

**MULTICOMPONENT DETERMINATION BY FLOW INJECTION
ANALYSIS USING PU 4021 DIODE ARRAY DETECTOR.
A DIRECT DETERMINATION OF LANTHANOIDS**

Vlastimil KUBÁŇ and Petr DOLEŽEL*

Department of Analytical Chemistry, J. E. Purkyně University, 611 37 Brno

Received May 11th, 1987

Flow injection analysis (FIA) using a multichannel UV-VIS diode array detector enables several components with sufficiently separate absorption bands to be determined simultaneously. The effects of the basic parameters of the FIA apparatus (geometry, flow rates, etc.), error of measurement of the analytical signal, mutual interactions between the components to be determined, and the data handling procedure on the accuracy and precision of the calculated concentrations of the components are demonstrated on a model case of binary and ternary mixtures of Cu(II), Ni(II), Co(II), and U(VI). The majority and minority components can be determined with relative errors of 1–3% and 2–20%, respectively, over the concentration region of 2 to 200 mmol l⁻¹ at concentration ratios from 1:1 to 50:1. The method has been applied to a simultaneous determination of Pr(III), Sm(III), and Nd(III) in oxidic concentrates of rare earths over the region of 1–20 mg ml⁻¹ at concentration ratios down to 1:10 with relative errors not exceeding 5%.

With the ever-increasing demands placed on the rapidity of analysis and with the introduction of automatic flow analyzers, simultaneous determination of several components using flow analyzers with segmented (SCFA) or continuous (nonsegmented) reaction mixture flow (NSCFA, FIA) has been gaining in importance¹. Electrochemical, optical and other types of detectors are employed, and several detectors linked in series or in parallel or a single detector with variable selectivity can be used^{1,2}.

A great potential is in the use of multichannel optical detectors enabling the analytical signal to be measured over a wide spectral region, such as UV-VIS diode array detectors. Scanning is performed repeatedly in trains while the reaction zone passes through the detector flow cell, in the region of the analytical signal maximum in time or in other characteristic points of the time dependence of the analytical signal (e.g., inflection points). The consecutive mathematical data handling allows a number of parameters such as the kinetic or equilibrium constants of the reactions involved or the instantaneous concentrations of all components to be evaluated^{3,4}.

* *Present address:* Institute of Analytical Chemistry, Czechoslovak Academy of Sciences 611 42 Brno.

Although some problems may arise from the occurrence of interactions between the reaction mixture components, these procedures give rather rapidly sufficiently accurate results for 3–5 or, occasionally, even a higher number of components. Little experience has been so far gained with mathematical handling of experimental data from multicomponent analysis in the dynamic conditions of flow injection analyzers^{1–6}.

In the present work, the potential of flow injection analysis in the simultaneous determination of several components with the use of a UV-VIS diode array detector is examined and discussed. A method for the determination of the components based on their light absorption is worked out on the case of binary and ternary mixtures of polyvalent metal ions, viz. Cu(II), Co(II), Ni(II), and U(VI), and applied to the determination of Pr(III), Sm(III), and Nd(III) in oxidic concentrates. Results of the FIA determinations are compared with data obtained in the classical stationary mode.

EXPERIMENTAL

Chemicals

Stock solutions of Cu^{2+} , Ni^{2+} , Co^{2+} , and UO_2^{2+} ions in concentrations of 1.0 mol l^{-1} (Cu, Ni, Co) or $0.1734 \text{ mol l}^{-1}$ (UO_2^{2+}) were obtained by dissolving the nitrates of reagent grade purity (Lachema, Brno, Czechoslovakia) in HNO_3 (1 mol l^{-1}). Stock solutions of Pr(III), Nd(III), and Sm(III) in a concentration of 0.1 mol l^{-1} were prepared by dissolving the nitrates (Pr, Nd) or oxide (Sm) in HNO_3 (1 mol l^{-1}) and diluting with water so that the final concentration of HNO_3 was 0.1 mol l^{-1} . The solutions were standardized chelometrically or gravimetrically.

The carrier liquid for FIA was nitric acid in a concentration of 1 mmol l^{-1} . Acidity of sample solutions containing the individual metal ions or their mixtures in concentrations of 4–200 $\text{mmol} \cdot \text{l}^{-1}$ was adjusted prior to injection so that the final concentration of HNO_3 was 0.1 or 1 mol l^{-1} for preventing the metal ions from hydrolysis in the zone region.

For analyses of oxidic concentrates of lanthanoids, 80–100 mg of sample was dissolved in a micro test tube by boiling with 0.1 ml of HNO_3 (1 : 5), or of HCl (1 : 1) with an addition of 20 drops of 30% H_2O_2 per 5 ml of HCl (1 : 1). After cooling, this solution was injected by means of a 30 μl sample loop injector through an in-line frit into the continuous stream of HNO_3 (1 mol l^{-1}).

The accuracy and precision of determination were tested in the stationary and flow modes on model mixtures of Cu(II), Ni(II), Co(II), and U(VI) in all binary and ternary combinations, with concentration ratios covering the range from 1 : 1 to 50 : 1.

Apparatus

Spectrophotometric measurements in the stationary mode in 1 cm quartz cells were carried out on a Superscan 3 double-beam digital spectrophotometer (Varian, Zug, Switzerland), on-line controlled with a Hewlett-Packard HP 9815A desktop computer⁸.

Acidity was measured with an OP 208/1 digital pH-meter equipped with an OP 0718P glass electrode and an OP 0830P calomel electrode and calibrated periodically with K21 and K71 standard buffers at pH 2.18 and 7.04, respectively, at 25°C (all Radelkis, Budapest, Hungary).

Measurements in the dynamic conditions were performed on a flow injection analyzer set up of conventional laboratory instrumentation (Fig. 1). Carrier liquid transport was provided by a HPP 4001 high-pressure plunger pump (Laboratorní přístroje, Prague, Czechoslovakia) with flow rates smoothly variable over the region of 0–5 ml min⁻¹ or adjustable at 0.2, 0.5, 1, 2, and 5 ml min⁻¹. An adapted loop injector⁷ with loop volumes variable from 10 to 100 µl or an adapted chromatographic six-way valve with a loop volume of 30 µl were employed for sample injection into the carrier stream. The sample loop was filled by means of a vacuum membrane pump (Varian, Zug, Switzerland).

Analytical signal was recorded and evaluated by using a PU 4021 multichannel UV-VIS diode array detector (Pye-Unicam, Cambridge, U.K.) equipped with an 8 µl flow cell 10 mm optical pathlength and interfaced to a TZ 4 200 two-line recorder (Laboratorní přístroje, Prague, Czechoslovakia). With this detector the time dependence of the analytical signal can be recorded continuously at one or two wavelengths, and up to nine complete absorption spectra over the regions of 190–390 or 390–590 nm can be scanned automatically or manually in any moment of passage of the reaction mixture zone through the flow cell. Automatic spectral recording in the peak maximum Autostore Mode was employed nearly exclusively.

In the FIA arrangement, sample and carrier liquid solutions were fed through Teflon capillaries 0.3 mm i.d. (Chemplast, Wayne, U.S.A), total pathlength from the injection spot to the detector 20 cm, which corresponds with the dimensions of the detector cell compartment.

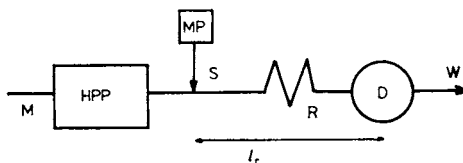
Calculations

Concentrations of the reaction mixture components were calculated by using simple programs for multicomponent analysis based on entered absorptivities of the components at selected wavelengths. A program relying on the Gauss–Jordan elimination of a system of linear equations where the number of wavelengths is identical with the number of components to be determined⁸ and two programs^{9,10} for overdetermined systems where the number of wavelengths exceeds several times that of the components were tested. In the two latter programs, the minimum of the function $U = \sum(A_{\text{obs}} - A_{\text{calc}})^2$ or $U' = \sum|(A_{\text{obs}} - A_{\text{calc}})|$ in dependence on the concentrations of the components is sought iteratively. The A_{obs} values at selected wavelengths are obtained from experimental spectra of sample mixtures, the A_{calc} values are obtained from the known absorptivities⁹; normalized absorbances $A_{\text{norm}} = A_{\text{obs}}/A_{\text{max}}$ where A_{max} is the absorbance in the absorption maximum of the species in question were also employed¹⁰. The programs seek for concentrations at which the U function reaches its minimum and, at the same time, the best "optical" agreement of the corresponding sum spectra is attained over the whole spectral region ($U' \rightarrow \min$) treated.

The accuracy of the obtained molar absorptivity values was assessed in terms of the relative differences between the calculated and observed absorbances $\Delta A = (A_{\text{obs}} - A_{\text{calc}})/A_{\text{calc}}$ for the entire wavelength set, or by applying the graphical Youden's method¹¹ where the A_{obs} values are plotted on one axis and the A_{calc} values on the other axis for the entire wavelength set. The accuracy of the concentration values was assessed likewise in terms of the relative dif-

FIG. 1

Block diagram of flow injection analyzer system used. M carrier medium, HPP high-pressure plunger pump, MP membrane pump, S sample loop, R reaction capillary, D detector, W waste; $l_r = 20$ cm, 0.3 mm i.d



ferences $\Delta c = (c_t - c_{calc})/c_t$ where c_t and c_{calc} are the theoretical and calculated concentrations, respectively.

RESULTS AND DISCUSSION

The relative standard deviations (RSD) of 10 repeated injections of 30 μl volumes of Co(II), $c = 0.05$ or 0.10 mol l^{-1} , at flow rates $F_m = 0.5$ – 3.0 ml min^{-1} lay within the regions of 0.1–0.5%, 0.6–1.9%, and 1–5% using the pulseless HPP 4 001 pump, membrane pump, and peristaltic pump, respectively⁶. Only the pulseless delivery of the carrier liquid thus suits to multicomponent FIA, because here the demands put on the accuracy of experimental data are considerably higher than for other FIA applications. The dispersion coefficient for the optimum volume injected (30 μl), $D = 1.3$, lies within the region of $D = 1$ – 2 suitable for direct FIA methods¹.

The optimum flow rates were about 1 ml min^{-1} (RSD = 1.4%). Although the reproducibility of measurement increased at lower flow rates (RSD = 0.35 and 0.75% at $F_m = 0.2$ and 0.5 ml min^{-1} , respectively), the time of an analysis increased to as much as 2 min from sample injection to the moment that the zero line was obtained in the record. By increasing the flow rate after the passage of the sample zone centre through the detector (after the peak maximum) to 5 ml min^{-1} the time of washing out the peak tail, and thereby the time of analysis, was reduced, the demands placed on the operation of the apparatus, however, grew considerably. At flow rates higher than 1 ml min^{-1} the time of an analysis was shortened to approximately 20 s and the sample zone retained its narrow peak shape, the reproducibility of measurement, however, was markedly poorer (RSD = 6.6% at $F_m = 2 \text{ ml min}^{-1}$).

The absorption spectra of the aquo ions and their mixtures measured in the stationary and dynamic (FIA) modes are identical in shape over the entire region of 350–850 or 390–590 nm, respectively (Fig. 2).

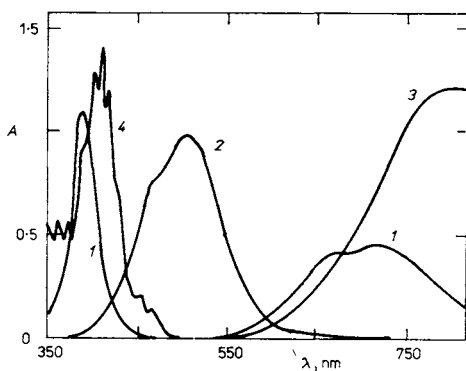


FIG. 2

Absorption spectra of Ni(II), Co(II), Cu(II), and U(VI) in nitric acid; $c(\text{HNO}_3) = 1 \text{ mol} \cdot \text{l}^{-1}$ (pH 1.1), $c_M = 0.2 \text{ mol l}^{-1}$ for Ni and Co, 0.1 mol l^{-1} for Cu, 0.173 mol l^{-1} for UO_2 , $d = 1 \text{ cm}$. Ion: 1 Ni^{2+} , 2 Co^{2+} , 3 Cu^{2+} , 4 UO_2^{2+}

The molar absorptivity or normalized absorbance values were evaluated in the stationary mode for 30 wavelengths within the region of 350–850 nm by the linear least squares method from the calibration plots for concentrations of 2–200 mmol \cdot l^{-1} ; several (usually five) replicate measurements were carried out for each concentration. For the dynamic FIA conditions the total number of wavelengths was reduced to ten with regard to the narrower usable spectral region (390–590 nm) and the more complex off-line data handling. The molar absorptivities were calculated similarly for the concentration region of 4–200 mmol l^{-1} .

The molar absorptivities calculated for the dynamic mode were invariably lower than those obtained in the stationary mode, viz. $\epsilon_{401} = 3.469$ and $5.030 \text{ cm}^2 \text{ mmol}^{-1}$ for Ni(II), $\epsilon_{510} = 3.872$ and $4.891 \text{ cm}^2 \text{ mmol}^{-1}$ for Co(II), and $\epsilon_{410} = 5.802$ and $7.474 \text{ cm}^2 \text{ mmol}^{-1}$ for U(VI). This is due to the calculation procedure being based on the instantaneous absorbances in the peak maxima and metal ion concentrations in the initial undispersed solution. The dispersion coefficient was $D \approx 1.3$.

The mean values of the molar absorptivities of the aquo ions determined in the stationary mode from the calibration curves of the ions of interest over the region of 2–200 mmol l^{-1} present in mixtures with other aquo ions in concentration ratios of 10 : 1 to 1 : 1 differ somewhat from those obtained in solutions of the individual ions ($\epsilon_{395} = 5.35$, $\epsilon_{660} = 1.973$, $\epsilon_{722} = 2.280 \text{ cm}^2 \text{ mmol}^{-1}$ for Ni(II), $\epsilon_{810} = 12.14 \text{ cm}^2 \text{ mmol}^{-1}$ for Cu(II), and $\epsilon_{401} = 7.250$, $\epsilon_{421} = 6.629 \text{ cm}^2 \text{ mmol}^{-1}$ for U(VI)). This indicates that interactions of the ions in solution also play a role (see later).

The experimental absorbances A_{obs} for the binary and ternary mixtures in all combinations of the aquo ions are compared with the values calculated based on the entered concentrations and absorptivities in Tables I and II.

In the stationary mode, the two values are identical to within the experimental error for the majority of binary mixtures, the relative differences ΔA are lower than 2%. Occasionally, particularly for the Cu(II)–Ni(II) system, the ΔA values are higher, in dependence on the aquo ion concerned and on the wavelength of measurement. This is demonstrated by the two tables where the mixtures with the highest ΔA values are deliberately included. For the ternary mixtures with approximately equimolar concentrations or with appreciable excess of one or two components, the ΔA values do not exceed 2.5%.

The concentrations of the aquo ions in the binary or ternary mixtures calculated from A_{obs} values by using programs^{8–10} approach the expected c_i values closely (Table III), the relative differences Δc largely amounting to tenths or units per cent. This applies to mixtures with approximately equimolar concentrations of the components as well as to systems with a marked excess of one or two components. Somewhat higher Δc values were obtained for some binary mixtures, particularly Ni(II)–Cu(II), Ni(II)–U(VI), and Cu(II)–U(VI) equimolar mixtures, where $\Delta c = 1–16\%$ ($\Delta A = 3–8\%$). Similar conclusions are derived from Youden's graphical

analysis¹¹ where the slopes and intercepts of the dependences differ statistically insignificantly from the values of 1 and 0, respectively, the data for the above-mentioned binary mixtures lying slightly beyond the data set (Fig. 3).

In the dynamic conditions of FIA, the effect of interionic interactions was marked particularly for Ni(II)-Co(II) and Ni(II)-U(VI) binary mixtures, where both the

TABLE I

Relative absorbance differences (ΔA , %) for binary and ternary mixtures of Ni(II), Co(II), Cu(II), and U(VI); stationary mode, pH 1.1, $c = 2-200 \text{ mmol l}^{-1}$

Ni : Co : Cu : U concentration ratio	λ , nm									
	401	410	421	470	510	525	600	660	720	810
1 : 1 : 0 : 0	—	—	—	—	2.2	2.6	—	3.3	4.2	—
1 : 0 : 1 : 0	—	—	—	—	—	—	—	8.1	5.0	3.9
1 : 0 : 0 : 1	-0.6	-0.4	0.0	—	—	—	2.2	2.5	2.2	—
0 : 1 : 1 : 0	—	—	—	0.0	0.0	0.6	—	—	—	1.2
0 : 1 : 0 : 1	-2.9	-2.2	-1.4	—	0.5	0.9	—	—	—	—
0 : 0 : 1 : 1	-5.0	-4.5	-3.6	—	—	—	—	—	—	1.9
1 : 1 : 1 : 0	—	—	—	2.3	0.8	—	0.6	—	0.3	-0.4
1 : 1 : 5 : 0	—	—	—	1.1	0.0	—	-0.4	—	-0.6	-2.1
1 : 1 : 10 : 0	0.7	—	—	-0.6	0.0	—	1.3	—	1.1	1.7
1 : 1 : 0 : 2	0.0	0.3	0.4	0.5	0.3	0.4	0.3	0.8	0.6	0.3

TABLE II

Relative absorbance differences (ΔA , %) for binary and ternary mixtures of Ni(II), Co(II), and U(VI); dynamic (FIA) mode, pH(sample) 1.2, pH(carrier) 3.0, $F_m = 1 \text{ ml min}^{-1}$, $c_t = 4-200 \text{ mmol l}^{-1}$

Ni : Co : U concentration ratio	λ , nm									
	401	410	421	475	480	485	510	515	520	525
1 : 1 : 0	9.2	11.9	13.3	3.6	3.3	3.1	3.0	3.7	3.7	4.4
1 : 0 : 1	0.8	-0.3	1.3	-11	-12	-13	-15	-16	-16	-16
0 : 1 : 1	-0.7	0.4	0.5	-4.2	-3.5	-2.3	-0.7	-0.9	-0.9	-1.1
1 : 1 : 1	2.4	2.5	3.6	-0.9	-0.4	-0.9	-0.2	-0.4	0.4	0.4
8 : 2 : 3	2.8	2.1	3.5	-3.3	-5.1	-5.0	-5.7	-4.9	-5.0	-4.9
5 : 5 : 1	1.1	1.5	5.1	-4.6	-4.7	-5.0	-3.6	-3.1	-3.0	-3.0
50 : 1 : 1	-2.2	-2.3	-2.5	-3.9	-5.2	-1.3	-4.1	-4.6	-4.1	-3.4

ΔA and Δc values were units or tens per cent, as demonstrated by Tables II and IV where mixtures exhibiting the highest differences are again deliberately included. For the remaining binary mixtures the two quantities are one or two orders of magnitude better.

TABLE III

Comparison of entered (c_t) and calculated (c_{calc}) concentrations of components of binary (left) and ternary (right) mixtures of Ni(II), Co(II), Cu(II), and U(VI); stationary mode, pH 1.1

Ion	c_t mmol l ⁻¹	c_{calc} mmol l ⁻¹	Δc %	Ion	c_t mmol l ⁻¹	c_{calc} mmol l ⁻¹	Δc %
Ni	120.0	125.0	4.2	Ni	100.0	105.7	5.7
Co	120.0	123.0	2.5	Co	100.0	100.3	0.3
				Cu	100.0	98.2	-1.8
Ni	80.0	94.4	18.0	Ni	100.0	98.3	-1.7
Cu	80.0	82.3	2.9	Co	20.0	20.0	0.0
				Cu	20.0	19.5	-3.0
Ni	80.0	80.2	0.3				
U	87.0	86.2	-0.6	Ni	200.0	201.4	0.7
				Co	20.0	20.1	0.5
Co	80.0	81.1	1.4	Cu	20.0	20.3	1.5
Cu	80.0	80.2	0.3				
				Ni	100.0	101.3	1.3
Co	120.0	121.2	1.0	Co	100.0	100.5	0.5
U	108.0	105.5	-2.3	Cu	100.0	98.8	-1.2
Cu	120.0	101.9	-15.9				
U	108.0	103.3	-4.4				

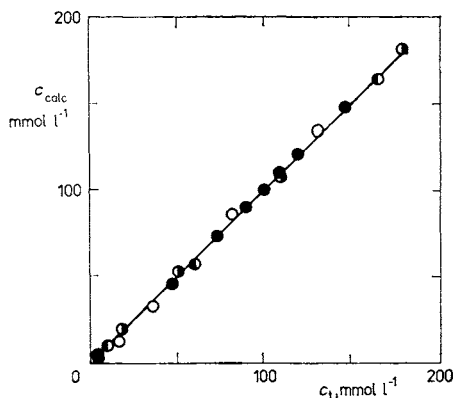


FIG. 3

Graphical comparison of entered (c_t) and calculated (c_{calc}) concentrations of Ni(II), Co(II), Cu(II), and U(VI) in binary and ternary mixtures in various concentration ratios; straight line equation $y = 1.003x + 0.274$. Ion: \circ Ni²⁺, \bullet Co²⁺, \ominus Cu²⁺, \bullet UO₂²⁺

In systems with different concentrations of the components the accuracy of the concentration values for the minority components decreases considerably as the concentration excess of the majority component is increased (from 5 : 1 to 50 : 1); in the extreme cases, $\Delta c = 10-30\%$. The accuracy of the concentration data for the majority components, on the contrary, is very high ($\Delta c = 0.3-3\%$) and comparable to that obtained by measurements in the stationary mode.

For Co(II)-Ni(II)-U(VI) ternary mixtures with approximately equimolar concentrations, the ΔA values are below 5% (Table II). The accuracy of the calculated concentrations is sufficient for practical purposes, the relative differences being lower than 3-5%. The accuracy of the determined concentrations of the majority components in mixtures with excess one or two components, $\Delta c < 2\%$, is comparable to that attained in the stationary mode, the concentrations of the minority components, however, involve large errors, as high as tens per cent; in the extreme cases of concentration ratios 50 : 1 and higher, the error is nearly 30% (Table IV). These conclusions are confirmed by Youden's graphical analysis (Fig. 3), the slope and intercept differing statistically insignificantly from the theoretical values. The variance of the values, however, is higher in the flow mode than in the stationary mode.

The FIA technique was applied to the simultaneous determination of Pr(III), Sm(III), and Nd(III) in oxidic concentrates of rare earths after their dissolution in nitric or hydrochloric acid. The molar absorptivities (Table V) were determined

TABLE IV

Comparison of theoretical entered (c_t) and calculated (c_{calc}) concentrations of components of binary and ternary mixtures of Ni(II), Co(II), and U(VI); dynamic (FIA) mode, pH(sample) 1.2, pH(carrier) 3.0, $F_m = 1 \text{ ml min}^{-1}$

Ion	c_t mmol l ⁻¹	c_{calc} mmol l ⁻¹	Δc %	Ion	c_t mmol l ⁻¹	c_{calc} mmol l ⁻¹	Δc %
Ni	200.0	219.6	9.8	Ni	200.0	195.7	-2.1
Co	200.0	203.0	1.5	Co	200.0	191.7	-4.1
				U	69.0	76.4	10.1
Ni	100.0	88.1	-12.9	Ni	200.0	197.0	-1.5
U	104.0	111.0	6.7	Co	50.0	44.2	-11.6
Co	100.0	98.9	-1.1	U	69.0	76.4	10.1
U	104.0	105.9	1.8				
Ni	100.0	101.0	1.0	Ni	200.0	196.2	-1.9
Co	100.0	99.0	-1.0	Co	4.0	3.6	-10.0
U	86.0	90.0	4.7	U	4.0	3.2	-23.0

TABLE V

Molar absorptivities (ϵ , $\text{cm}^2 \text{mmol}^{-1}$) of Pr(III), Nd(III), and Sm(III) obtained in the FIA mode; $F_m = 1 \text{ ml min}^{-1}$, $\rho = 2\text{--}20 \text{ mg ml}^{-1}$

Ion	λ , nm				
	402	444	450	522	575
Pr	0	8.391	1.030	0	0.082
Nd	0	0	0.020	3.526	5.545
Sm	2.642	0.035	0	0	0

TABLE VI

FIA determination of Pr(III), Nd(III), and Sm(III) in model samples of oxides (A, B) and in oxidic concentrates (C, D); $F_m = 1 \text{ ml min}^{-1}$, $D = 1.25$

Ion	Content, wt. %		
	found ^a	found by FIA	Δ , %
A			
Pr	0.102	0.100 ± 0.002	1.9
Nd	0.153	0.151 ± 0.004	1.3
Sm	0.146	0.147 ± 0.003	0.6
B			
Pr	0.075	0.076 ± 0.003	1.3
Nd	0.242	0.239 ± 0.005	0.8
Sm	0.196	0.196 ± 0.005	0.0
C			
Pr	0.073 ± 0.009	0.069 ± 0.007	5.5
Nd	0.212 ± 0.027	0.210 ± 0.026	0.9
Sm	0.062 ± 0.014	0.059 ± 0.012	4.8
D			
Pr	0.047 ± 0.017	0.050 ± 0.009	6.0
Nd	0.139 ± 0.018	0.133 ± 0.020	4.3
Sm	0.022 ± 0.008	0.018 ± 0.004	18.2

^a Calculated from the amount of Ln_2O_3 added for samples A, B, and determined by emission spectral analysis for samples C, D.

by the linear least squares method from calibration plots of the individual ions in the presence of approximately equal concentrations of the remaining ions, as can be expected in the concentrates, applying the standard addition method. The values, on conversion, agree well with published data^{1,2}, with a dispersion coefficient of $D \approx 1.25$.

The resultant mass fractions of the rare earth ions, determined for several sample batches, were compared with those obtained by other methods (Table VI). The data are in a very good agreement particularly for Nd(III); for Sm(III) and Pr(III) the agreement can be classed as satisfactory.

It can be concluded that a characteristic feature of measurements in flow conditions is a somewhat poorer repeatability of absorbance determination as compared to the stationary mode, which results in a poorer accuracy and precision of determination of components in a multicomponent system. Among the primary factors affecting the repeatability is the rapidity and repeatability of sample injection into the carrier stream, putting high demands on the experimenter's skill or calling for the use of an automatic injector. A next factor is pressure pulses occurring while the injector valve is switching between injection and filling; these have a negative effect particularly at high flow rates, even if the by-pass arrangement is used. A constant flow of the carrier stream, also, can be only achieved by employing a pulseless plunger pump.

For the sake of accuracy it is advised to apply repeated sample injections (3–10 times) and to use the average A_{obs} value eliminating outliers.

Of intrinsic factors, interionic interactions affect the molar absorptivities of the components, thereby causing variations in their values with changing concentration ratios. This effect can be partly eliminated by using absorptivity values obtained in conditions approaching closely the expected composition of the actual mixtures to be analyzed or by employing programs that take these interactions into account.

In summary, the FIA technique, which is rapid and shows great promise to the analytical practice, gives accurate and precise results for systems with negligible interionic interactions.

REFERENCES

1. Růžička J., Hansen E. H.: *Flow Injection Analysis*, p. 207. Wiley-Interscience, New York 1981.
2. Luque de Castro M. D., Cases M. V.: *Analyst (London)* 109, 413 (1984).
3. Otto M., Wegscheider W.: *Anal. Chem.* 57, 63 (1985).
4. Maris M. A., Brown C. W., Lavery D. S.: *Anal. Chem.* 55, 1694 (1983).
5. Lazaro F., Rios A., Luque de Castro M. D., Valcarcel M.: *Anal. Chim. Acta* 179, 279 (1986).
6. Doležel P., Kubáň V.: *Collect. Czech. Chem. Commun.*, in press.
7. Anderson L.: *Anal. Chim. Acta* 110, 123 (1979).
8. Kubáň V.: *Chem. Listy* 74, 862 (1980).
9. Havel J., Novák V.: *Scr. Fac. Sci. Nat. Univ. Purk. Brun.*, in press.
10. Buršík V., Kubáň V., Sommer L.: *Collect. Czech. Chem. Commun.* in press.

11. Eckschlager K., Horsák I., Kodejš Z.: *Vyhodnocování analytických výsledků a metod*, p. 44. Published by SNTL — Nakladatelství technické literatury, Prague 1982.
12. Ryabchikov D. I., Ryabukhin V. A.: *Analiticheskaya khimiya redkozemelnykh elementov i itriya*, p. 178. Nauka, Moscow 1966.

Translated by P. Adámek.