Interval regularization approach to the Firodt method of the spectroscopic analysis of the nonseparated mixtures

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Overview

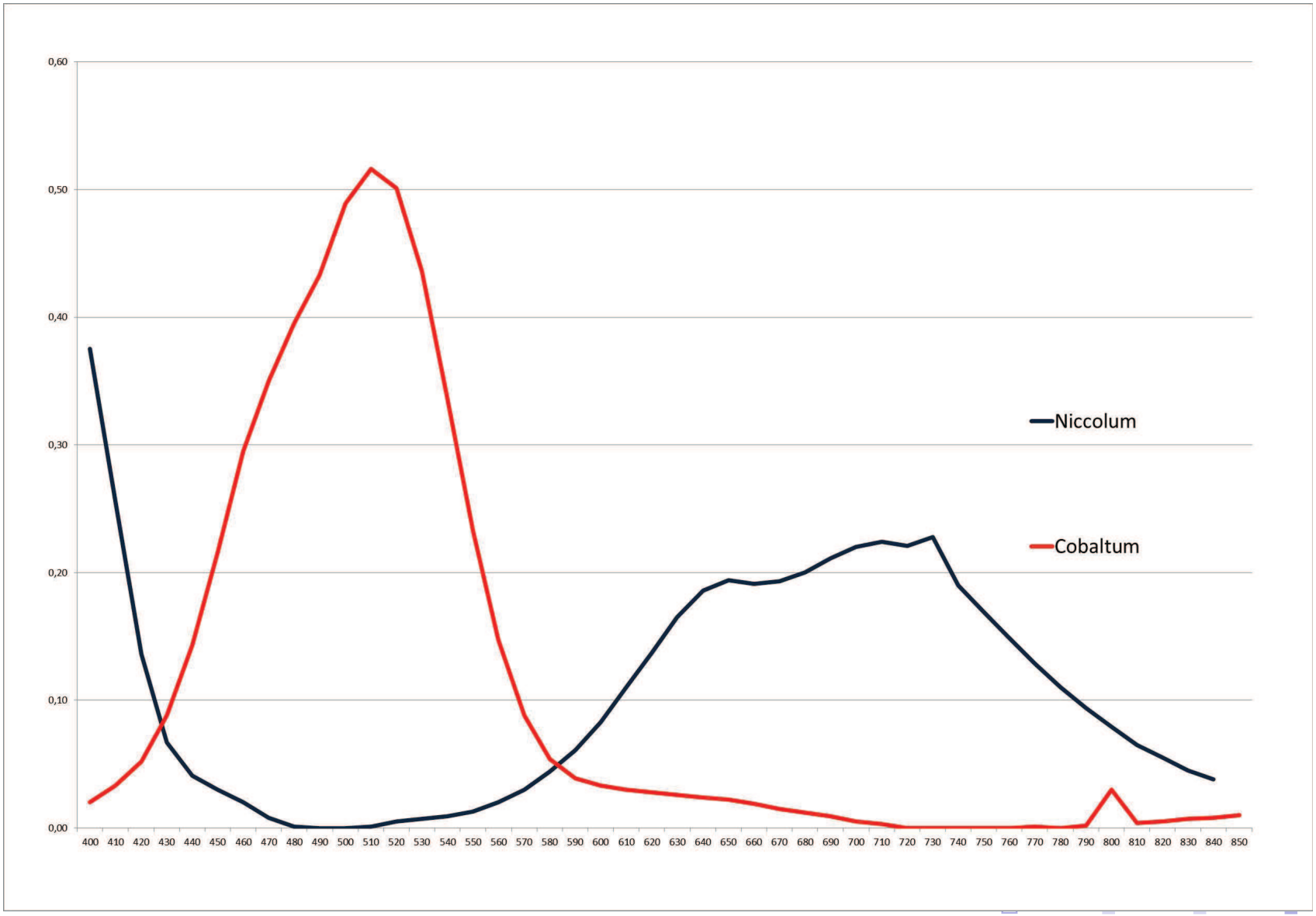
- Traditional formulation of the Firordt method
- Interval formulation of problem
- Interval reguarization approach
- Examples
- Conclusions

To find concentrations c_x, c_y of the components X, Y of the nonseparated mixture you should to solve

$$\begin{cases} a_{x1} \cdot c_x + a_{y1} \cdot c_y = A_1, \\ a_{x2} \cdot c_x + a_{y2} \cdot c_y = A_2, \end{cases} \quad \text{where}$$

- a_{x1}, a_{x2} — X absorption levels for the wave lengths λ_1, λ_2,
- a_{y1}, a_{y2} — Y absorption levels for the wave lengths λ_1, λ_2,
- c_x и c_y — *required* molar concentration of the components X and Y in the given mixture,
- A_1 и A_2 — absorption level of the mixture corresponding to wave lengths λ_1, λ_2.

Measurements sample



More measurements for the same number of components

$$\begin{cases} a_{x1} \cdot c_x & + & a_{y1} \cdot c_y = & A_1, \\ a_{x2} \cdot c_x & + & a_{y2} \cdot c_y = & A_2, \\ \cdots & & & \\ a_{xm} \cdot c_x & + & a_{ym} \cdot c_y = & A_m. \end{cases}$$

$$\begin{cases} \boldsymbol{a}_{x1} \cdot c_x + \boldsymbol{a}_{y1} \cdot c_y = \boldsymbol{A}_1, \\ \boldsymbol{a}_{x2} \cdot c_x + \boldsymbol{a}_{y2} \cdot c_y = \boldsymbol{A}_2, \\ \quad \cdots \\ \boldsymbol{a}_{xm} \cdot c_x + \boldsymbol{a}_{ym} \cdot c_y = \boldsymbol{A}_m. \end{cases}$$

$$\Xi_{tol}(\boldsymbol{A}, \boldsymbol{b}) = \{x \in \mathbb{R}^n \mid (\forall A \in \boldsymbol{A})(\exists b \in \boldsymbol{b})(Ax = b)\}, \tag{1}$$

$$\Xi_{tol}(\boldsymbol{A}, \boldsymbol{b}) = \bigcap_{A \in \boldsymbol{A}} \left\{ x \in \mathbb{R}^n \,\middle|\, (\exists b \in \boldsymbol{b})\,(Ax = b) \right\}, \tag{2}$$

In the above formula, $\left\{ x \in \mathbb{R}^n \,\middle|\, (\exists b \in \boldsymbol{b})(Ax = b) \right\}$ is the solution set to the interval system $Ax = \boldsymbol{b}$ with the interval uncertainty concentrated only in the right-hand side vector.

Straight forward replacement $Ax = b$ to $\boldsymbol{A}x = \boldsymbol{b}$ often leads to empty $\Xi_{tol}(\boldsymbol{A}, \boldsymbol{b})$.

Right-hand part of the interval system may be extended using some positive parameter $z \in \mathbb{R}$, $z > 0$.

So we have to find point which belong to the tolerable solution set of the system $\Xi_{tol}(\boldsymbol{A}, \boldsymbol{b}(z))$
For the Firordt method it is useful $\boldsymbol{b}(z) = [\underline{b}_i - z, \overline{b}_i + z]$, $i = 1, \ldots, m$

One of the simpliest way to find both minimum extension ($z^* \in \mathbb{R}$ and $\boldsymbol{b}(z^*)$) and point from $\Xi_{tol}(\boldsymbol{A}, \boldsymbol{b}(z^*))$ is to solve linear programming task.

Theorem

There exists a solution x^{+^*} and $x^{-^*} \in \mathbb{R}^n$, $z^* \in \mathbb{R}$ to the linear programming problem

$$z \rightarrow \min_{x^+,\ x^-,\ z}, \tag{3}$$

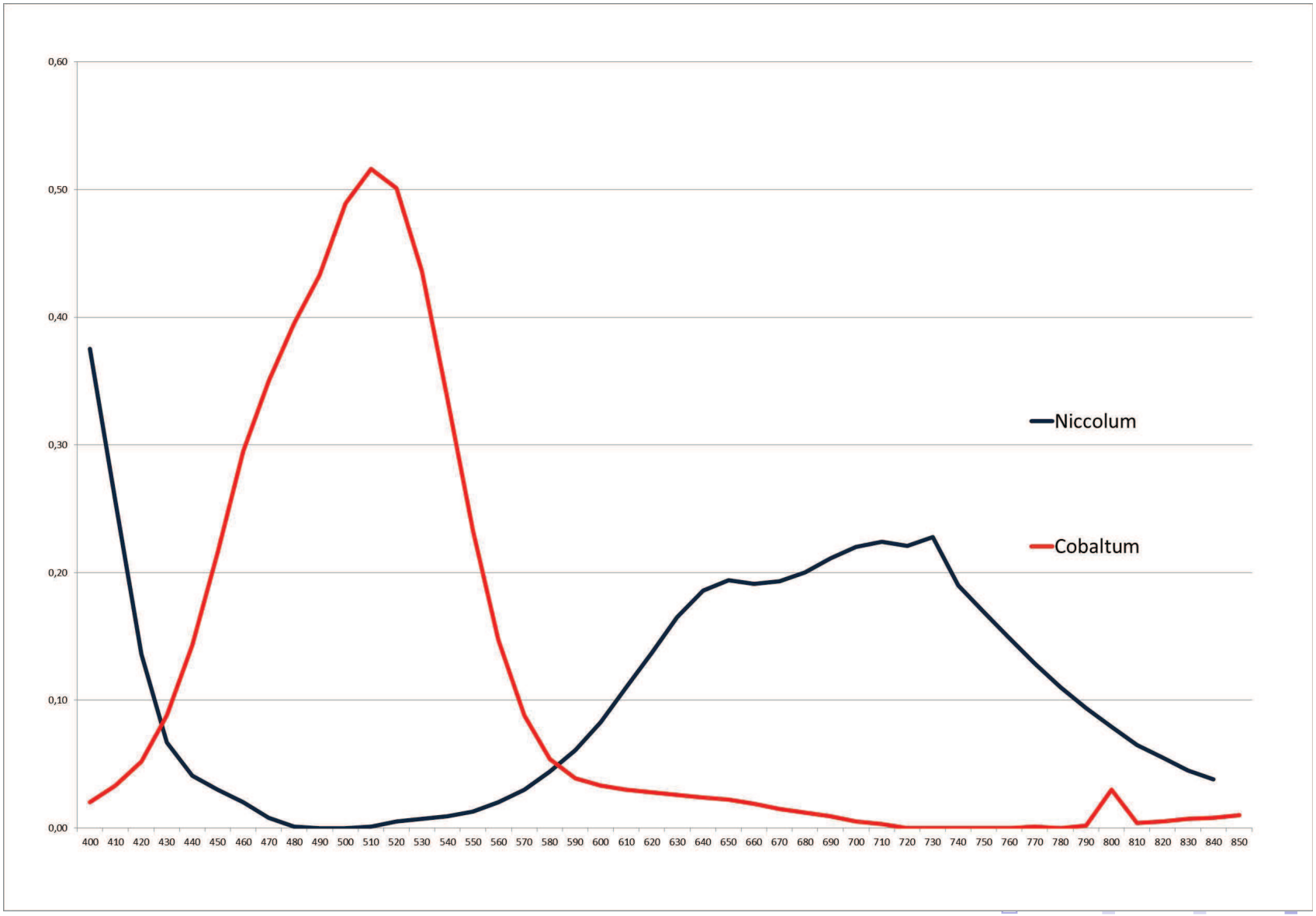
$$\sum_{j=1}^{n} (\underline{a}_{ij} x_j^+ - \overline{a}_{ij} x_j^-) \geq \underline{b}_i - z, \qquad i = 1, 2, \ldots, n, \tag{4}$$

$$\sum_{j=1}^{n} (\overline{a}_{ij} x_j^+ - \underline{a}_{ij} x_j^-) \leq \overline{b}_i + z, \qquad i = 1, 2, \ldots, n, \tag{5}$$

$$x_j^+, x_j^-, z \geq 0, \qquad j = 1, 2, \ldots, n. \tag{6}$$

In addition, the vector $x^* = x^{+^*} - x^{-^*}$ belongs to $\Xi_{tol}(\boldsymbol{A}, \boldsymbol{b}(z^*))$.

Measurements sample



Measurements under interval uncertainty

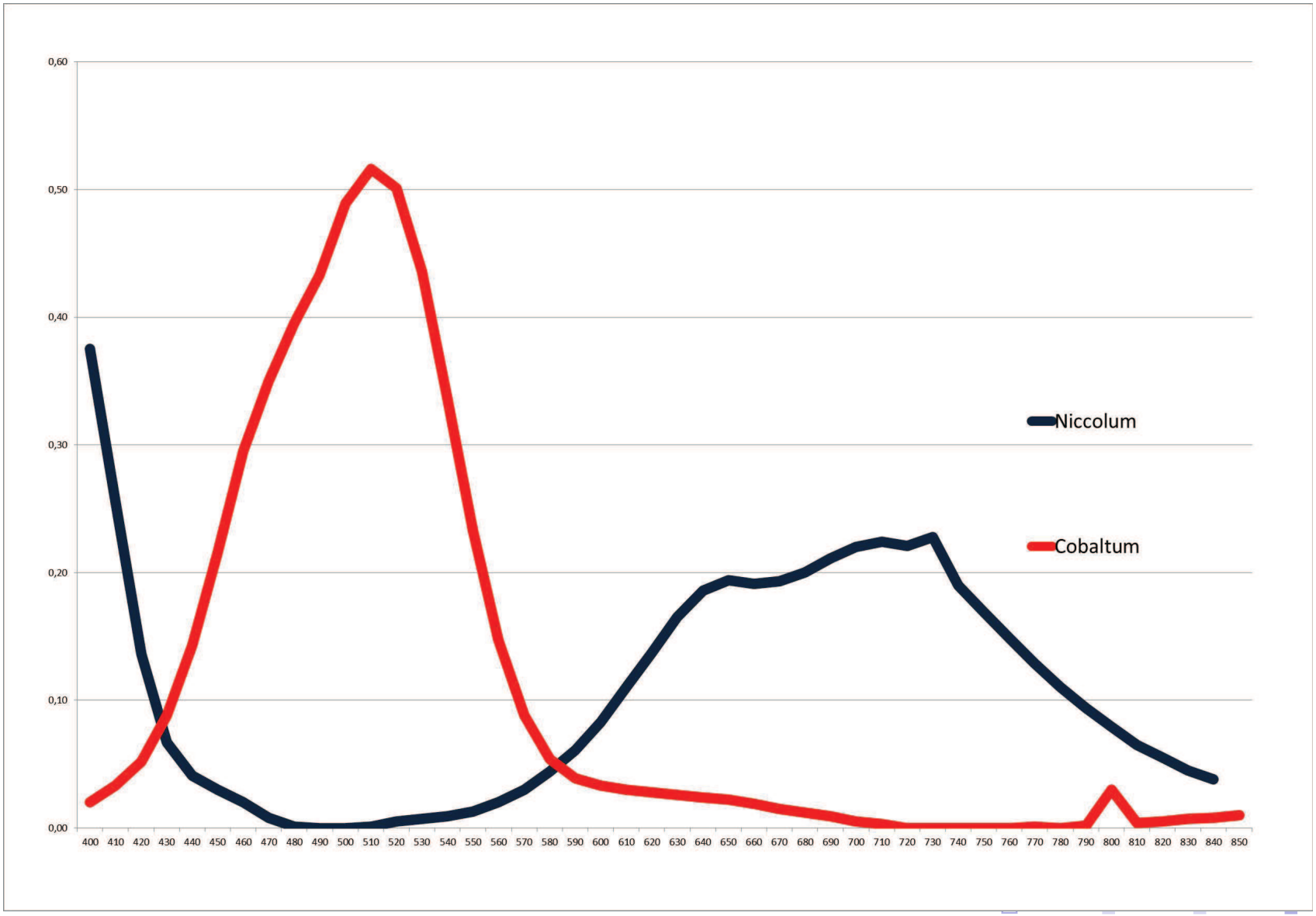


Table: Mixture of $Ni : Co$ at a ratio (1:2).

	Mixture $Ni : Co(1:2)$					
	$c = (c_x, c_y)$	Δ in %	$c = (c_x, c_y)(1\%)$	Δ in %	N_{ps}	Δ in %
	0.0323	2.8197	0.0321	3.4512	0.033	1
	0.0610	9.9509	0.0610	9.8862	0.063	13.4
z^*	0.02143	—	0.02144	—	—	—

Table: Mixture of Ni : Co at a ratio of (1:1).

	Mixture Ni : $Co(1:2)$					
	$c = (c_x, c_y)$	Δ in %	$c = (c_x, c_y)(1\%)$	Δ in %	N_{ps}	Δ in %
	0.0467 0.0483	6.4847 16.0296	0.0471 0.0480	5.6110 15.2289	0.04811 0.0458	3.78 10.136
z^*	0.01531	—	0.01624	—	—	—

Table: Mixture of Ni : Co at a ratio of (2:1).

	Mixture Ni : $Co(1:2)$					
	$c = (c_x, c_y)$	Δ in %	$c = (c_x, c_y)(1\%)$	Δ in %	N_{ps}	Δ in %
	0.0651 0.0312	2.3320 12.5	0.0650 0.0311	2.3820 12.0534	0.0648 0.0306	2.665 10.196
z^*	0.01244	—	0.01250	—	—	—

Conclusions

- In general Firordt method has poor accuracy.
- In all cases applied approach gives stable solution.
- In most cases results are not worse than other approaches.
- Because of its stability the applied approach may be used for short the sequense of measurements.

References

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Thanks for your attention!