Numerical analysis of an inverse coefficient problem for a chemical transformation model

A V Penenko$^{1,2}$, Zh S Mukatova$^{1,2}$, A B Salimova$^2$

$^1$Institute of Computational Mathematics and Mathematical Geophysics SB RAS, ICM&MG SB RAS, prospekt Akademika Lavrentjeva 6, Novosibirsk, 630090, Russian Federation
$^2$Novosibirsk State University, Pirogova st. 1, Novosibirsk, 630090, Russian Federation

a.penenko@yandex.ru

Abstract. Inverse coefficient problems for a non-stationary chemical transformation model are considered. The objective of this work is to test an approach consisting in reducing the inverse problem to a quasi-linear matrix equation based on sensitivity operators constructed from an ensemble of independent solutions of adjoint equations. A Newton-Kantorovich-type algorithm is used to solve the thus obtained matrix equations. This approach is tested on a chemical transformation scheme with 22 species and 20 reactions. The reconstruction results are compared with several sets of unknown reaction rates according to the influence characteristics. The analysis seems to be useful for selecting sets of reaction rates that can be reconstructed by the inverse problem solution.

1. Introduction
Production-destruction type models are used in a wide range of applications, including modeling of the chemical transformation process. The chemical reaction rates can be potentially determined in laboratory conditions. Another way is to identify them implicitly by solving the inverse problems. A possible application of this approach is to indirectly estimate the reaction conditions that affect the reaction rates, e.g., temperature, pressure, or incoming solar radiation fluxes in the case of photochemical reactions.

In this paper, we study an approach based on the idea of G.I. Marchuk [1]. In this approach the inverse problems are reduced to the family of quasi-linear matrix equations based on the ensemble of independent solutions of adjoint equations. A Newton-Kantorovich-type method is used to solve the resulting quasilinear matrix equations. In the general case Newton-type algorithms are locally-convergent, i.e., their performance strongly depends on the choice of the initial guess.

In previous works we considered the inverse problems when the number of unknowns is comparable to the number of measurement data elements [2], [3]. In the case being considered the number of unknowns is less than the number of measurement data elements. The objective of this paper is to study numerically the local convergence properties of the adjoint ensemble-based algorithm, with regard to the different number of reconstructed reaction rates for an atmospheric chemistry transformation model with 22 species and 20 chemical reactions. This work is an extension of [4] by the application to the chemical transformation model.
2. Inverse Problem
Consider the time interval \([0,T]\) and the Cauchy problem for the system of ordinary differential equations in the form of production-destruction:

\[ \frac{\partial \varphi_l}{\partial t} + P_l(t, \varphi, y) \varphi_l = \Pi_l(t, \varphi, y) + f_l, \quad t \in [0,T]. \]  

where \( N \) is the number of components under consideration, \( \varphi_l(t) \) is the value of component \( l \) at the time moment \( t \), and \( \varphi(t) \in \mathbb{R}^{N \times} \) is a vector function with elements \( \varphi_l(t) \). Let \( Y \) be a set of admissible coefficients. According to the inverse modeling approach developed in [5], the constant coefficients vector \( y \in \mathbb{Y} \subset \mathbb{R}^{N \times} \) is called the uncertainty vector. The vector-functions \( \Pi_l : [0,T] \times \mathbb{Y} \rightarrow \mathbb{R}^{N \times} \) describe the destruction and production processes, respectively. The set \( \Phi \subset L^2(0,T; \mathbb{R}^{N \times}) \) denotes the solutions of (1)-(2) corresponding to \( Y \). Suppose that all involved functions are smooth enough for all subsequent calculations to make sense.

The problem of determining \( \varphi \) from (1)-(2) by known \( \varphi^0 \in \mathbb{R}^{N \times} \) and \( y \in \mathbb{Y} \) is called a direct problem. Let us denote its solution by \( \varphi[y] \in \Phi \).

The set of indices \( \text{L}_{\text{meas}} \) denotes the observed state function components. Define the subspace \( \text{L}_{\text{meas}} \subset L^2(0,T; \mathbb{R}^{N \times}) \) and the operator that maps the coefficients to the observed time-series at their respective positions and place zero time-series in the rest of the positions:

\[ \text{L}_{\text{meas}} = \{ \{ h_i \} \}_{i=1}^{N \times} \text{L}_{\text{meas}} \ni \{ h_i \} \in L_2(0,T), \quad A : \{ \{ y \} \} \ni \{ \{ y \} \} \rightarrow \{ \{ \varphi[y] \} \} \text{L}_{\text{meas}}. \]

where \( \{ a_i \} \) is a vector with elements \( a_i, \ldots, a_N \). Let there be some \( y^{(\*)} \in \mathbb{Y} \), which we call the “exact solution”, and define measurements data vector:

\[ \text{I} = A(y^{(\*)}). \]  

The problem of finding \( y^{(\*)} \) by \( \text{I} \) and (3) is called the inverse coefficient problem.

In practical applications, instead of the continuous concentration function available, there is usually a sequence of concentration measurements at separate time moments. We need the following definitions:

\[ \# : \mathbb{R}^{N \times} \times \mathbb{R}^{N \times} \rightarrow \mathbb{R} \]

\[ \{ a, b \} \mapsto a^T \text{diag}(r)b = \sum_{i=1}^{N} a_i b_i \rho_i, \]

\[ .^* : \mathbb{R}^{N \times} \times \mathbb{R}^{N \times} \rightarrow \mathbb{R} \]

\[ \{ a, b \} \mapsto a^T \text{diag}(c)b = \sum_{i=1}^{N} a_i b_i \chi_i, \]

where the points "below" in the notation of the scalar products mean that the corresponding entry contains two arguments, \( T \) is the transposition operation, \( \rho_i, \chi_i > 0 \) are some weights, and \( \rho = \{ \rho_i \}_{i=1}^{N} \), \( c = \{ \chi_i \}_{i=1}^{N} \), \( \text{diag}(x) \) is the diagonal matrix with elements of the vector \( X \) on the diagonal, \( \mathbb{R}^{N \times} \) is the Euclidean space with the scalar product \# . and \( \mathbb{R}^{N \times} \) is the Euclidean space with the scalar product .*. Let \( S^* \) denote the adjoint operator for \( S : \mathbb{R}^{N \times} \rightarrow \mathbb{R}^{N \times} \) and \( S \), the adjoint operator for \( S : \mathbb{R}^{N \times} \rightarrow \mathbb{R}^{N \times} \). The matrices for the operators in the canonical bases are

\[ S^* = (\text{diag}(r))^{-1} S^T \text{diag}(r), \quad S^* = (\text{diag}(c))^{-1} S^T \text{diag}(r). \]
Let there be a sequence of time moments $\Theta = \{\theta^m\}_{m=1}^M \subset [0,T]$, $\theta^0 > 0$, $\theta^M = T$ and a set of matrices $\{H(\xi) \in \mathbb{R}^{N\times M} | \xi = 1,...,\Xi\}$. This type of reduction [3] can correspond to an in situ monitoring system that performs measurements regularly. We define a bilinear map corresponding to one composite measurement result and the corresponding operator $H_0$:

$$\left\langle \cdot, \cdot \right\rangle_0 : \begin{cases} \mathbb{R}^{N\times M} \times \Phi \to \mathbb{R} \\
\{h, \varphi\} \mapsto \sum_{m=1}^M h_m \# \varphi(\theta^m) \\
H_0 : \begin{cases} \Phi \to \mathbb{R}^\Xi \\
\varphi \mapsto \sum_{m=1}^M \left\langle H(\xi), \varphi \right\rangle_0 e^{(\xi)}
\end{cases}
\end{cases}$$

where $h_m$ is the $m$-th column of the matrix $h$. For example, the results of the measurements of the $l$-th component of the state function $j$ at the time moment $\theta^m$ can be written as $\varphi_j(\theta^m) = \left\langle h, \varphi \right\rangle_0$, where $h \in \mathbb{R}^{N\times M}$ is the matrix with all zero columns except for the $m$-th one, and the $m$-th column is the vector whose $l$-th element is 1 and the others are zeros. Let $H(i)$ rows be nonzero only for the indices from $L_{meas}$.

### 3. Quasi-linear matrix equation

The solution algorithm of the inverse problem is taken from [4]. It is based on the ensembles of adjoint problem solutions. To define the adjoint problem, we need the definition of the divided difference operators $\overline{V}_\varphi$ and $\overline{V}_\varphi$ that map the vector function $S : [0,T] \times \mathbb{R}^N \times \mathbb{R}^N \to \mathbb{R}^N$ to vector functions $\overline{V}_\varphi S : [0,T] \times \mathbb{R}^N \times \mathbb{R}^N \to \mathbb{R}^N$ and $\overline{V}_\varphi S : [0,T] \times \mathbb{R}^N \times \mathbb{R}^N \to \mathbb{R}^N$ such that for any $t \in (0,T]$ and $\varphi^{(m)} \in \mathbb{R}^N$, $y^{(m)} \in \mathbb{R}^N$, $m = 1,2$,

$$S(t, \varphi^{(2)}, y) - S(t, \varphi^{(1)}, y) = \overline{V}_\varphi S(t, \varphi^{(2)}, \varphi^{(1)}; y) \left( \varphi^{(2)} - \varphi^{(1)} \right),$$

$$S(t, \varphi, y^{(2)}) - S(t, \varphi, y^{(1)}) = \overline{V}_\varphi S(t, \varphi, y^{(2)}, y^{(1)}) \left( y^{(2)} - y^{(1)} \right).$$

Let $\varphi^{(m)} = \varphi(\varphi^{(m)})$, $m = 1,2$. We define the adjoint problem with the solution $Y$ for any function $h \in L^2(0,T;\mathbb{R}^N)$ and matrix $H \in \mathbb{R}^{N\times M}$:

$$\frac{-\partial \Psi}{\partial t} + W(t, \varphi^{(2)}, y^{(2)}, \varphi^{(1)}, y^{(1)}) \psi = 0, \quad t \in [\theta^m, \theta^{m+1}], m = 0, \ldots, M - 1,$$

$$W(t, \varphi^{(2)}, y^{(2)}, \varphi^{(1)}, y^{(1)}) = \text{diag} \left( P(t, \varphi^{(2)}, y^{(2)}) \right) + \overline{V}_\varphi P(t, \varphi^{(2)}, \varphi^{(1)}; y^{(2)}) \left( \varphi^{(2)} - \varphi^{(1)} \right) + \overline{V}_\varphi \Pi(t, \varphi^{(2)}, \varphi^{(1)}; y^{(2)}) \left( y^{(2)} - y^{(1)} \right),$$

$$\left[ \Psi \right]_{\theta^m} = \Psi^m, m = 1, \ldots, M,$$

$$\Psi(T+) = 0,$$

where $\theta^0 = 0$, the expressions $f(t-)$ and $f(t+)$ denote the limits from below and top, respectively, $[f]_{\theta^m} = f(\theta^m) - f(\theta^m)$ is the jump of the function $f$. Let us denote the solution of the adjoint problem (4)–(7) with $\Psi[y^{(2)}, y^{(1)}; H]$ and define the sensitivity function $M[y^{(2)}, y^{(1)}; H]$ in the following way:

$$M[y^{(2)}, y^{(1)}; H] = \int_0^T K(t, \varphi^{(2)}, \varphi^{(1)}, y^{(2)}, y^{(1)}) \Psi[y^{(2)}, y^{(1)}; H] dt,$$

$$K(t, \varphi^{(2)}, y^{(2)}, \varphi^{(1)}, y^{(1)}) = \overline{V}_\varphi \Pi(t, \varphi^{(2)}, y^{(2)}, y^{(1)}) - \overline{V}_\varphi P(t, \varphi^{(2)}, y^{(2)}, y^{(1)}) \text{diag}(\varphi^{(1)}).$$

Hence, the measurement data projection system defines the adjoint problem solution ensemble. We call the aggregate of an ensemble of the sensitivity functions as the sensitivity operator. The elements of the ensemble are evaluated in parallel. For any $y^{(m)} \in Y$, $m = 1,2$ the following relation holds:

$$H_0 A(y^{(2)}) - H_0 A(y^{(1)}) = M_0[y^{(2)}, y^{(1)}] \delta y.$$
where

\[ M_n[y^{(2)}, y^{(1)}]: \begin{cases} Y \to \mathbb{R}^{\sum \alpha} \\ z \to \sum_{i=1}^{\sum \alpha} e^{(i)} M[y^{(2)}, y^{(1)}; H^{(2)}] \end{cases} \]

Choosing \( y^{(2)} = y^{(*)} \) in (9), we come to a parametric family of operator equations, which can be used to solve the inverse problem:

\[ H_\alpha(I - A(y)) = M_\alpha[y, y](y^{(*)} - y) + Q[y^{(*)}, y], \]

\[ Q[y^{(*)}, y] = (M_\alpha[y^{(*)}, y] - M_\alpha[y, y])(y^{(*)} - y). \]

Thus, any pair of measurement data reduction operator \( H_\alpha \) and “uncertainty” of the model (in our case it is \( y \)) generates the sensitivity operator, which is the characteristic of this inverse problem. To solve the matrix equation we use a Newton-Kantorovich-type algorithm similar to [2]. In the algorithm, the ill-conditioned sensitivity operator matrix inversion is regularized by the truncated SVD with the sequential increase of the singular values being considered.

4. Numerical experiments

Let us consider a numerical experiment on the identification of the reaction rates for the atmospheric chemistry transformation model with 22 species and 20 chemical reactions from [6] augmented with a \( SO_2 \) reaction from [7]:

\[
\begin{align*}
NO_2 + h\nu & \rightarrow NO + O_3 P \\
HCHO + h\nu & \rightarrow CO + 2H_2O \\
O_2 + O_3 P & \rightarrow O_3 \\
O_3 + O_2 & \rightarrow O_3 + O_3 P \\
NO_2 + NO & \rightarrow NO_2 + OH \\
NO + OH & \rightarrow HCHO + HO_2 + NO_2 \\
HC + OH & \rightarrow H_2O + RO_2 \\
NO_2 + OH & \rightarrow HNO_3 \\
H_2O + 2HO_2 & \rightarrow H_3O + H_2O_2 + O_3 \\
2RO_2 & \rightarrow Prod
\end{align*}
\]

As the «exact» solution \( y^{(*)} \), we consider the reaction rates from [6], [7], and [8] corresponding to noon (Figure 1a).

Similarly to [2], for the numerical computations we use a first-order discrete-analytical numerical scheme, which is equivalent to the QSSA scheme [9]. The scheme is explicit and preserves nonnegative concentrations. The numerical schemes for the direct and adjoint problems are constructed to satisfy the discrete analog of the sensitivity relation that links the variation of the state function to the variation of the model coefficients. The grid parameters in the computations are \( T = 3600s \), \( N_t = 500 \), \( N_c = 22 \), \( N_y = 20 \), where \( N_t \) is the number of the temporal grid points. The point-wise measurements are taken with the uniform time interval \( \Delta \theta = 360 \). In this case the number of the adjoint ensemble members is \( \Xi = \lfloor T / \Delta \theta \rfloor \). Let all concentrations be measured \( (I_{\text{meas}} = 1,..., N_c) \).
In the first experiment we calculate the sensitivity operator matrices for \( M_y[y^{(o)}, y^{(0)}] \) and \( M_y[y^{(0)}, y^{(0)}] \) with \( y^{(0)} = 2y^{(o)} \). The norm of the column of a sensitivity operator matrix describes the sensitivity of measurements to the variation of a particular reaction rate. The norms are presented in Figure 1 b). Let us call these norms the influences of the reaction rates.

Let us evaluate the reconstruction efficiency for the reaction rates corresponding to the reaction rates from different sensitivity groups. In Figure 3 we present examples of the outcomes of reconstruction for different sets of reconstructed rates \( L_{cons} \) and for different initial guesses:

\[
y^{(0)}_i = y^{(o)}_i + \begin{cases} 0, & l \notin L_{cons} \\ (g-1)y^{(o)}_l, & l \in L_{cons} \end{cases}
\]

In Figure 2 a) we present a relative reconstruction error for the set of rates \( L_{cons} = \{y_1, y_3, y_4\} \). As we see, \( y_1 \) has the highest influence among \( L_{cons} \) (see Figure 1), but its reconstruction is not the best one. In Figure 2 b) c) and d), \( \{y_1, y_3, y_4\} \) is augmented with \( y_{18}, y_{20}, \) and \( y_{10}, \) respectively: \( y_{18} \) has the lowest influence, \( y_{20} \) has a medium one, and \( y_{10} \) has the highest one. In the experiment with \( y_{18}, \) the reconstruction error of \( \{y_1, y_3, y_4\} \) was not affected (Figure 2 b). In the experiment with \( y_{20}, \) it was slightly modified (Figure 2 c)), and the reconstruction was unsuccessful in the experiment with \( y_{10}, \) i.e. the resulting reconstruction error is equal to the initial guess error (Figure 2 d).

5. Discussion
In the numerical experiments, the resulting reconstruction error is dependent on the initial guess, i.e., the algorithm shows local convergence. The efficiency of reconstruction of an individual reaction rate is affected by the complete set of unknowns (i.e., it depends on the context). The reaction rate with a high influence can change the reconstruction efficiency of the other rates from the set. In the case being considered the highest influence was not connected with better reconstruction within the set of reaction rates.
Figure 2. Relative reconstruction error for different sets $L_{\text{cons}}$ of the unknown reaction rates (a), (b), (c), (d)) and for different initial guesses (different colors) with all concentrations measured.

6. Conclusions
In the paper, an inverse coefficient problem solution algorithm was tested for a 0-D atmospheric chemistry transformation model. With the help of an adjoint equation solutions ensemble, the inverse problem can be reduced to a parametric quasi-linear matrix equations family. In the above-considered numerical experiment, there were sets of reaction rates that can be reconstructed by the solution of the inverse problem. We considered the reconstruction error together with a characteristic that measures the influence of the reaction rate on the measurement data. In the numerical experiment presented above the reaction rates with high influence characteristics were able to modify the reconstruction efficiency of a set of reaction rates. This analysis seems to be useful for selecting sets of reaction rates that can be reconstructed by the inverse problem solution.

Acknowledgments
The work was supported by the Russian Foundation for Basic Research under grant 19-07-01135 (inverse coefficient problem with point-wise measurements).
References
[1] Marchuk G 1964 Reports of the USSR Academy of Sciences Ed. Science 156 503–06 (In Russian)
[2] Penenko A V 2019 Numerical Analysis and Applications 12 51-69
[3] Penenko A V 2018 Numerical Analysis and Applications 11 73-88
[4] Penenko A, Mukatova Z, Salimova A 2019 preprint URL https://www.researchgate.net/publication/334249101 Numerical study of the coefficient identification algorithm based on ensembles of adjoint problem solutions for a product ion-destruction model
[5] Penenko V V 1996 Bull. Nov. Comp. Center, Series Num. Model. Atmosph. 4 31-52
[6] Stockwell W and Goliff W 2002 Journal of Geophysical Research 107 4643–50
[7] Visscher A D 2013 Air Dispersion Modeling: Foundations and Applications (JOHN WILEY & SONS INC).
[8] Schaap M, Roemer M, Sauter F, Boersen G, Timmermans R and Builtjes P J H 2005 LOTOS-EUROS Documentation (TNO report)
[9] Hesstvedt E, Hov O and Isaksen I 1978 International Journal of Chemical Kinetics 10 971-94