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

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• Traditional formulation of the Firordt method
• Interval formulation of problem
• Interval regularization approach
• Examples
• Conclusions
To find concentrations $c_x, c_y$ of the components $X, Y$ of the nonseparated mixture you should to solve

\[
\begin{align*}
    a_{x1} \cdot c_x + a_{y1} \cdot c_y &= A_1, \\
    a_{x2} \cdot c_x + a_{y2} \cdot c_y &= A_2,
\end{align*}
\]

where

- $a_{x1}, a_{x2}$ — $X$ absorption levels for the wave lengths $\lambda_1, \lambda_2$,
- $a_{y1}, a_{y2}$ — $Y$ absorption levels for the wave lengths $\lambda_1, \lambda_2$,
- $c_x$ 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 $\lambda_1, \lambda_2$. 
Overdefined linear equation system

More measurements for the same number of components

\[
\begin{align*}
 a_{x1} \cdot c_x + a_{y1} \cdot c_y &= A_1, \\
 a_{x2} \cdot c_x + a_{y2} \cdot c_y &= A_2, \\
 \cdots \\
 a_{xm} \cdot c_x + a_{ym} \cdot c_y &= A_m.
\end{align*}
\]
Interval formulation of the problem

\begin{align*}
  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{align*}
\[ \Xi_{tol}(A, b) = \{ x \in \mathbb{R}^n \mid (\forall A \in A)(\exists b \in b)(Ax = b) \}, \] 

(1)

\[ \Xi_{tol}(A, b) = \bigcap_{A \in A} \{ x \in \mathbb{R}^n \mid (\exists b \in b)(Ax = b) \}, \] 

(2)

In the above formula, \( \{ x \in \mathbb{R}^n \mid (\exists b \in b)(Ax = b) \} \) is the solution set to the interval system \( Ax = b \) with the interval uncertainty concentrated only in the right-hand side vector.
Straight forward replacement $Ax = b$ to $Ax = b$ often leads to empty $\Xi_{tol}(A, b)$.

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 $\Xi_{tol}(A, b(z))$.

For the Firordt method it is useful $b(z) = [b_i - z, \overline{b_i} + z], i = 1, \ldots, m$.
One of the simpliest way to find both minimum extension ($z^* \in \mathbb{R}$ and $b(z^*)$) and point from $\Xi_{tol}(A, b(z^*))$ 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*

\[
 z \rightarrow \min_{x^+, x^-, z},
\]

\[
 \sum_{j=1}^{n} (a_{ij}x_j^+ - \bar{a}_{ij}x_j^-) \geq b_i - z, \quad i = 1, 2, \ldots, n, \tag{4}
\]

\[
 \sum_{j=1}^{n} (\bar{a}_{ij}x_j^+ - a_{ij}x_j^-) \leq \bar{b}_i + z, \quad i = 1, 2, \ldots, n, \tag{5}
\]

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

*In addition, the vector $x^* = x^{+*} - x^{-*}$ belongs to $\Xi_{tol}(A, b(z^*))$.*
Table: Mixture of $Ni : Co$ at a ratio (1:2).

<table>
<thead>
<tr>
<th>$c = (c_x, c_y)$</th>
<th>$\Delta$ in %</th>
<th>$c = (c_x, c_y)(1%)$</th>
<th>$\Delta$ in %</th>
<th>$N_{ps}$</th>
<th>$\Delta$ in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0323</td>
<td>2.8197</td>
<td>0.0321</td>
<td>3.4512</td>
<td>0.033</td>
<td>1</td>
</tr>
<tr>
<td>0.0610</td>
<td>9.9509</td>
<td>0.0610</td>
<td>9.8862</td>
<td>0.063</td>
<td>13.4</td>
</tr>
<tr>
<td>$z^*$</td>
<td>—</td>
<td>0.02144</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>( c = (c_x, c_y) )</th>
<th>( \Delta ) in %</th>
<th>( c = (c_x, c_y)(1%) )</th>
<th>( \Delta ) in %</th>
<th>( N_{ps} )</th>
<th>( \Delta ) in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0467</td>
<td>6.4847</td>
<td>0.0471</td>
<td>5.6110</td>
<td>0.04811</td>
<td>3.78</td>
</tr>
<tr>
<td>0.0483</td>
<td>16.0296</td>
<td>0.0480</td>
<td>15.2289</td>
<td>0.0458</td>
<td>10.136</td>
</tr>
<tr>
<td>( z^* )</td>
<td>0.01531</td>
<td>0.01624</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
Table: Mixture of $Ni:Co$ at a ratio of (2:1).

<table>
<thead>
<tr>
<th>$c = (c_x, c_y)$</th>
<th>$\Delta$ in %</th>
<th>$c = (c_x, c_y)(1%)$</th>
<th>$\Delta$ in %</th>
<th>$N_{ps}$</th>
<th>$\Delta$ in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0651</td>
<td>2.3320</td>
<td>0.0650</td>
<td>2.3820</td>
<td>0.0648</td>
<td>2.665</td>
</tr>
<tr>
<td>0.0312</td>
<td>12.5</td>
<td>0.0311</td>
<td>12.0534</td>
<td>0.0306</td>
<td>10.196</td>
</tr>
<tr>
<td>$z^*$</td>
<td>—</td>
<td>0.01250</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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• In general Firdort 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 sequence of measurements.
Vlasova I.V., Vershinin V.I., Determination of binary mixture components by the Firordt method with errors below the specified limit, *Journal of Analytical Chemistry*, vol. 64(2009), No. 6, pp. 553–558.


Thanks for your attention!