MULTICOMPONENT SPECTROPHOTOMETRIC ANALYSIS OF METAL IONS BASED ON SIMULTANEOUS OR CONSECUTIVE APPLICATION OF SEVERAL REAGENTS

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This paper deals with nonconventional approaches to multicomponent spectrophotometric analysis consisting of (i) simultaneous or consecutive addition of several nonselective reagents in the multi-component determination of metal ions, and (ii) the use of absorbance data which have been measured at different pH values or in different experimental conditions and subsequently combined into a single data set, evaluated by the partial least squares method. The following multicomponent mixtures of metal ions with reagents were examined: Co^{2+} and Fe^{3+} with nitroso-R-salt and 1,10-phenanthroline; Co^{2+}, Cu^{2+} and Fe^{3+} with nitroso-R-salt and zincon; Co^{2+}, Cu^{2+} and Zn^{2+} with nitroso-R-salt and zincon; and Cu^{2+}, Zn^{2+} and Ni^{2+} with zincon and PAR. The average relative error of determination was 2% (two metal ions) and 5% (three metal ions). Cu^{2+}, Zn^{2+} and Ni^{2+} were also quantitated in ALPAKA alloy with relative errors of 4 – 9%.

The majority of methods of multicomponent determination of metal ions by UV-VIS spectrometry is based on the use of a single, more or less selective reagent[1–4]. This conventional approach has the following shortcomings:

1. Many elements combined with the reagents exhibit similar or identical spectra. If the mixture contains many components, the bands overlap considerably and large errors of determination arise (the relative standard deviations are high).

2. Many elements form unstable complexes with the reagent used and/or the reaction of the metal ion with the reagent is not very sensitive and/or the components interact, giving, for instance, mixed complexes.

3. The effect of interfering ions in conventional spectrophotometry using a single reagent is sometimes difficult to eliminate, by the generalized standard addition method (GSAM) for instance[5]. Alternatively, preliminary separation must be applied.

Owing to the availability of sophisticated computer techniques, analytical chemists are making efforts to eliminate the above-mentioned shortcomings of the conventional approach to spectrophotometric multicomponent analysis (SMA) by mathematical means. Attention is paid to calibration (particularly to finding the optimum calibration set patterns and the optimum number of calibration solutions as well as to a proper

choice of analytical wavelengths) and to a comparison of the individual modern or conventional SMA methods[1–4,6–8].

The present paper addresses the potential of the use of several nonselective reagents, each reacting preferentially with a different metal ion (or group of ions). Some partial results have been published[9–12].

The data were evaluated by the partial least squares (PLS) method, whose assets have been highlighted[1,6,8,13–15]. This method is fast and simple, does not require the molar absorptivities of the components to be known, and nonlinearities and interactions between the components, if any, are addressed by the calibration procedure. The application of the PLS method is particularly well suited for systems exhibiting considerable absorption band overlap and/or involving many components, and/or if a small number of calibration solutions is used.

The algorithm of the PLS method has been described and discussed in detail in refs[8,14–19], and therefore will not be dealt with in this paper.

EXPERIMENTAL

Chemicals

Standard metal solutions. Stock solutions of $Co(NO_3)_2$ (3.65 mmol l^{-1}), $Cu(NO_3)_2$ (3.62 mmol l^{-1}), $Fe(ClO_4)_3$ (6.51 mmol l^{-1}), $Zn(NO_3)_2$ (2.0 mmol l^{-1}), and $Ni(NO_3)_2$ (49 mmol l^{-1}) were prepared from chemicals supplied by Lachema, Brno. The concentrations were checked gravimetrically. Fresh working solutions were prepared from the stock solutions before the measurements.

Standard solutions of reagents. 1,10-Phenanthroline (PEN) of reagent grade purity (Lachema, Brno) was dissolved in HCl (1.0 mol l^{-1}) and diluted to volume with water. The stock solution ($c = 252$ mmol l^{-1}) was stable for several months.

1-Nitroso-2-naphthol-3,6-disulfonic acid, disodium salt, known as nitroso-R-salt (NRS), of reagent grade purity (Lachema, Brno) was dissolved in water. Stock solution ($c = 13.25$ mmol l^{-1}) stored in a dark bottle was stable for several months.

2-Carboxy-2μ-hydroxy-5μ-sulfoformazylbenzene (zincon, ZNC) of reagent grade purity (Lachema, Brno) was dissolved in NaOH of reagent grade purity ($c = 1.0$ mol l^{-1}) (Lachema, Brno) and diluted to volume with water. Fresh solution ($c = 0.93$ mmol l^{-1}) was prepared prior to each measurement.

4-(2-Pyridylazo)resorcinol (PAR) of reagent grade purity (Lachema, Brno) was dissolved in water. Fresh stock solution ($c = 2.0$ mmol l^{-1}) was prepared prior to each measurement.

Buffers. Acetate buffer (1.0 mol l^{-1}, pH 5.2) was made up of 136.08 g of sodium acetate and 21 ml of concentrated acetic acid (both Lachema, Brno), which were diluted to 1 000 ml with water. Clark–Lubs buffer (0.2 mol l^{-1}, pH 9.0) was prepared from 12.4 g of boric acid and 14.9 g of KCl (both Lachema, Brno), which were diluted to 1 000 ml with water; 50 ml of this solution was mixed with 42.8 ml of NaOH, $c = 0.1$ mol l^{-1} (Lachema, Brno) and diluted to 200 ml with water.

Other chemicals. Hydroxylamine hydrochloride (NH_2OH . HCl) of reagent grade purity (Lachema, Brno) was dissolved in water to a concentration of 3.0 mol l^{-1}. Ethanol was redistilled. $KBrO_3$ of reagent grade purity (Lachema, Brno) was used as a 5 wt.% aqueous solution. CHELATON III (Lachema, Brno) was used at a concentration of 1.9 mmol l^{-1}.

Alloys. Specimens of ALPAKA E2 and E6, supplied by Armaturka Ceska Trebova, were standard reference materials conforming to Czechoslovak Standard CSN 42 3356. Samples were dissolved in

10 ml of concentrated nitric acid of reagent grade purity (Lachema, Brno) and diluted to 250 ml with water. The stock solutions were diluted so that the expected ion concentrations lay within the concentration region of the calibration set.

Apparatus

Absorbances were measured and spectra recorded on a HP 8452A diode array spectrophotometer, controlled by a HP Vectra 386SX/25 computer (Hewlett–Packard, U.S.A.). The pH was measured with an OP 0808P combined electrode interfaced to an OP-208 pH-meter (both Radelkis, Hungary). Spectrophotometric data were evaluated by using an IBM-compatible PC AT.

Procedures

The concentrations of reagents, buffers and other chemicals were as reported in Chemicals, metal concentrations applied are given in Table I. All solutions were diluted to 50 ml with water.

Procedure I. Determination of Co^{2+} and Fe^{3+} with nitroso-R-salt: solutions of metal ions, 1 ml of acetate buffer, 1 ml of NRS, 0.5 ml of NH_2OH . HCl.

Determination of Co^{2+} and Fe^{3+} with 1,10-phenanthroline and nitroso-R-salt: metal ion solutions, 5 ml of acetate buffer, 1 ml of NRS, heating for 1 min, addition of 0.5 ml of $KBrO_3$, heating nearly to boil, addition of 0.5 ml of concentrated HNO_3, pH adjustment to 3.5, addition of 5 ml of NH_2OH . HCl and 0.2 ml of PEN.

Determination of Fe^{3+} with 1,10-phenanthroline in the presence of Co^{2+}: metal ion solutions, 1 ml of NH_2OH . HCl, 10 ml of PEN.

Procedure II. Determination of Co^{2+}, Cu^{2+} and Fe^{3+} with nitroso-R-salt and zincon: metal ion solutions, 2 ml of acetate buffer, 1 ml of NRS, 5 ml of ZNC, 0.5 ml of NH_2OH . HCl.

Procedure III. Determination of Cu^{2+} and Zn^{2+} with zincon at pH 9.0: metal ion solutions, 15 ml of Clark–Lubs buffer, 9 ml of ZNC.

Determination of Cu^{2+} with zincon in the presence of Zn^{2+} at pH 5.0: metal ion solutions, 2 ml of acetate buffer, 5 ml of ZNC.

Determination of Co^{2+}, Cu^{2+} and Zn^{2+} with nitroso-R-salt and zincon: metal ion solutions, 15 ml of Clark–Lubs buffer, 0.7 ml of NRS, 10 ml of ZNC.

Procedure IV. Determination of Cu^{2+}, Zn^{2+} and Ni^{2+} with zincon and PAR: metal ion solutions, 10 ml of Clark–Lubs buffer, 2 ml of PAR, 5 ml of ZNC.

The procedures were tested experimentally and the order of addition was optimized with respect to time stability and to the maximum attainable response (absorbances). Absorbances were measured 20 min after mixing the solutions.

The reagents were selected based on published data[20,21] so that the highest possible differences in the absorption maxima of the complexes of the various elements be achieved.

Data Evaluation

The PLS-G program[7,8] was employed for data evaluation. A suitable calibration set design was set up by the experiment planning approach[3,4,7,22]. A complete factorial design emerged as the optimum, i.e. 3^2 (9 calibration solutions) for 2 components at 3 concentration levels, and 3^3 (27 calibration solutions) for 3 components at 3 concentration levels of the components.

Agreement of the true (added) concentrations of the components and those calculated (predicted) by the PLS program was the basic criterion of correctness of the approach. This can be expressed by the relative error of prediction for the individual components (CRPE) and by the average relative error of prediction for all components and test solutions[7] (MRPE), viz. as

TABLE I
Composition of the analytical systems

System	Calibration (test) set	pH	c_L, µmol l^{-1} PEN	NRS	ZNC	PAR	c_M, µmol l^{-1} Fe	Co	Cu	Zn	Ni	Σ^a	I^b
	3^2						1.95	2.19	–	[c]	–		
							7.82	8.78	–	–	–		
IA		5.0	–	265	–	–	32.6	36.6	–	[d]	–	16	1, 2
	(2^2)						3.26	3.66	–	[c]	–		
							18.2	20.5	–	[d]	–		
	3^2						5.04	1.46	–	–	–		
							20.2	7.32	–	–	–		
IB		3.3	1 000	265	–	–	80.6	36.6	–	–	–	16	1
	(2^2)						37.3	7.32	–	–	–		
							50.4	10.2	–	–	–		
	3^2						5.20	2.19	–	–	–		
							19.5	8.78	–	–	–		
IC		3.3	1 000	265	–	–	78.2	36.6	–	–	–	16	1
	(2^2)						8.60	3.66	–	–	–		
							44.3	8.60	–	–	–		
	3^2						1.95	2.19	2.17	–	–		
							7.82	8.78	7.96	–	–		
II		5.0	–	265	93	–	32.5	36.5	29.0	–	–	24	2, 3, 4
	(2^2)						3.26	3.66	3.62	–	–		
							18.2	20.5	17.4	–	–		
	3^2						–	–	2.17	2.00	–		
IIIA		9.2	–	–	190	–	–	–	7.96	6.40	–		
IIIB		5.0	–	–	93	–	–	–	29.0	20.0	–	16	4, 5
	(2^2)						–	–	3.62	3.20	–		
							–	–	17.4	12.8	–		
	3^3						–	2.19	2.17	2.00	–		
							–	8.78	7.96	6.40	–		
IIIC		9.2	–	190	190	–	–	36.5	29.0	20.0	–	24	3, 5
	(2^3)						–	3.66	3.62	3.20	–		
							–	20.5	17.4	12.8	–		
	$3^3 - 12$						–	–	2.89	0.84	0.89		
IVA							–	–	9.41	2.65	2.76		
IVB		9.2	–	–	190	79	–	–	28.9	8.40	8.87	36	6, 7, 8
	(2^3)						–	–	5.07	1.51	1.58		
							–	–	16.6	4.62	4.93		

[a] Number of wavelengths; [b] wavelength region (nm): 1 428 – 528, 2 652 – 750, 3 410 – 480, 4 528 – 640, 5 646 – 674, 6 450 – 494, 7 500 – 544, 8 550 – 638; [c] lowest and [d] highest concentration level in the calibration (test) set.

$$\mathrm{CRPE}\ (\%) = \left[\sum_{i=1}^{T}(c_{ij} - c'_{ij})^2 \Big/ \sum_{i=1}^{T} c_{ij}^2\right]^{1/2} . 100 \tag{1}$$

and

$$\mathrm{MRPE}\ (\%) = \left\{\sum_{i=1}^{T}\left[\sum_{i=1}^{M}(c_{ij} - c'_{ij})^2 \Big/ \sum_{i=1}^{M} c_{ij}^2\right]^{1/2}\right\} T^{-1} . 100 . \tag{2}$$

In these equations, T is the number of test solutions (samples), M is the number of components, and c_{ij} and c'_{ij} are the true and calculated concentrations of the components.

RESULTS AND DISCUSSION

Determination of Co^{2+} and Fe^{3+} with Nitroso-R-Salt and 1,10-Phenanthroline

Absorption spectra of the Fe^{2+} and Co^{2+} complexes with PEN are nearly identical, with absorption maxima at 510 nm. The reaction of Fe^{2+} with PEN is sufficiently sensitive whereas the reaction of Co^{2+} is not. The spectra of the complexes of the two metals overlap considerably, so that simultaneous determination of the two metal ions with PEN is difficult. Fe^{3+} itself can be determined in the presence of Co^{2+}, and Co^{2+} itself can be determined in the presence of Fe^{3+}: Co^{2+} is oxidized by Fe^{3+} to Co^{3+} and the resulting absorbance of the Fe^{2+} complex with PEN then corresponds to the amount of Co^{2+} in sample[20].

NRS, on the other hand, is a reagent with which the two metal ions react at a nearly identical sensitivity. Their absorption bands are well discriminated (Fig. 1), and so they are well suited to the simultaneous determination of the two metal ions. The results of determination by this procedure are given in Table II (set *IA*).

When using both reagents, NRS was first reacted with Co^{2+} and Fe^{3+}, excess NRS was removed with $KBrO_3$ and HNO_3, and PEN was added. The latter reagent formed a complex with Fe^{2+} (after reducing Fe^{3+} with hydroxylamine), and the absorption band of the Fe^{2+}–NRS complex in the long-wavelength region vanished (Tables I and II, set *IB*).

A third, also nonconventional approach was examined, viz. application of the reagents separately. For a solution containing Co^{2+} and Fe^{3+} with NRS, absorbances were measured at wavelengths where the contribution of Co^{2+} was most marked, whereas for a solution containing the two metal ions with PEN, absorbances were measured at wavelengths where Fe^{3+} manifested itself most. Data so obtained were combined into a single data set and processed by the PLS method (Table II, set *IC*).

The optimum pH values, excess concentrations of the reagents over those of the metals sufficient for a quantitative complexation, and linearity regions of the calibration dependences for the various systems are given in Tables III, IV, and V.

Application of nitroso-R-salt and 1,10-phenanthroline to the simultaneous determination of Co^{2+} and Fe^{3+} gives results similar to those obtained by using nitroso-R-salt

TABLE II
Relative errors of metal ion determination (CRPE) and mean relative prediction errors (MRPE) for the systems measured

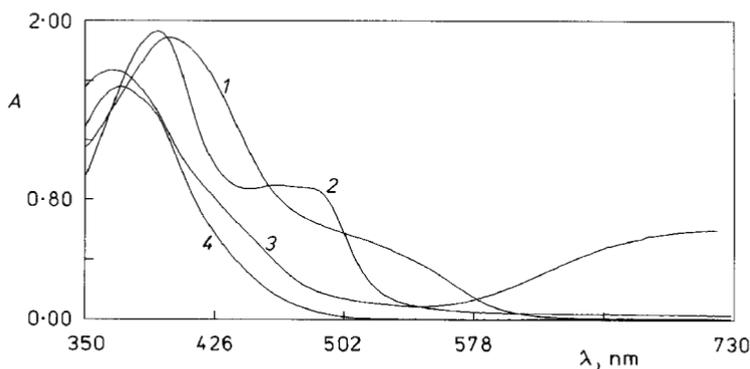| System	CRPE, rel.%					MRPE, rel.%
	Fe	Co	Cu	Zn	Ni	
IA	3.1	1.1	–	–	–	2.4
IB	1.8	5.9	–	–	–	2.5
IC	2.3	1.4	–	–	–	2.2
II	4.5	4.8	3.6	–	–	4.6
IIIA	–	–	0.5	7.6	–	5.8
IIIB	–	–	1.7	8.6	–	5.3
IIIC	–	3.5	4.6	2.8	–	4.1
IVA	–	–	2.1	2.2	2.4	2.2

FIG. 1
Absorption spectra of complexes of Co^{2+}, Cu^{2+} and Fe^{2+} ions with nitroso-R-salt at pH 5.0; concentrations (µmol l^{-1}): Co^{2+} 36, Cu^{2+} 63, Fe^{2+} 32, NRS 265. Systems: *1* Co^{2+} + NRS; *2* Cu^{2+} + NRS; *3* Fe^{2+} + NRS; *4* NRS

alone. In both cases, Co^{2+} and Fe^{3+} are determined with roughly the same error, viz. 2 rel.%. The results of analysis do not improve appreciably by the separate use of the two reagents. This is due to the fact that the absorption peaks of the Co^{2+} and Fe^{2+} complexes with nitroso-R-salt are well separated, so that the multicomponent determination by the PLS method is sufficiently accurate also if one reagent only is used. The results of determination are given in Table II.

Determination of Co^{2+}, Cu^{2+} and Fe^{3+} with Nitroso-R-Salt and Zincon

NRS on its own as well as ZNC on its own is unsuitable for the simultaneous quantitation of Co^{2+}, Cu^{2+} and Fe^{3+}. Cobalt and copper ions form complexes with NRS (Fig. 1) which absorb at wavelength at which NRS alone also absorbs considerably, so that the

TABLE III
Optimum pH values derived from A vs pH dependences

System	Metal	Reagent	c_M μmol l^{-1}	c_L μmol l^{-1}	λ, nm	pH region	pH$_{opt}$
I	Fe^{2+}	PEN	8.0	8 000	350 – 750	2.2 – 7.3	3.1 – 7.1
	Fe^{2+}	NRS	32.5	260	350 – 750	3.1 – 7.1	4.5 – 6.0
	Co^{2+}	NRS	36.0	260	350 – 750	3.5 – 7.0	4.6 – 5.3
II	Cu^{2+}	ZNC	8.0	92.0	350 – 750	4 – 11	4.6 – 9.5
IV	Ni^{2+}	PAR	8.9	79.6	350 – 750	6 – 11	8.5 – 10.0
	Zn^{2+}	PAR	8.4	79.6	350 – 750	6 – 11	6.5 – 10.5

TABLE IV
Reagent-to-metal ratios sufficient for complete complexation, as derived from A vs c_L dependences

System	Metal	Reagent	c_M μmol l^{-1}	c_L μmol l^{-1}	pH	λ, nm	Sufficient c_L/c_M
I	Fe^{2+}	NRS	8.0	30 – 8 000	4	350 – 750	20
	Fe^{2+}	NRS	32.5	53 – 260	5	350 – 750	5
	Co^{2+}	NRS	8.0	8 – 260	5	350 – 750	2
II	Cu^{2+}	ZNC	14.5	37 – 110	5	350 – 750	6
III	Zn^{2+}	ZNC	20.0	37 – 110	9	350 – 750	5
IV	$Ni^{2+,a}$	PAR	8.9	30 – 200	9.2	350 – 750	8

[a] In the presence of Zn^{2+} (8.4 μmol l^{-1}) and Cu^{2+} (29 μmol l^{-1}).

resulting absorbances A in multicomponent analysis attain very high values (in excess of 2.5), whereas iron(III) gives with ZNC a nearly colourless complex (Fig. 2).

The two reagents can be elegantly combined to determine all the three metal ions. A good band separation is achieved because Cu^{2+} reacts with ZNC while Co^{2+} and Fe^{3+} react with NRS (Fig. 3). ZNC decomposes at pH < 3.1 and haze appears. As the alkalinity is increased to above pH 9.5, the absorption band of this reagent shifts to longer wavelengths, viz. from 470 nm at pH 3.2 – 9.2 to 500 nm at pH 11.0.

The time stability of solutions containing the three metal ions and two reagents at pH 5.0 was examined at 410, 440, 560, 608, 708, and 750 nm in dependence on the concentration of $NH_2OH . HCl$ across the region of $c = 15 – 60$ mmol l^{-1}. The stability was best at an $NH_2OH . HCl$ concentration of 30 mmol l^{-1} and at the following concentrations of the remaining components (μmol l^{-1}): Co^{2+} 36, Cu^{2+} 29, Fe^{3+} 32, NRS 260, and ZNC 93.

The optimum pH values, values of excess concentrations of the reagents over those of the metal ions sufficient for a quantitative complexation, and the linearity regions of the calibration plots are given in Tables III – V.

The application of nitroso-R-salt and zincon to the determination of Co^{2+}, Cu^{2+} and Fe^{3+} proved to give very good results. The relative error of determination of each of the analytes was lower than 5%.

The calibration solution design and the results of simultaneous determination of Co^{2+}, Cu^{2+} and Fe^{3+} with NRS and ZNC are given in Tables I and II (set *II*).

TABLE V
Linearity ranges of the calibration dependences

System	Metal	Reagent	c_L μmol l^{-1}	Reagent	c_L μmol l^{-1}	pH	λ, nm	Linearity range c_M, μmol l^{-1}
I	Fe^{2+}	–	–	PEN	8 000	4	460, 510, 540, 560	2.6 – 78.0
	Fe^{2+}	NRS	260	–	–	5	700, 710, 720, 730	1.9 – 32.5
	Co^{2+}	NRS	260	–	–	5	420, 440, 460, 480	2.2 – 36.5
II	$Cu^{2+,a}$	NRS	265	ZNC	93	5	528, 608	2.2 – 28.9
	$Fe^{3+,b}$	NRS	265	ZNC	93	5	700, 710, 720	3.9 – 35.0
	$Co^{2+,c}$	NRS	265	ZNC	93	5	420, 440, 460	2.2 – 36.5
III	Zn^{2+}	–	–	ZNC	72	9	650, 660, 670	2.0 – 16.0
	$Zn^{2+,d}$	NRS	190	ZNC	190	9	650, 666, 670, 674	2.0 – 20.0

Accompanying ions (concentrations in μmol l^{-1}): [a] Co^{2+} (36) + Fe^{3+} (32); [b] Co^{2+} (36) + Cu^{2+} (29); [c] Cu^{2+} (29) + Fe^{3+} (32); [d] Co^{2+} (36) + Cu^{2+} (29).

Determination of Co^{2+}, Cu^{2+} and Zn^{2+} with Nitroso-R-Salt and Zincon

The application of NRS alone or ZNC alone to the simultaneous determination of Co^{2+}, Cu^{2+} and Zn^{2+} is inappropriate. The reasons for this were partly outlined above. The reaction of Co^{2+} with ZNC is not very sensitive and the spectra of the complexes of the three metal ions with ZNC overlap considerably (Fig. 4).

The possibility of a simultaneous determination of Cu^{2+} and Zn^{2+} with ZNC was first investigated. While only Cu^{2+} reacts at pH 5.0, both metals react at pH 9.0 (Fig. 4).
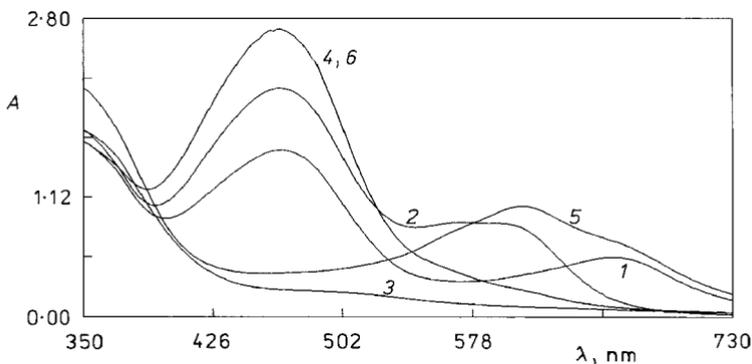
FIG. 2
Absorption spectra of complexes of Co^{2+}, Cu^{2+}, Zn^{2+} and Fe^{2+} with zincon at pH 5.0; concentrations (μmol l^{-1}): Co^{2+} 36, Cu^{2+} 29, Fe^{2+} 32, Zn^{2+} 20, ZNC 280. Systems: *1* Co^{2+} + ZNC; *2* Cu^{2+} + ZNC; *3* Fe^{2+} + ZNC; *4* Zn^{2+} + ZNC; *5* Co^{2+} + Cu^{2+} + Fe^{2+} + ZNC; *6* ZNC
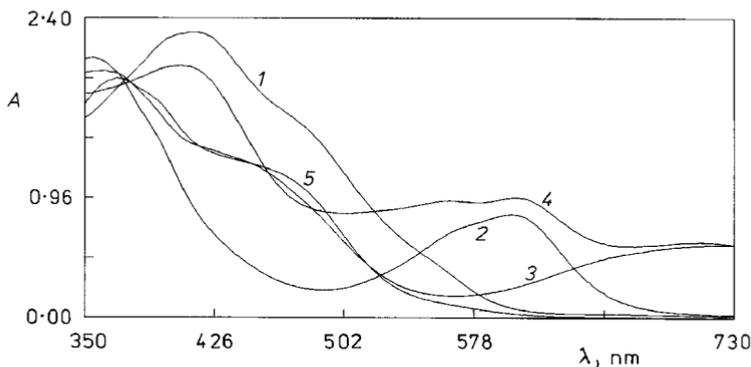

FIG. 3
Absorption spectra of complexes of Co^{2+}, Cu^{2+} and Fe^{2+} ions with nitroso-R-salt and zincon at pH 5.0; concentrations (μmol l^{-1}): Co^{2+} 36, Cu^{2+} 29, Fe^{2+} 32, ZNC 93, NRS 260. Systems: *1* Co^{2+} + NRS + ZNC; *2* Cu^{2+} + NRS + ZNC; *3* Fe^{2+} + NRS + ZNC; *4* Co^{2+} + Cu^{2+} + Fe^{2+} + NRS + ZNC; *5* NRS + ZNC

Simultaneous determination of the two metals was tested at pH 9.0 (Tables I and II, set *IIIA*); alternatively, the absorbances were measured at pH 5.0 and at pH 9.0 and the two sets of data were combined into one (Tables I and II, set *IIIB*). The results obtained by the two procedures were nearly identical.

Simultaneous determination of Co^{2+}, Cu^{2+} and Zn^{2+} with NRS and ZNC was accomplished at pH 9.0 (Tables I and II, set *IIIC*).

The time stability of this system was examined under conditions given in Table V (set *III*, note [d]). The system was stable in 20 min.

The excess concentrations of the reagents over those of the metals sufficient for a quantitative complexation and the linearity regions of the calibration plots are given in Tables IV and V.

Very good results were achieved by using nitroso-R-salt and zincon for the quantitation of Co^{2+}, Cu^{2+} and Zn^{2+}. All components were determined with relative errors lower than 6%. The results of the multicomponent analysis are given in Table II.

Determination of Cu^{2+}, Zn^{2+} and Ni^{2+} with Zincon and PAR

The spectra of the Cu^{2+}, Zn^{2+} and Ni^{2+} complexes with PAR overlap considerably, the three absorption maxima lying all at 500 nm (Fig. 5). Moreover, the reagent itself absorbs strongly at 390 – 450 nm, so that multicomponent determination of the three metal ions with PAR is very difficult.

The complexes of the three ions with ZNC absorb at 550 – 700 nm and the bands overlap considerably (Fig. 4). The reaction of Ni^{2+} with ZNC is less sensitive.
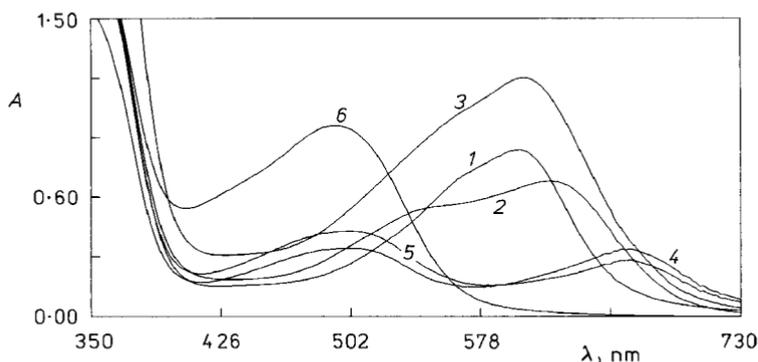

FIG. 4

Absorption spectra of complexes of Co^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} with zincon at pH 9.2; concentrations ($\mu mol\ l^{-1}$): Co^{2+} 36, Cu^{2+} 29, Zn^{2+} 20, Ni^{2+} 25, ZNC 93. Systems: *1* Cu^{2+} + ZNC; *2* Zn^{2+} + ZNC; *3* Cu^{2+} + Zn^{2+} + ZNC; *4* Co^{2+} + ZNC; *5* Ni^{2+} + ZNC; *6* ZNC

The two reagents can be employed simultaneously with advantage, whereby the selectivity of the system increases appreciably. Cu^{2+} will react with ZNC solely whereas Zn^{2+} and Ni^{2+} will react with PAR solely (Fig. 5).

The three metals were determined with PAR and ZNC in a model mixture (Tables I and II, set *IVA*) and, in addition, in ALPAKA alloy specimens (Tables I and VI, set *IVB*).

The concentrations of the metal ions in the calibration solutions were consistent with their contents in the ALPAKA alloy. The analysis of the alloy was performed under identical conditions and using the same calibration set as with the model blend.

The time stability of the solution at pH 9.2 was monitored at 460, 488, 490, 546, 550, and 648 nm using the following concentrations ($\mu mol\ l^{-1}$): Ni 9.2, Cu 29, Zn 9.7, PAR 79.6, ZNC 93. The system was stable in 20 min.

Cation Cu^{2+} was determined with ZNC in conditions which were found optimum in the measurements described above. The values of the optimum pH and excess reagent concentrations over the metal concentration sufficient for quantitative complexation are given in Tables III and IV.

The simultaneous application of zincon and PAR to the determination of Cu^{2+}, Zn^{2+} and Ni^{2+} gave very good results. The relative errors of determination of the three components in the model solutions were all lower than 2.5% (Table II).

ALPAKA Alloy

The metal ions in sample were determined three times at weekly intervals. In the first week, each solution of the calibration set was prepared and measured in triplicate and
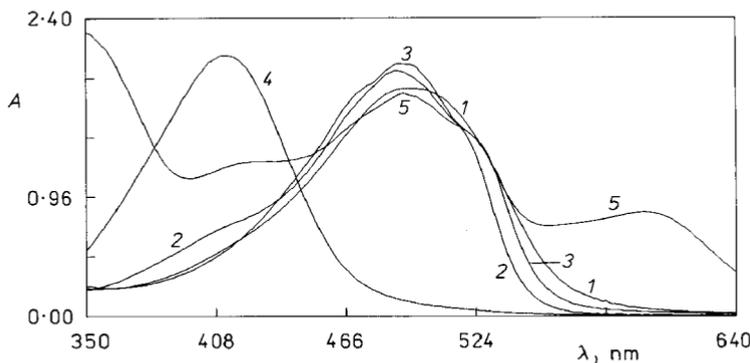

FIG. 5

Absorption spectra of complexes of Cu^{2+}, Zn^{2+} and Ni^{2+} ions with PAR at pH 9.2; concentrations ($\mu mol\ l^{-1}$): Cu^{2+} 29, Zn^{2+} 21, Ni^{2+} 25, PAR 80. Systems: *1* Cu^{2+} + PAR; *2* Zn^{2+} + PAR; *3* Ni^{2+} + PAR; *4* PAR; *5* Cu^{2+} + Zn^{2+} (8 $\mu mol\ l^{-1}$) + Ni^{2+} (9 $\mu mol\ l^{-1}$) + PAR + ZNC

the average absorbance value was used. Since the relative standard deviation of absorbance for all calibration solutions and all wavelengths was 0.004_3 absorbance units, which is roughly at the limit of measurement precision, the calibration solutions were measured only once in the second and third weeks. Each of the unknown ALPAKA samples (E2, E6) was determined fivefold each week.

The results of statistical processing are summarized in Table VI. This table demonstrates that the Cu^{2+}, Zn^{2+} and Ni^{2+} ions were determined with relative errors of $4 - 9\%$. This level is probably due to the matrix effect (microcomponents). Moreover, the fact that the Zn^{2+} and Ni^{2+} contents were many times lower than the Cu^{2+} content also contributed to the errors.

TABLE VI
Results of determination of copper, zinc and nickel in ALPAKA alloy samples

Metal	True content wt.%	1st week			2nd week			3rd week		
		content wt.%	s_{rel} %	CRPE %	content wt.%	s_{rel} %	CRPE %	content wt.%	s_{rel} %	CRPE %
				ALPAKA E2						
Cu	57.89	54.73	1.79	−5.45	53.90	1.55	−6.89	55.07	1.17	−4.87
Zn	19.90	18.44	2.02	−7.33	18.53	1.26	−6.88	18.42	1.11	−7.43
Ni	18.43	17.09	2.80	−7.27	16.73	1.97	−9.22	16.91	1.54	−8.24
				ALPAKA E6						
Cu	57.21	55.90	0.91	−2.29	54.71	1.26	−4.37	55.16	0.89	−3.58
Zn	19.92	18.62	1.79	−6.53	18.55	1.88	−6.87	18.35	2.21	−7.88
Ni	18.45	17.05	2.08	−7.58	17.18	1.59	−6.88	17.27	1.09	−6.40

[a] Average of 5 determinations.

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