol} \cdot \text{dm}^{-3}$ ) and  $\text{NaIO}_4$  ( $0.3 \text{ mmol dm}^{-3}$ ) indicate the optimal pH intervals (see Fig. 1) in which the individual chelates are formed quantitatively under the given experimental conditions. The plateau on the absorbance pH curve for the  $\text{NiL}(\text{LH})^-$  chelate is located in the pH region 4–7, for the  $\text{CoL}_2^-$  chelate in the region pH 4.5–7, and for the  $\text{CuL}_2^{2-}$  chelate in the region pH 5–8. Because of the low interference from other di- and higher valent metal ions, the lower limit of the given optimal interval pH 5–7 was selected for all three ions, i.e.  $\text{pH} \approx 5.0$ .

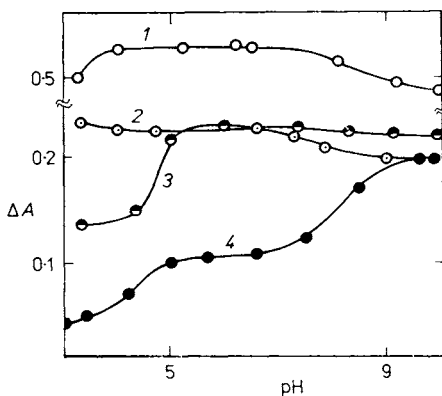


FIG. 1

The absorbance pH curves for the Ni(II), Cu(II), and Co(III) chelates with 1PAN4S in aqueous medium.  $c(1\text{PAN4S}) = 60 \mu\text{mol} \cdot \text{dm}^{-3}$ ,  $c_M \approx 6 \mu\text{mol dm}^{-3}$ ,  $I = 0.10$  ( $\text{HNO}_3 + \text{NaOH}$ ), 560 nm; 1 Ni(II), 2 Co(III), 3 Cu(II), 4 1PAN4S

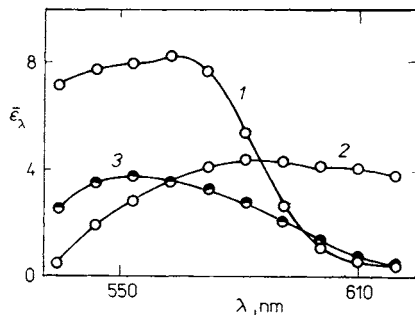


FIG. 2

The absorption spectra of the chelates of Ni(II), Cu(II), and Co(III) with 1PAN4S.  $c(1\text{PAN4S}) = 60 \mu\text{mol dm}^{-3}$ ,  $c_M \approx 10 \mu\text{mol dm}^{-3}$ , acetate buffer with  $c(\text{Ac}^-) = 80 \text{ mmol dm}^{-3}$ , pH 5.00,  $c(\text{NaIO}_4) = 0.6 \text{ mmol dm}^{-3}$ ; 1 Ni(II), 2 Co(III), 3 Cu(II)

An acetate buffer with pH 5.00 was selected as the best buffer for regulating the acidity; up to a concentration of  $c(\text{Ac}^-) = 0.2 \text{ mol dm}^{-3}$ , no effect on the optical characteristics of the individual chelates was observed. A pyridine buffer with the same pH exhibited a higher blank absorbance value in the whole concentration interval  $c(\text{Py}) \leq 0.1 \text{ mol dm}^{-3}$ .

The absorption spectra of the chelates of Cu(II), Ni(II), and Co(III) with 1PAN4S were measured under the above experimental conditions in acetate buffer medium ( $c(\text{Ac}^-) = 80 \text{ mmol dm}^{-3}$ ) with pH 5.00 and are depicted in Fig. 2 for the region 530–610 nm. The absorption bands of the individual chelates are sufficiently separated with marked changes in the molar absorption coefficients. Compared with other N-heterocyclic azodyes, the differences in the optical characteristics of the chelates are greater<sup>7</sup>. This system is especially suitable for the simultaneous determination of several ions in multicomponent analysis in spite of the lower sensitivity compared with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, 2-(2-pyridylazo)-resorcinol, etc.<sup>8</sup>.

The maxima of the absorption bands of the individual chelates lie in the wavelength region 500–650 nm, which is most advantageous for measuring these multicomponent systems. The lower limit is determined by the characteristic absorption of the ligand form  $\text{LH}^-$  (i.e. the acid-base form of 1PAN4S), which has marked absorption maxima<sup>4</sup> at 359 and 478 nm ( $\epsilon_{\text{max}}$  0.96 and 1.45  $\text{m}^2 \text{ mmol}^{-1}$ , respectively).

Under the above experimental conditions, the calibration curves are linear in the concentration range of metal 0.12–10  $\mu\text{mol dm}^{-3}$  for Ni(II), 0.23–10  $\mu\text{mol dm}^{-3}$  for Co(III), and 0.27–10  $\mu\text{mol dm}^{-3}$  for Cu(II). The slopes of the calibration curve decrease at higher metal cation concentrations.

The parameters for the FIA analyzer were optimized for injection of 30  $\mu\text{l}$  of a solution with  $c(1\text{PAN4S}) = 0.12 \text{ mmol dm}^{-3}$  and  $c(\text{NaIO}_4) = 1.2 \text{ mmol dm}^{-3}$  in acetate buffer medium with  $c(\text{Ac}^-) = 0.2 \text{ mol dm}^{-3}$  and pH 5.00 into a continuous stream of distilled water with a flow rate of 1  $\text{cm}^3 \text{ min}^{-1}$  in a capillary system with  $L = 50 \text{ cm}$ .

Various types of pumps were tested for continuous, pulseless transport of the carrier liquid and the sample in the FIA capillary system, as the requirements on the precision and accuracy in multicomponent analysis are far greater than for the other FIA analysis procedures. The mathematical treatment of the experimental data leads to a great increase in the experimental errors<sup>9</sup>.

In addition to the previously described linear, high-pressure HPP 4001 injector (Laboratorní přístroje, Prague, Czechoslovakia), which has been found to be most useful for work with a multicomponent FIA analyzer<sup>2</sup>, the carrier liquid was transported from the stock bottle by hydrostatic pressure. The flow rate was varied in the range 0.1–1.0  $\text{cm}^3 \text{ min}^{-1}$  by changing the liquid level in the stock bottle above the level of the flow-through cuvette; however, these manipulations were complicated by the high hydrodynamic resistance of the flow-through cuvette in the detector

(the reservoir height was adjusted to up to 250 cm). In spite of the continuous decrease in the flow rate ( $<0.1\%$  per hour) as a result of the change in the liquid volume in the reservoir and change in the hydrostatic pressure, the reproducibility of the absorbance measurement for 10 repeated injections of a 1PAN4S solution was comparable with that using a HPP 4 001 injector ( $s_r$  0.2–0.35 and 0.1–0.25% for  $c(1PAN4S) = 0.12–0.06 \text{ mmol dm}^{-3}$ ).

When a membrane pump MC 706 (Mikrotechna, Prague, Czechoslovakia) or five-channel peristaltic pump with a modified rotation head, Unipan 304 (Domet, Poland), the reproducibility of the measurement was much worse, primarily as a result of pulsation of the carrier liquid in the tubing ( $s_r = 0.9–1.4$  and  $2.2–2.9\%$  for the above conditions), even when small diameter tubing and high rotor rates were used. Pulsation of the liquid could not be completely removed even by using a pulse damper consisting of a T-piece with a dead-end filled with air.

The volume of the injection solution was varied in the range 10–50  $\mu\text{l}$  using a loop injector with a flow rate of  $1 \text{ cm}^3 \text{ min}^{-1}$  of a solution with  $c(\text{Ni(II)}) = 30 \mu\text{mol dm}^{-3}$ . The best results were obtained for injection of 25 and 30  $\mu\text{l}$  of 1PAN4S solution. Because of the high hydrodynamic resistance of the flow-through cuvette, a six-way chromatographic stop-cock with minimal injection loop volume of 30  $\mu\text{l}$  was used in the actual measurement, as the simple injection loop was subject to leakage after prolonged use.

The chelates of Ni(II), Cu(II), and Co(III) with 1PAN4S are formed quite rapidly, as the maximal absorbance value was attained for an overall length of the reaction capillary between the injection point and detector of c. 35–45 cm in the whole range of flow rates  $0.2–1.0 \text{ cm}^3 \text{ min}^{-1}$  (see Fig. 3). An optimal length of the reaction capillary of  $L = 42 \text{ cm}$  was selected from the maxima on the individual curves, for all the chelates. When a longer capillary is used, the absorbance decreases as a result of predominance of sample dispersion over increased reaction yield. On the other hand, a shorted capillary results in decreased reaction yield reflected in a marked decrease in the absorbance in spite of the assumed decreased degree of sample dispersion.

The highest sensitivity for the optimal length of the reaction capillary of  $L = 42 \text{ cm}$  was attained for a flow rate of  $0.2 \text{ cm}^3 \text{ min}^{-1}$  (see Fig. 3) with very good reproducibility ( $s_r \leq 0.15\%$ ). However, the time for a single analysis was up to 2 minutes as the return of the absorbance to the zero value was slow as a result of marked tailing of the sample zones. A flow rate of  $0.5 \text{ cm}^3 \text{ min}^{-1}$  was selected as optimal as it permitted faster (c. 15–20 s) measuring of the absorbance with comparable reproducibility of the measurement ( $s_r \approx 0.20\%$ ). At higher flow rates, the time for a single analysis decreased slightly to c. 10–15 s, but the reproducibility was much worse ( $s_r = 0.5$  and  $0.9\%$  for flow rates of 1 and  $2 \text{ cm}^3 \text{ min}^{-1}$ ). At flow rates above  $0.5 \text{ cm}^3 \text{ min}^{-1}$  the peaks retained a sharp, narrow shape suitable for evaluation.

The dependence of the absorbance on the concentration of 1PAN4S under the above optimal conditions for FIA analysis and for metal cation concentrations of  $30 \mu\text{mol dm}^{-3}$  exhibits a plateau in the range  $c(1\text{PAN4S}) = 0.08 - 0.15 \text{ mmol dm}^{-3}$ . A concentration of  $c(1\text{PAN4S}) = 0.12 \text{ mmol dm}^{-3}$  was selected as optimal.

Under the above experimental conditions, the calibration curves were linear in the concentration range  $5 - 50 \mu\text{mol dm}^{-3}$  for Ni(II) and Cu(II) and  $5 - 60 \mu\text{mol dm}^{-3}$  for Co(III). The values of the molar absorption coefficients of the individual chelates,  $\bar{\epsilon}_\lambda$ , were determined from the calibration curves for the wavelength range 530 to 590 nm; Fig. 4 depicts their dependence on the wavelength. The value of  $\bar{\epsilon}_\lambda$  is decreased by up to one order of magnitude under flow conditions compared to the value found under stationary conditions, corresponding to a value of the dispersion coefficient of  $D \approx 2$  for the Cu(II) chelate and  $D \approx 6$  for the Ni(II) chelate.

The average values of the molar absorption coefficient  $\bar{\epsilon}'_\lambda$  were determined for all the binary and ternary mixtures of Cu(II), Ni(II), and Co(III) by the method of standard additions of one component at a constant nonzero concentration of the other components by the linear least squares method. As the  $\bar{\epsilon}'_\lambda$  values depend on the

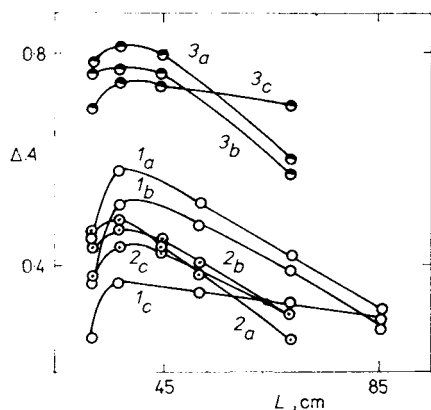


FIG. 3

The dependence of the absorbance on the length of the reaction coil  $L$  for various flow rates and for the individual chelates of 1PAN4S.  $c(1\text{PAN4S}) = 0.12 \text{ mmol dm}^{-3}$ ,  $c(\text{Ni(II)}) = 55 \mu\text{mol dm}^{-3}$ ,  $c(\text{Co(III)}) = 61 \mu\text{mol dm}^{-3}$ ,  $c(\text{Cu(II)}) = 51 \mu\text{mol dm}^{-3}$ , acetate buffer with  $c(\text{Ac}^-) = 0.2 \text{ mol dm}^{-3}$ , pH 5.00,  $c(\text{NaIO}_4) = 1.2 \text{ mmol dm}^{-3}$ ; 1 Ni(II), 2 Co(III), 3 Cu(II), a  $0.2 \text{ cm}^3 \text{ min}^{-1}$ , b  $0.5 \text{ cm}^3 \text{ min}^{-1}$ , c  $1.0 \text{ cm}^3 \text{ min}^{-1}$

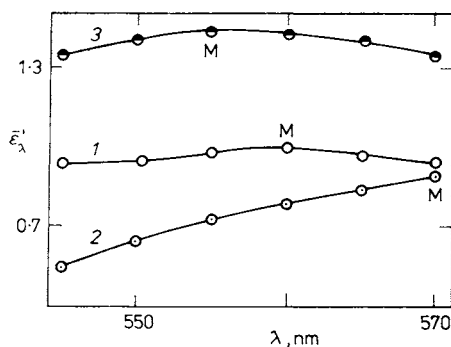


FIG. 4

The dependence of the molar absorption coefficient values ( $\bar{\epsilon}'_\lambda, \text{m}^2 \text{ mmol}^{-1}$ ) of 1PAN4S chelates on the wavelength. Curves: 1 Ni(II), 2 Co(III), 3 Cu(II), M designates the absorption maximum

overall concentrations of the components and their ratios, the values determined as the arithmetic means of all the determined values were employed in the subsequent calculations. These values are 5–10% lower than the  $\bar{\epsilon}_\lambda$  values determined for the individual components for the same linearity range of the calibration dependences.

In the calculation of the concentration of individual components using simple program for multicomponent analysis, the binary and ternary mixtures of the individual metal cations were mixed in concentration ratios of 1 : 1 to 1 : 10, where one or two concentrations were changed simultaneously. The measurement was carried out at wavelengths of 540–590 nm in steps of 5 nm so that these wavelengths overlapped the regions of the absorption maxima for all the studied chelates in the spectral range of the detector employed (390–590 nm). The overall concentration of the mixture of cations varied in the interval 5–50  $\mu\text{mol dm}^{-3}$  for Ni(II) + Cu(II) + Co(III), to ensure a sufficient concentration excess of 1PAN4S, ensuring quantitative formation of all the chelates.

The measured absorbance values  $A_{\text{exp}}$  for the individual binary and ternary mixtures in the whole spectral range were compared with the  $A_{\text{calc}}$  values calculated from the known metal ion concentrations and their molar absorption coefficients

TABLE I

Selected values of the relative deviation in the absorbance,  $\Delta A(\%)$  and  $\Delta A'(\%)$ , for some binary and ternary mixtures;  $c(\text{1PAN4S}) = 0.12 \text{ mmol dm}^{-3}$ ,  $c(\text{M}) = 6-30 \mu\text{mol dm}^{-3}$  ( $\text{M} \equiv \text{Ni(II) + Cu(II) + Co(III)}$ ),  $c(\text{NaIO}_4) = 1.2 \text{ mmol dm}^{-3}$ , acetate buffer with  $c(\text{Ac}^-) = 0.2 \text{ mol dm}^{-3}$ , pH 5.00

Mixtures Ni : Co : Cu	$\lambda$ , nm					
	545	550	555	560	565	570
0 1 1 <sup>a</sup>	-15.6	-15.0	-15.0	-15.6	-13.0	-16.4
0 1 1 <sup>b</sup>	1.2	0.0	-1.1	-1.7	-0.2	-1.3
1 1 0 <sup>a</sup>	-27.3	-26.2	-25.1	-24.7	-23.5	-22.8
1 1 0 <sup>b</sup>	0.0	-0.8	-2.2	-2.4	0.7	1.4
2 2 1 <sup>a</sup>	-29.2	-26.9	-25.7	-25.0	-24.5	-24.1
2 2 1 <sup>b</sup>	-7.4	-6.3	-6.7	-6.1	-4.0	-5.3
1 1 1 <sup>a</sup>	-22.7	-22.6	-22.7	-22.3	-22.3	-23.0
1 1 1 <sup>b</sup>	-2.3	-3.4	-5.3	-4.3	-3.5	-5.2
1 1 2 <sup>a</sup>	-12.0	-9.8	-8.3	-8.4	-8.7	-9.3
1 1 2 <sup>b</sup>	7.7	9.1	9.3	8.0	8.5	9.6
1 1 5 <sup>a</sup>	-13.4	-11.5	-11.1	-11.5	-12.4	-13.8
1 1 5 <sup>b</sup>	2.7	3.4	3.2	3.3	3.0	2.0

<sup>a</sup>  $\Delta A(\%)$ ; <sup>b</sup>  $\Delta A'(\%)$ .

$\bar{\epsilon}_\lambda$  and  $\bar{\epsilon}'_\lambda$  found in the two above-mentioned procedures. It can be seen from the results (see Table I) that far better agreement of the two absorbance values, expressed in terms of the  $\Delta A(\%)$  values, is attained using the average value,  $\bar{\epsilon}'_\lambda$ . The maximal deviation values,  $\Delta A'(\%)$  then vary in units of per cent, while use of the  $\bar{\epsilon}_\lambda$  values yields  $\Delta A(\%)$  values in the units to tens of per cent range. In addition, when the  $\bar{\epsilon}_\lambda$  values are used, the corresponding  $A_{\text{calc}}$  values are much lower than the  $A_{\text{exp}}$  values, while the number of lower and higher  $A_{\text{calc}}$  values is roughly the same when the  $\bar{\epsilon}'_\lambda$  values are used, indicating that there is a systematic error in the calculated  $\bar{\epsilon}_\lambda$  values.

The concentrations of the individual ions was calculated from the experimentally measured absorbance values,  $A_{\text{exp}}$ , attained as the average of 5 independent determinations for each mixture of cations, using the average  $\bar{\epsilon}'_\lambda$  values. Part of the results, calculated for 35 binary and ternary metal cation mixtures, is given in Table II and compared with the results for the determination of these cations under similar experimental conditions in stationary systems. It can be seen that the relative con-

TABLE II

Relative deviations  $\Delta c(\%)$  for selected binary and ternary mixtures of Ni(II), Cu(II), and Co(III) with 1PAN4S  $c(1\text{PAN4S}) = 0.12 \text{ mmol dm}^{-3}$ ,  $c(\text{M}) = 5-50 \text{ } \mu\text{mol dm}^{-3}$  ( $\text{M} \equiv \text{Cu(II)} + \text{Ni(II)} + \text{Co(III)}$ ),  $c(\text{NaIO}_4) = 1.2 \text{ mmol dm}^{-3}$ , acetate buffer with  $c(\text{Ac}^-) = 0.2 \text{ mol dm}^{-3}$ , pH 5.00, 530–590 nm

Ion	$c_t^a$	$c_{\text{calc}}^a$	$\Delta c(\%)^b$	Ion	$c_t^a$	$c_{\text{calc}}^b$	$\Delta c(\%)^b$
Co	24.6	24.50	-0.3	Ni	21.9	20.81	-5.0
Cu	20.0	20.03	0.2	Co	24.6	25.10	2.5
Ni	21.9	24.21	10.0	Ni	10.9	11.48	4.8
Cu	20.0	22.07	10.0	Co	31.4	30.98	-0.8
Ni	21.9	19.64	-10.0	Ni	10.9	10.88	-0.6
Co	24.6	23.35	-5.0	Co	12.3	12.30	0.0
Cu	10.00	9.81	-1.5	Cu	10.0	9.01	-10.0
Ni	10.9	12.54	14.5	Ni	6.6	8.07	22.8
Co	12.3	13.53	10.0	Co	7.4	8.40	13.9
Cu	20.0	21.45	-7.3	Cu	30.0	29.60	-1.0
Ni <sup>c</sup>	5.47	5.438	-0.7	Ni <sup>c</sup>	2.19	2.526	15.3
Co <sup>c</sup>	1.23	1.601	30.3	Co <sup>c</sup>	9.83	9.629	-2.1
Cu <sup>c</sup>	5.00	4.937	-1.3	Cu <sup>c</sup>	2.00	1.872	-6.1
Ni <sup>c</sup>	1.09	1.014	-7.4	Ni <sup>c</sup>	5.48	5.580	1.9
Cu <sup>c</sup>	5.00	5.117	2.3	Co <sup>c</sup>	1.23	1.075	-12.5

<sup>a</sup> In  $\mu\text{mol dm}^{-3}$ ; <sup>b</sup>  $\Delta c(\%) = 100(c_{\text{calc}} - c_t)/c_t$ ; <sup>c</sup> measured under stationary conditions (see text).



centration deviations  $\Delta c(\%)$  vary in the units of per cent range and only rarely exceed 10%, while the use of the  $\bar{\epsilon}_\lambda$  values determined for the individual components resulted in  $\Delta c(\%)$  values in the tens of per cent range and exceptionally values of 30 to 50% were obtained. The relative deviations  $\Delta c(\%)$  were lower (max. 10%) for metal cations present in the mixtures in concentration excesses or equimolar ratios, while the relative deviations  $\Delta c(\%)$  increased to up to 30% for cations present in much lower concentrations. No dependence was found on the type of cation, as was found for the direct determination of Cu(II), Co(II), Ni(II), and U(VI) by multicomponent FIA analysis<sup>2</sup>.

It follows from the above results that the precision and accuracy of the determination of the concentrations of the individual components is somewhat worse in FIA systems than for classical stationary measurements. The most important factor is the decreased reproducibility of the measurement of the analytical signal for relatively fast passage of the zones of the reaction mixture through the flow-through cuvette of the detector. Where the dependences of the analytical signal on time are characterized by sharp narrow peaks and the integration time of the analytical signal in the electronic part of the detector is comparable or even longer than the time of passage of the central part of the zone through the flow-through cuvette, the reproducibility of the measurement is understandably worse.

A further factor that negatively affects the precision and accuracy of the calculated concentrations of the individual components is the precision and accuracy of the determination of the values of the molar absorption coefficients of all the absorbing species in the reaction mixture. Measuring the values for pure solutions containing only a single component of the reaction mixture under broad concentration conditions does not seem optimal in FIA determinations. The theoretically calculated absorption spectra of mixtures using the values thus obtained for the molar absorption coefficients  $\bar{\epsilon}_\lambda$  differ more or less from the experimentally measured absorption spectra. This often appears as a systematic deviation of the absorbance in part or all of the spectral interval. Far better results were obtained using the mean values,  $\bar{\epsilon}'_\lambda$ , found for various combinations of mixtures of metal cations by the standard addition method.

The differences in the optical characteristics of the individual absorbing species in the reaction mixture is also a significant factor. While in the direct determination of the Cu(II), Co(II), Ni(II), and U(VI) ions<sup>2</sup> or in a multiligand FIA determination of Cu and Fe ions using the bathocuproine disulfonate and bathophenanthroline disulfonate mixed reagent<sup>9</sup> described earlier the absorption bands of the individual ions could be considered as completely independent<sup>2</sup>, this is no longer possible for a mixture of the chelates of Ni(II), Cu(II), and Co(III) with 1PAN4S. The changes in the optical characteristics are much smaller, reflected in the precision and accuracy of the calculated concentrations. The relatively high absorption of the free acid-base form  $LH^-$  of 1PAN4S is also comparable or even higher than the absorbance of the

chelate mixture in the lower part of wavelength region 500–540 nm, so that a small change in the concentration of 1PAN4S is strongly reflected in the overall value of the absorbance of the reaction mixture.

The marked differences between the values of the dispersion coefficients of the individual chelates,  $D \approx 2$  for Cu(II) and  $D \approx 6$  for Ni(II) should also be noted. These differences are connected with the different rates of formation of the individual chelates, as the retention time of the reaction mixture in the capillary system is not sufficient for quantitative formation of all the chelates. In addition, differences in the diffusion rates of the individual cations within the reaction zone can also be important.

In spite of these problems, flow injection analysis combined with multicomponent analysis can be a very useful method in a number of regions. The increased effectiveness and increased information yield obtained from direct connection of the detector with a fast signal recorder and a computer permit more effective processing of the experimental data.

#### REFERENCES

1. Luque de Castro M. D., Valcárcel C. M.: *Analyst* (London) *109*, 413 (1984).
2. Kubáň V., Doležel P.: *Collect. Czech. Chem. Commun.* *53*, 543 (1988).
3. Lazaro F., Rios A., Luque de Castro M. D., Valcárcel M. C.: *Anal. Chim. Acta* *179*, 279 (1986).
4. Koblížková V., Kubáň V., Sommer L.: *Collect. Czech. Chem. Commun.* *43*, 2711 (1978).
5. Buršík V., Kubáň V., Sommer L.: *Collect. Czech. Chem. Commun.*, submitted.
6. Eckschlager K., Hořsák I., Kodejš Z.: *Vyhodnocování analytických výsledků a metod*, p. 44. SNTL, Prague 1982.
7. Ivanov V. M.: *Geterotsiklicheskie azotsoderzhashchie azosodineniya*, p. 41. Nauka, Moscow 1982.
8. Zbiral K., Sommer L.: *Scr. Fac. Sci. Nat. Univ. Brun.* *12*, 283 (1982).
9. Kubáň V., Gládilovič D. B.: *Collect. Czech. Chem. Commun.*, in press.

Translated by M. Štullková.