



SPECIATION FINGERPRINTS OF BINARY MIXTURES
BY THE OPTIMIZED SEQUENTIAL TWO-PHASE SEPARATION

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At the SIS'93 Conference we reported the analysis of the separation methods suitable for chemical speciation of radionuclides and metals, and the advantages of sequential (double) distribution technique were discussed [1]. The equilibria are relatively easy to control and the method enables to minimize a matrix composition adjustment, and therefore it minimizes also the disturbance of original (native) state of elements.

The technique may consist in the repeated solvent extraction of sample, or the replicate equilibration with sorbent. The common condition of applicability is a linear separation isotherm of the species, what is mostly a reasonable condition in case of trace concentrations.

The equations used for simultaneous fitting [1] can be written in general form.

(i) In the case when the species are independent (interconversion does not occur) the concentration of analyte occurring in form of two species as a total concentration in respective phase j and step i :

$$\frac{c_{1j}}{c_0} = \frac{(K_B)^{j-1}}{(1+rK_B)^i} + \left[\frac{(K_A)^{j-1}}{(1+rK_A)^i} - \frac{(K_B)^{j-1}}{(1+rK_B)^i} \right] x_A \quad (1)$$

where

$$x_A = 1 - x_B = \frac{1}{1+p} \quad (2)$$

is the mole fraction of species A in mixture with species B, where the matrix of indexes (identical with the exponents) is as follows:

	i	j	fingerprints phase
original solution	0	1	0
1st raffinate / filtrate	1	1	1
1st extract / sorbate	1	2	2
2nd raffinate / filtrate	2	1	3
2nd extract / sorbate	2	2	4

(ii) When the species are genetically tied, i.e. an equilibrium

$$p = \frac{[B]_{10}}{[A]_{10}} = \frac{[B]_{11}}{[A]_{11}} = \frac{[B]_{21}}{[A]_{21}} = K_1 \quad (3)$$

exists both in the original sample and that contacted with separation phase 2, but no interconversion takes place in the organic or solid separation phase 2,

$$c_{ij} = c_0 \frac{(K_A + K_B K_1)^{j-1} (1 + K_1)^{i+1-j}}{[1 + r K_A + K_1 (1 + r K_B)]^i} \quad (4)$$

These equations can be used not only for predictive calculation of c_{ij} values at known K_A , K_B and K_1 , but also for finding the constants K 's by routine methods of non-linear programming.

As a realistic example, the distribution of two species, A and B, having individual distribution ratios $K_A = 10$ and $K_B = 0.06$ in liquid - liquid system¹ was modeled mathematically for 6 and 10% uncertainty of the apparent distribution constants respectively, and variance in $p = c_B/c_A$ ratio in original samples 8% (Table 1).

The experimental concentration data can be well displayed in Tukey box plot diagrams, which for each set of data display the mean (dotted) line and the box indicating the range e.g. between the 25th and 75th percentiles of the data (and the 10th and 90th percentiles as capped error bars, as in our case). The characteristic patterns obtained may serve as fingerprints of the binary chemical species mixture (FIG 1.).

¹ See data in paper [2] on distribution of arsenic(V) (=A) and arsenic(III) (=B) between 5M H_2SO_4 - 1M NaBr aqueous phase and chloroform.

REFERENCES

1. F.MACÁSEK, *Separation methods for chemical speciation of radionuclides and metals in environmental matrices*, J.Radioanal.Nucl.Chem.Articles 183 (1994) 5.
2. N.SUZUKI, K.SATO, H.SHOJI, H.IMURA, *Liquid-liquid extraction behavior of arsenic(III), arsenic(V), methylarsonate and dimethylarsinate in various systems*, Anal.Chim.Acta 185 (1986) 239.

TABLE 1. The parameters found from concentration data at various conditions (standard Marquardt-Levenberg algorithm of fitting from SigmaPlot™ Scientific Graph System Version 5.01). "True" values : $K = 10.0 \pm 0.6$, $K = 0.060 \pm 0.006$, permissible variance of p was 8% of the initial value indicated.

The mode of fitting:

- A - all sets c_{11} - c_{22} were considered with constant weight 1
- B - first, the sets c_{11} and c_{22} were fitted with weights of individual values $1/c^2$ and then the set c_{12} was added and fitted with the same weights.
- B(0.1) - the same for data at phase ratio $r=0.1$
- C - the value K_A was considered to be known
- D - both the values K_A and K_B were considered to be known.

Fitting mode	p		K_A	K_B
	"true"	fitted	fitted	fitted
A	0.10	0.57	290	1.1
B	0.10	0.076	8.5	0.0
B(0.1)	0.10	0.18	7.9	7.9
C	0.10	0.17	-	0.56
D	0.10	0.1055±0.0006	-	-
A	1.0	1.1	17	0.084
B	1.0	1.17	12	0.08
B(0.1)	1.0	1.04	7.5	0.66
C	1.0	0.998	-	0.061
D	1.0	0.990±0.023	-	-
A	10	3.1	1.2	0.004
B	10	3.8	1.5	0.015
B(0.1)	10	8.5	5.6	0.11
C	10	5.5	-	0
D	10	9.20±0.13	-	-

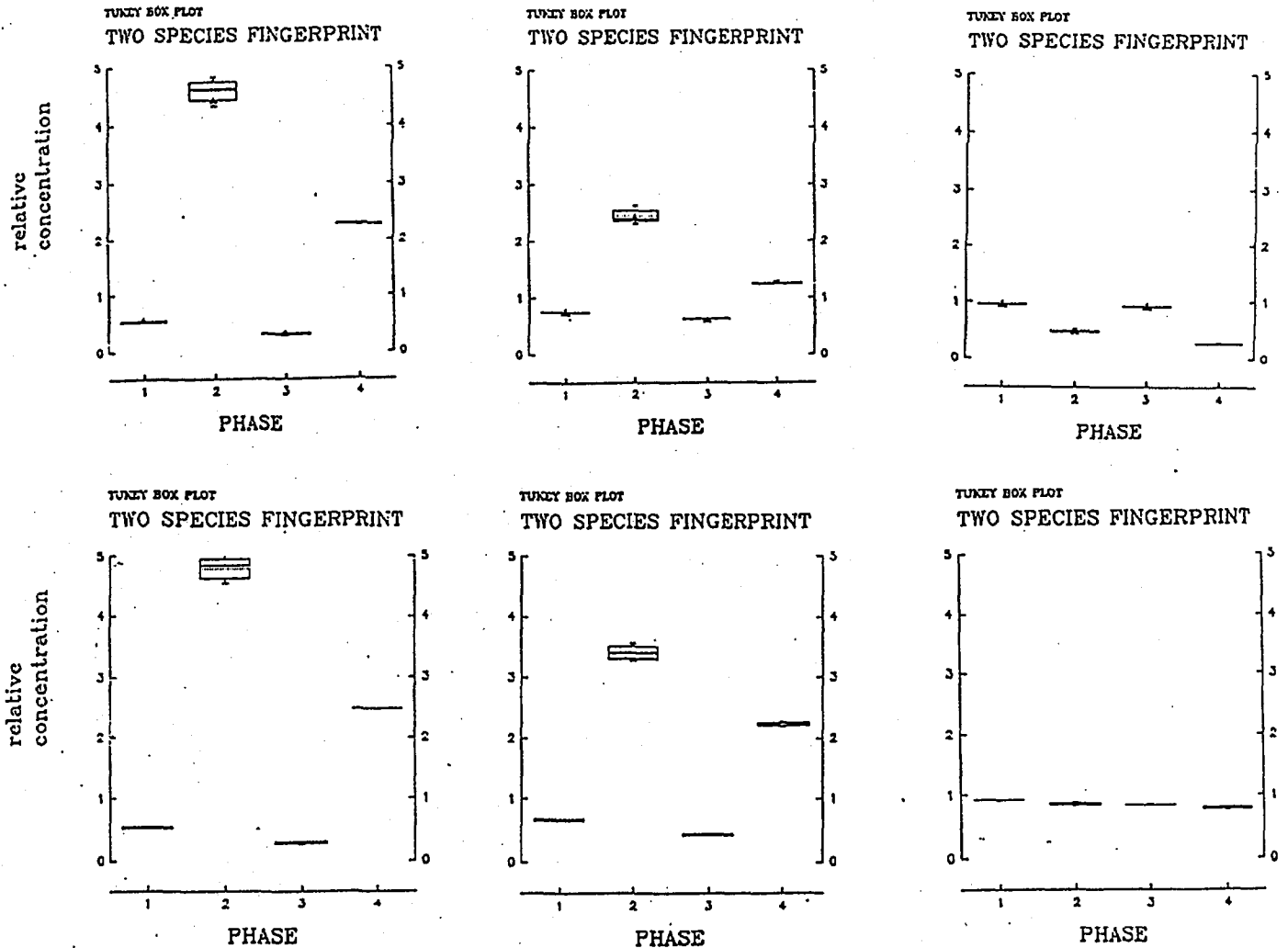


FIG.1. Distribution patterns (fingerprints) for binary mixture of the species having distribution constants $K_A=10$, $K_B=0.06$ and $r=0.1$) at the Tukey box diagram. Full triangles correspond to the values found by fitting with known constants K_A and K_B and unknown ratio p .

(i) Independent species ratio:
 1a: $p = 0.1$, 1b: $p = 1$, 1c: $p = 10$.

(ii) Equilibrium of species reestablished at various K_1 :
 2a: $K_1 = 0.1$, 2b: $K_1 = 1$, 2c: $K_1 = 10$.

SECTION B

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