Pergamon

Atmospheric Environment Vol. 29, No. 3, pp. 403 410, 1995

1352-2310/95 $9.50 + 0.00

1352-2310(94)00282-7

EXTRAPOLATION TECHNIQUES USED IN THE SOLUTION OF STIFF ODEs ASSOCIATED WITH CHEMICAL KINETICS OF AIR QUALITY MODELS

DONALD DABDUB and JOHN H. SEINFELD*

Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, U.S.A.

(*First received* 22 *May* 1994 *and in final form* 19 *August* 1994)

Abstract—The solution of chemical kinetics is generally the most computationally intensive step in atmospheric air quality models. The incorporation of ever more complex chemical mechanisms and physicochemical phenomena into these models stimulates the search for more accurate and efficient numerical ODE integration methods. We report here on a new method based on Richardson extrapolation to solve the chemical kinetics in air quality models. The extrapolation method presents high accuracy consistently for wide ranges of ROG/NO_x ratios. The method is robust during sunrise and sunset transitions, when the rate of change of concentrations of a number of photochemically driven species is the greatest. In addition, the extrapolation algorithm is one of the most efficient computationally tested.

Key word index: Ordinary differential equations, chemical mechanism, air quality model, extrapolation method.

1. INTRODUCTION

In three-dimensional Eulerian air quality models (AQMs) the computation of the rate of chemical reaction is the most intensive calculation component, requiring 75–90% of the total CPU time (Shin and Carmichael, 1992; Saylor and Fernandes, 1993; Dabdub and Seinfeld, 1994). To compute the rate of chemical reaction one must essentially solve a system of stiff nonlinear ordinary differential equations (ODEs) of the form

$$\frac{dc_i}{dt} = P_i(\mathbf{c}, t) - L_i(\mathbf{c}, t)c_i, \tag{1}$$

where P_i and $L_i c_i$ are the production and loss rate of species i, respectively, and $\mathbf{c}$ is the vector of concentrations. The chemistry in urban and regional ozone and acid deposition AQMs is becoming more comprehensive and complex as these models continue to be refined and developed. The CIT urban photochemical model, for example, incorporates a modified version of the LCC chemical mechanism (Lurmann *et al.*, 1987), consisting of 106 reactions involving 36 chemical species (Harley *et al.*, 1993). The urban airshed model (UAM) employs the Carbon Bond Mechanism version IV (CB-IV) (Morris and Myers, 1990) containing 87 reactions and 38 species. The regional acid deposition model (RADM) chemical mechanism consists of 157 reactions involving 59 chemical species (Stockwell *et al.*, 1990).

The numerical solution of stiff ODEs has been the subject of considerable attention in the numerical analysis literature (Gear, 1971; Lapidus and Seinfeld, 1971; Enright *et al.*, 1975; Hairer, 1987). There exist a number of general purpose software packages to obtain accurate solutions to stiff ODE systems. Byrne and Hindmarsh (1987) compare some of the most popular packages. This study focuses on the Livermore solver for ordinary differential equations (LSODE), the variable-coefficient ordinary differential equation package (VODPK), the quasi-steady-state (QSSA) method, the hybrid method, and the extrapolation method which is developed here. LSODE (Hindmarsh, 1980) is generally regarded as one of the most accurate routines available and is frequently used as a benchmark to evaluate other methods. In LSODE the Jacobian matrix of the system must be computed and a set of algebraic equations must be solved at each time step, relatively time-consuming operations. To overcome the time requirements of LSODE other methods have been introduced that are specifically designed to solve the ODEs resulting from chemical kinetics in a more rapid manner. VODPK is an alternative that might offer dramatic storage and CPU time improvements in comparison with elimination solvers. It uses Krylov subspace projection methods and the Nordisieck formulation of backward differentiation formulas (Brown and Hindmarsh, 1989). The implementation

* Author to whom correspondence should be addressed.

of VODPK studied here uses Krylov projections with unpreconditioned iterations. Two of the most widely used integrators, as applied to solving chemical kinetics associated with atmospheric chemistry, are the QSSA method (Hesstvedt *et al.*, 1978) and the Hybrid method (Young and Boris, 1977). Table 1 outlines the characteristics of the methods compared in this study.

The QSSA method as proposed by Hesstvedt *et al.* (1978) uses the following formulas for advancing the solution over a time step Δt:

(a) If $L_i(\mathbf{c})\Delta t < 0.01$, where $L_i(\mathbf{c})c_i$ is the species loss rate as defined in equation (1), the equations are non-stiff and are advanced in time by a simple Euler step

$$c_i(t + \Delta t) = c_i(t) + \frac{\mathrm{d}c_i}{\mathrm{d}t}\Delta t. \tag{2}$$

(b) If $10 \geqslant L_i(\mathbf{c})\Delta t \geqslant 0.01$, the equations are deemed stiff and are advanced in time using

$$c_i(t + \Delta t) = \frac{P_i(\mathbf{c})}{L_i(\mathbf{c})} + \left(c_i(t) - \frac{P_i(\mathbf{c})}{L_i(\mathbf{c})}\right) \times \exp(-L_i(\mathbf{c})\Delta t), \tag{3}$$

which comes from the analytical solution of equation (1) assuming that P_i and L_i are constants.

(c) If $L_i(\mathbf{c})\Delta t > 10$, the species i is considered to be in a quasi-steady state and

$$c_i(t + \Delta t) = \frac{P_i(\mathbf{c})}{L_i(\mathbf{c})}. \tag{4}$$

The Hybrid method (Young and Boris, 1977) uses the following predictor–multi-corrector algorithm.

(a) If $L_i(\mathbf{c})\Delta t < 1$, the equations are considered non-stiff and are integrated with the following predictor (p)–corrector (c) method:

$$c_i^{\mathrm{p}}(t + \Delta t) = c_i(t) + \frac{\mathrm{d}c_i}{\mathrm{d}t}\Delta t, \tag{5}$$

$$c_i^{\mathrm{c}}(t + \Delta t) = c_i(t) + \left(\frac{\mathrm{d}c_i}{\mathrm{d}t} + \frac{\mathrm{d}c_i^{\mathrm{p}}}{\mathrm{d}t}\right)\frac{\Delta t}{2}. \tag{6}$$

(b) If $L_i(\mathbf{c})\Delta t \geqslant 1$, the equations are considered stiff and are integrated with the following asymptotic predictor and corrector formulas:

$$c_i^{\mathrm{p}}(t + \Delta t) = \frac{c_i(t)(2/L_i(\mathbf{c}) - \Delta t) + 2\,\Delta t P_i(\mathbf{c})/L_i(\mathbf{c})}{2/L_i(\mathbf{c}) + \Delta t}, \tag{7}$$

$$c_i^{\mathrm{c}}(t + \Delta t) = \frac{c_i(t)(\psi_i - \Delta t) + \Delta t(P_i(\mathbf{c}) + P_i(\mathbf{c}^{\mathrm{p}}))\psi_i/2}{\psi_i + \Delta t}, \tag{8}$$

where $\psi_i = 1/L_i(\mathbf{c}) + 1/L_i(\mathbf{c}^{\mathrm{p}})$, and c_i^{p} and c_i^{c} are the predicted and corrected concentrations, respectively.

The QSSA and hybrid methods applied to atmospheric chemistry have been compared to LSODE by Odman *et al.* (1992), who determined that the hybrid method is more robust and accurate than the QSSA scheme, even though QSSA is a faster algorithm. Because of stability problems associated with simulating day-to-night transitions (Odman, 1992), the QSSA is not a viable method to be used as the integrator in photochemical AQMs.

The critical need for ODE integration algorithms for AQMs is high efficiency while maintaining accuracy and robustness. Although the hybrid method has been proved to be a robust integration method for atmospheric chemistry, its accuracy is not

Table 1. ODE integration methods for chemical kinetics of air quality models

Method	Reference	Characteristics
LSODE	Hindmarsh (1980)	General stiff and non-stiff solver. Uses Adams methods (predictor–corrector) in the non-stiff case, and backward differentiation methods for the stiff case. Treats Jacobian matrix as a full or banded matrix. The linear systems that arise are solved by direct methods (LU factor/solve).
VODPK	Brown and Hindmarsh (1989)	General stiff and non-stiff solver. Uses Adams methods in the non-stiff case, and backward differentiation methods for the stiff case. Uses Krylov subspace iterative methods with right, left or no preconditioners and scaling.
QSSA	Hesstvedt *et al.* (1978)	Stiff solver specifically designed for chemical kinetics problems. Uses analytical characteristics of rate equations for integration. Fixed time step. Some stability problems in long-time simulations. Equations (2)–(4) in text.
Hybrid	Young and Boris (1977)	Stiff solver specifically designed for chemical kinetics problems. Uses asymptotic approximations to rate equations for integration. Variable time step. Predictor–multi-corrector algorithm. Equations (5)–(8) in text.
Extrapolation	This work	A general solver that uses Richardson extrapolation to improve accuracy over single time step solution. To solve chemical kinetics problems the algorithm proposed in this work uses a modified QSSA scheme. Equations (2)–(4) and (12)–(15) in text.

as good as one might seek. In addition, the incorporation of ever more complex chemical mechanisms and physical phenomena, such as aerosol processes, into AQMs stimulates the search for even more accurate and efficient integration methods. This paper presents a new chemical integrator for AQMs based on extrapolation techniques. The performance of the extrapolation method is compared to that of the LSODE, QSSA, and hybrid method using a test case of organic/NO_x chemistry as well as a full implementation of the method in the CIT model.

2. DESCRIPTION OF THE METHOD

Extrapolation methods, or the so-called Richardson extrapolation, consist of solving a system of ODEs repeatedly using the same scheme, but with ever decreasing time steps, and then combining the results of the solutions to obtain a result that is more accurate than any of the individual solutions (Lapidus and Seinfeld, 1971; Stoer and Burlisch, 1980). For example, in a two time step implementation, the ODEs are first solved with scheme $\mathscr{L}_h$, with time step h. This produces

$$\mathscr{L}_h\{\mathbf{c}(t)\} = \mathbf{c}(t+\Delta t; h) = \mathbf{c}(t+\Delta t) + \mathbf{R}_m(\mathbf{c})h^m + O(h^{m+1}), \quad (9)$$

where $\mathbf{c}(t+\Delta t; h)$ is the approximation of the species concentrations, $\mathbf{c}(t+\Delta t)$ is the true solution to the differential equations, m is the order of the scheme, and $\mathbf{R}_m$ and O represent the error inherent in $\mathscr{L}_h$ of order h^m and h^{m+1}, respectively. The equations are solved again with the same scheme but with a different time step k. This produces

$$\mathscr{L}_k\{\mathbf{c}(t)\} = \mathbf{c}(t+\Delta t; k) = \mathbf{c}(t+\Delta t) + \mathbf{R}_m(\mathbf{c})k^m + O(k^{m+1}). \quad (10)$$

Then, equations (9) and (10) are combined using Richardson extrapolation to yield the approximation,

$$\mathbf{c}(t+\Delta t; h, k) = \frac{k^m \mathbf{c}(t+\Delta t; h) - h^m \mathbf{c}(t+\Delta t; k)}{k^m - h^m}, \quad (11)$$

which is accurate to order $h^{m+2} + k^{m+2}$.

While any scheme can be selected as the basis for the extrapolation method, since $\mathscr{L}$ must be called at least twice, its speed is central to the efficiency of the method. We introduce here a version of the QSSA method that has been modified by including a corrector step as well as a convergence test as the basic scheme for the extrapolation method described by equations (9)–(11).

The modified QSSA first predicts the concentration of species, i, $c_i^{\mathrm{p}}(t+\Delta t; \Delta t)$ using the QSSA method, equations (2)–(4). After the prediction step is completed P, L, and $\mathrm{d}c_i/\mathrm{d}t$ are re-evaluated using the predicted concentration $c_i^{\mathrm{p}}(t+\Delta t; \Delta t)$. Then, the predicted concentrations are corrected. The correction step is introduced in QSSA to increase the robustness of the method since it has been demonstrated that in long-time simulations QSSA presents instability problems (Odman *et al.*, 1992).

The corrector step of the modified QSSA is performed in the following manner:

(a) If $L_i(\mathbf{c}^{\mathrm{p}})\Delta t < 0.01$, the equations are non-stiff and are corrected using the trapezoidal rule

$$c_i^{\mathrm{c}}(t+\Delta t; \Delta t) = c_i(t) + \left(\frac{\mathrm{d}c_i}{\mathrm{d}t} + \frac{\mathrm{d}c_i^{\mathrm{p}}}{\mathrm{d}t}\right)\frac{\Delta t}{2}. \quad (12)$$

(b) If $10 \geqslant L_i(\mathbf{c}^{\mathrm{p}})\Delta t \geqslant 0.01$, the equations are corrected using

$$c_i^{\mathrm{c}}(t+\Delta t; \Delta t) = \psi_i + (c_i(t) - \psi_i) \times \exp\left[-\left(\frac{1}{L_i(\mathbf{c})} + \frac{1}{L_i(\mathbf{c}^{\mathrm{p}})}\right)\frac{\Delta t}{2}\right]. \quad (13)$$

(c) If $10 < L_i(\mathbf{c}^{\mathrm{p}})\Delta t$, the following numerical approximation is used

$$c_i^{\mathrm{c}}(t+\Delta t; \Delta t) = \psi_i, \quad (14)$$

where

$$\psi_i = \tfrac{1}{4}(P_i(\mathbf{c}) + P_i(\mathbf{c}^{\mathrm{p}}))\left(\frac{1}{L_i(\mathbf{c})} + \frac{1}{L_i(\mathbf{c}^{\mathrm{p}})}\right). \quad (15)$$

Note that: (1) If the modified QSSA is used by itself (not as part of extrapolation) then the convergence of the corrector must be checked by assuring that $|c_i^{\mathrm{p}} - c_i^{\mathrm{c}}|/c_i^{\mathrm{c}} < \varepsilon$ for all i, where ε is a small number provided by the user. If convergence is not achieved the time step is decreased. On the other hand, if the modified QSSA is used as part of extrapolation then h and k are kept constant. (2) All the species must be determined to be stiff or non-stiff for every time step. (3) There is no steady-state assumption that requires equating first-order time derivatives of steady-state species to zero and solving the resulting nonlinear algebraic equations.

3. NUMERICAL EXPERIMENTS

In this section we compare the speed and accuracy of the extrapolation method against the LSODE, VODPK, QSSA, and hybrid algorithms. The comparison is based on two test cases: (1) a single cell simulation used by Odman *et al.* (1992) based on that of Lurmann *et al.* (1987); (2) a full implementation in the CIT model

3.1. *Single cell test*

The test case consists of simulating the 8 h photooxidation of a complex organic/NO_x mixture inside a single cell at a constant temperature, 298 K. Table 2 lists the initial mixing ratios for the cases studied. The cases differ only in the NO and NO_2 initial concentration by a factor of α so as to encompass (ROG)/NO_x ratios between 0.2 and 20.2. The photolytic reaction rates are calculated at a constant zenith angle of 0°. The modified LCC mechanism was used with the initial conditions described by Lurmann *et al.* (1987). Table 3 lists all the species in the modified LCC mechanism used. There are no emissions or deposition.

Table 2. Initial mixing ratios in parts-per-billion (ppb) for the three single cell cases

Species		Case 1 $\alpha = 1$	Case 2 $\alpha = 10$	Case 3 $\alpha = 100$
NO	$\alpha \times 7.5$; $\alpha = 1, 2, \ldots, 100$	7.5	75	750
NO_2	$\alpha \times 2.5$; $\alpha = 1, 2, \ldots, 100$	2.5	25	250
O_3	0.01	0.01	0.01	0.01
CO	1000	1000	1000	1000
HCHO	30	30	30	30
ALD2	10	10	10	10
ALKA	82.7	82.7	82.7	82.7
ETHE	15	15	15	15
ALKE	29.4	29.4	29.4	29.4
TOLU	22.9	22.9	22.9	22.9
AROM	11.9	11.9	11.9	11.9
H_2O	2×10^7	2×10^7	2×10^7	2×10^7

Table 3. Species in chemical kinetic mechanism used in this study

Species number	Species name	Species number	Species name	Species number	Species name
1	NO	13	MEK	25	CRES
2	NO_2	14	MGLY	26	NPHE
3	O_3	15	PAN	27	H_2O_2
4	HONO	16	RO_2	28	MEOH
5	HNO_3	17	MCO_3	29	NH_3
6	HNO_4	18	ALKN	30	NIT
7	N_2O_5	19	ALKA	31	ISOP
8	NO_3	20	ETHE	32	EOTH
9	HO_2	21	ALKE	33	MTBE
10	CO	22	TOLU	34	SO_2
11	HCHO	23	AROM	35	SO_3
12	ALD2	24	DIAL		

The integrators used are LSODE, VODPK, QSSA, hybrid, and extrapolation method. LSODE is called with the following error control parameters: RTOL = 1.0d-6 and ATOL = 1.0d-9. QSSA is implemented with a fixed time step of 30 s, the value suggested by Hesstvedt *et al.* (1977) as appropriate for most simulations of photochemical air pollution. The extrapolation method is implemented using the modified QSSA as the basic scheme with constant time steps of 60 and 30 s for the extrapolation. All the integrators were called at 5 min intervals.

When implementing the extrapolation method, the following two questions must be addressed: (1) How to compute the order of accuracy m? (2) How often should extrapolation be performed? We have used the following approach to address these questions. First, m is computed numerically. This is done by calling the modified QSSA scheme with a constant step of 3 s from $t = 0$ to 5 min to obtain an accurate value for c_i. The accurate value of c_i is used as the left-hand side of equation (11) to solve for m. The value of m associated with each species is then used through the simulation for the first 100 min. Since m changes slightly with time due to the fact that the degree of stiffness of the equations is also changing as the simulation progresses, at each 100 min it is recomputed. The Richardson extrapolation is performed every 5 min. This time corresponds to the time interval between integrator calls. The extrapolated values are then used as the initial conditions for the next integrator calls.

Figure 1 shows the ozone (O_3) mixing ratio in parts-per-billion (ppb) for Case 1 using the four integrators mentioned. Odman *et al.* (1992) presented similar results using the LSODE, QSSA, and hybrid methods. While the QSSA results deviate most from those obtained by LSODE, and the extrapolation results agree most closely with those of LSODE, none of the four integrators yields major differences for ozone in this particular test.

Ozone, however, is not the most sensitive indicator of the performance of an integration method for atmospheric chemistry. Rather, free radical species such as the hydroperoxyl (HO_2) and nitrate (NO_3) radicals should reflect more strongly the differences in the performance of numerical integration routines. Tables 4–6 show the maximum relative error for VODPK, QSSA, hybrid, and extrapolation methods for each of the three simulations. Tables 4–6 also show the average normalized relative error, which is the computed using the maximum relative errors for all the species during the entire time interval. It can also be noted that the performance of QSSA varies among all the cases. The accuracy of QSSA could be improved by taking smaller time steps, which would decrease the efficiency of the method. The average error of VODPK is the greatest of all the methods compared for all the cases studied. The reason for this behavior is that to obtain the best results with VODPK, one would need to implement right and/or left preconditioners. The selection of an effective preconditioner is problem dependent and there is no method that can be followed to obtain the optimum preconditioner for a given problem. The average errors presented in Tables 4–6 indicate that hybrid and extrapolation are the most accurate methods. Figure 2 shows the average error of the hybrid and

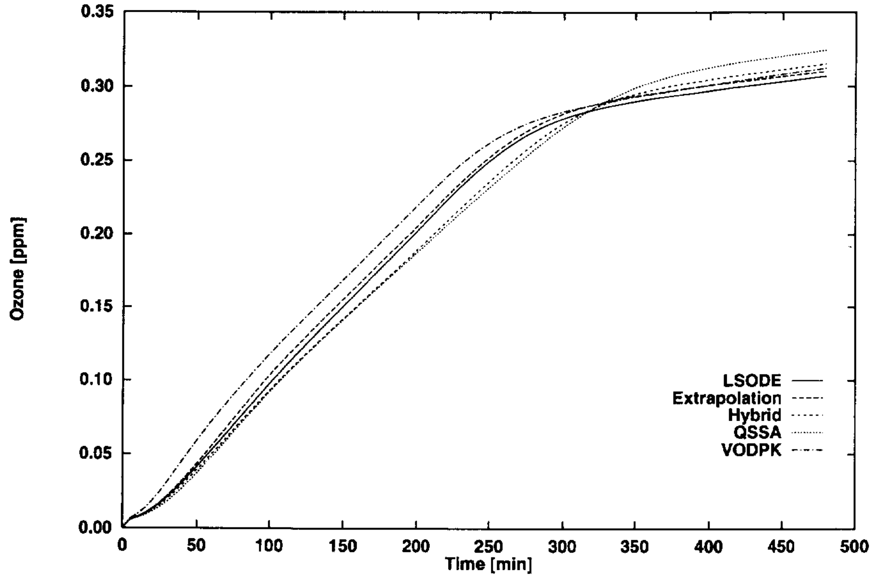

Fig. 1. Ozone mixing ratios from single cell simulation of Case 1 using LSODE, QSSA, VODPK, hybrid, and extrapolation algorithms.

Table 4. Normalized maximum error relative to LSODE for VODPK, QSSA, hybrid, and extrapolation methods for Case 1 simulation of 480 min duration

	Max error			
Species number	VODPK	QSSA	Hybrid	Extrapolation
1	0.2326	0.3817	0.0498	0.1123
2	0.4783	0.3244	0.0256	0.0430
3	0.1282	0.1737	0.0319	0.0663
4	0.4282	0.2069	0.0361	0.0310
5	0.2748	0.2801	0.0449	0.1003
6	0.4827	0.4575	0.0735	0.1588
7	0.7790	0.5999	0.1312	0.2812
8	0.5754	0.5357	0.1056	0.2181
9	0.2740	0.3433	0.0525	0.1121
10	0.0068	0.0026	0.0001	0.0003
11	0.2558	0.0420	0.0031	0.0072
12	0.5493	0.0854	0.0127	0.0289
13	0.4278	0.2036	0.0296	0.0683
14	1.3955	0.3255	0.0478	0.1091
15	0.2064	0.3422	0.0633	0.1359
16	0.4096	0.3485	0.0526	0.1136
17	0.8642	0.1391	0.0273	0.0573
18	0.5583	0.2018	0.0291	0.0673
19	0.0035	0.0330	0.0007	0.0025
20	0.1189	0.0766	0.0014	0.0057
21	0.8718	0.3465	0.0069	0.0296
22	0.0774	0.0451	0.0009	0.0034
23	0.4622	0.2770	0.0051	0.0199
24	0.2407	0.3134	0.0450	0.1044
25	0.2760	0.3210	0.0470	0.1074
26	0.1986	0.2634	0.0263	0.0643
27	0.2993	0.0492	0.0256	0.0437
28	0.0000	0.0000	0.0000	0.0000
29	0.0000	0.0000	0.0000	0.0000
30	0.0000	0.0000	0.0000	0.0000
31	0.0000	0.0000	0.0000	0.0000
32	0.0000	0.0000	0.0000	0.0000
33	0.0000	0.0000	0.0000	0.0000
34	0.0000	0.0000	0.0000	0.0000
35	0.0000	0.0000	0.0000	0.0000
Average error	0.3107	0.1920	0.0279	0.0598

Table 5. Normalized maximum error relative to LSODE for VODPK, QSSA, hybrid, and extrapolation methods for Case 2 simulation of 480 min duration

	Max error			
Species number	VODPK	QSSA	Hybrid	Extrapolation
1	0.2813	0.2879	0.0984	0.0094
2	0.3443	0.7481	0.7997	0.0798
3	0.4551	0.1849	0.0639	0.0103
4	0.3041	0.4902	0.1737	0.0512
5	0.1980	0.2122	0.0807	0.0316
6	0.8821	0.6870	0.6699	0.1019
7	1.0593	0.9037	1.6993	0.1916
8	0.6198	0.6340	0.5066	0.0819
9	0.2674	1.2471	0.3563	0.0432
10	0.0090	0.0021	0.0008	0.0007
11	0.2178	0.0765	0.0407	0.0123
12	0.7106	0.1333	0.0518	0.0140
13	0.9215	0.0803	0.0485	0.0330
14	2.3878	0.1240	0.0822	0.0409
15	0.9266	0.1701	0.0822	0.0363
16	0.5682	1.7878	0.4093	0.0577
17	0.7615	2.5013	0.4501	0.0998
18	1.1069	0.1187	0.0473	0.0340
19	0.1519	0.1159	0.0264	0.0088
20	0.1796	0.2320	0.0548	0.0166
21	0.9292	0.0945	0.0908	0.0313
22	0.1380	0.1607	0.0360	0.0120
23	0.7891	0.0774	0.1196	0.0494
24	0.4758	0.2323	0.1650	0.0538
25	0.7206	0.2159	0.1214	0.0403
26	0.1284	0.5599	0.1469	0.0358
27	0.4201	1.9260	0.5426	0.0729
28	0.0000	0.0000	0.0000	0.0000
29	0.0000	0.0000	0.0000	0.0000
30	0.0000	0.0000	0.0000	0.0000
31	0.0000	0.0000	0.0000	0.0000
32	0.0000	0.0000	0.0000	0.0000
33	0.0000	0.0000	0.0000	0.0000
34	0.0000	0.0000	0.0000	0.0000
35	0.0000	0.0000	0.0000	0.0000
Average error	0.4844	0.4001	0.1990	0.0357

extrapolation methods for 100 different mixing ratios. Except for the very first point (Case 1) the average error presented by extrapolation is smaller than hybrid algorithm.

As expected, the QSSA algorithm is the fastest of all those tested but with low accuracy. VODPK is the least accurate integrator tested. LSODE, VODPK, extrapolation, and hybrid integrators are 8.09, 5.90, 2.27, and 2.09 times slower than QSSA, respectively. These timing results for LSODE, hybrid, and QSSA agree with those reported by Odman *et al.* (1992). The hybrid and extrapolation integrators are similar in speed, however the extrapolation method is superior in accuracy for the test case studied. If a higher initial mixing ratio for ozone is used, the relative performance of the integrators is not affected.

3.2. *Three-dimensional model test*

This section describes a comparison of the extrapolation, LSODE, and hybrid methods when implemented in the three-dimensional CIT model. The QSSA integrator is not discussed further since it is unstable under the conditions tested. VODPK is not discussed further since it presented the lowest accuracy. The integrators were used in the CIT model to simulate photochemical smog in the South Coast Air Basin during the 27–28 August 1987 episode. A simulation that includes daytime and nighttime conditions tests the robustness of an integration method, since the night-to-day and day-to-night transitions lead to rapidly varying concentrations of a number of photochemically driven species. This test compares the performance of the integrators interacting with other physical phenomena present in typical air quality models.

The LSODE and hybrid integrators were implemented as described in the single cell test. The calculation of m in the extrapolation method was carried out as described previously but only for a single vertical column of the model grid. The computed value of m is then used for all columns during the length of the chemistry step specified by the model. The Richardson extrapolation is performed every 5 min as in the single cell test case described previously.

To test the accuracy of the integrators the averaged normalized absolute errors were computed:

$$\mathrm{error}_{i,x,y}(t) = \frac{|c^*_{i,x,y}(t) - c_{i,x,y}(t)|}{c^*_{i,x,y}(t)} \times 100, \qquad (16)$$

where $c^*_{i,x,y}(t)$ and $c_{i,x,y}(t)$ are the predicted concentrations of species i at vertical column located at ground-level location x, y at time t by LSODE and the integrator being tested, respectively. The average normalized error is reported, instead of the average maximum error, since some of the mixing ratios predicted are below machine accuracy.

Table 6. Normalized maximum error relative to LSODE for VODPK, QSSA, hybrid, and extrapolation methods for Case 3 simulation of 480 min duration

	Max error			
Species number	VODPK	QSSA	Hybrid	Extrapolation
1	0.0707	0.0162	0.0109	0.0074
2	0.0952	0.0324	0.0230	0.0220
3	0.1733	0.0494	0.0334	0.0290
4	0.1690	0.0288	0.0270	0.0219
5	0.2173	0.0291	0.0083	0.0045
6	0.4996	0.0564	0.0202	0.0175
7	0.4844	0.1331	0.0855	0.0767
8	0.4017	0.0971	0.0982	0.0557
9	0.4360	0.0212	0.3161	0.0065
10	0.0044	0.0002	0.0002	0.0001
11	0.0735	0.0070	0.0087	0.0075
12	0.6996	0.0041	0.0019	0.0009
13	2.2658	0.0088	0.0097	0.0081
14	2.6767	0.0142	0.0130	0.0118
15	1.1724	0.0560	0.0229	0.0121
16	0.6988	0.0245	0.1725	0.0099
17	1.0652	0.0179	0.0533	0.0120
18	1.3820	0.0144	0.0135	0.0111
19	0.0596	0.0017	0.0018	0.0015
20	0.0291	0.0026	0.0028	0.0023
21	0.8641	0.0028	0.0014	0.0007
22	0.0195	0.0023	0.0024	0.0020
23	0.6086	0.0128	0.0134	0.0107
24	0.5991	0.0159	0.0163	0.0146
25	0.8453	0.0108	0.0067	0.0049
26	1.0411	0.0134	0.0099	0.0073
27	1.0115	0.0352	0.0090	0.0057
28	0.0000	0.0000	0.0000	0.0000
29	0.0000	0.0000	0.0000	0.0000
30	0.0000	0.0000	0.0000	0.0000
31	0.0000	0.0000	0.0000	0.0000
32	0.0000	0.0000	0.0000	0.0000
33	0.0000	0.0000	0.0000	0.0000
34	0.0000	0.0000	0.0000	0.0000
35	0.0000	0.0000	0.0000	0.0000
Average error	0.5047	0.0202	0.0281	0.0104

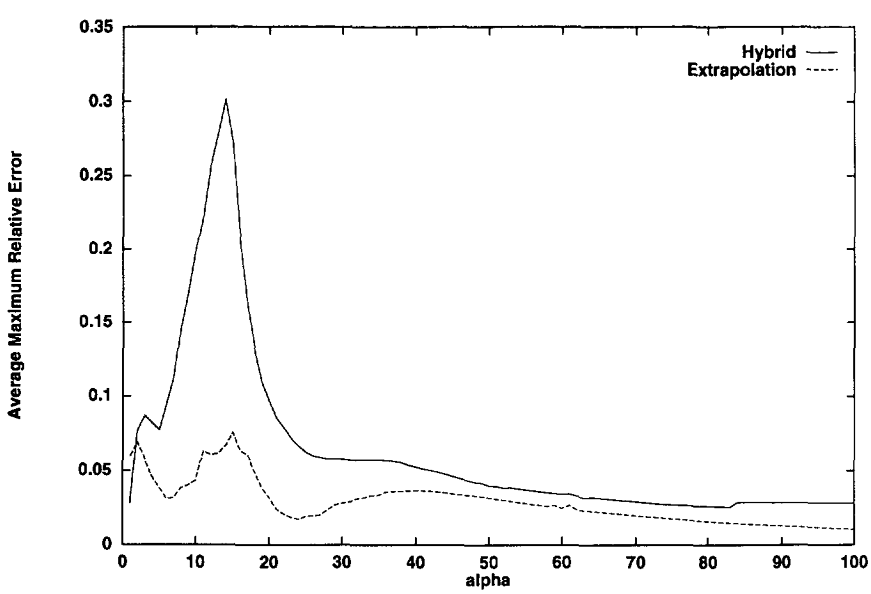

Fig. 2. Average maximum relative errors computed over all species using hybrid and extrapolation algorithms for the 100 different ROG/NO_x ratios as described in Table 2.

The error was determined for the hybrid and extrapolation integrators for each hour of a 24 h simulation averaged over all the species and columns. Both integrators produce average errors in the order of 0.005% with no noticeably greater accuracy of one algorithm over the other. Thus a typical South Coast Air Basin episode presents ROG/NO_x ratios that do not affect the performance of the integrator. Extrapolation and LSODE were 1.13 and 14.33 times slower, respectively, than the hybrid method.

4. CONCLUSION

This paper presents a new method based on Richardson extrapolation to solve the ODEs associated with chemical kinetics of reactive-flow problems, such as the atmospheric chemical mechanism of air quality models. The extrapolation method is a general technique that can be used to solve any system of ODEs using different schemes as the basis for the extrapolation procedure. The basis method selected here is a version of the QSSA method (Hesstvedt *et al.*, 1978) modified by adding a corrector step and by checking the convergence of the corrector.

Numerical experiments show that the extrapolation method consistently achieves high accuracy for wide ranges of ROG/NO_x ratios. The speed of the extrapolation methods compares to that of the hybrid method. In addition, there were no stability problems observed for the different single cell tests as well as the three-dimensional model tests. Overall the use of extrapolation methods in air pollution appears to be a promising alternative to available methods.

Acknowledgements—This work was supported in part by a grant from the IBM Environmental Research Program. Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the IBM corporation. The information in this document has been funded in part by the United States Environmental Protection Agency High Performance Computing and Communication Program under cooperative agreement CR 822051-01-0.

REFERENCES

Brown P. N. and Hindmarsh A. C. (1989) Reduced storage matrix methods in stiff ODE systems. *J. Appl. Math. Comput.* **31,** 40–91.

Byrne G. D. and Hindmarsh A. C. (1987) Stiff ODE solvers: a review of current and coming attractions. *J. Comput. Phys.* **70,** 1–62.

Byrne G. D. (1992) Pragmatic experiments with Krylov methods in the stiff ODE setting. In *Numerical ODEs* (edited by Cash J. and Duff I.). Oxford University Press, London, U.K.

Dabdub D. and Seinfeld J. H. (1994) Air quality modeling on massively parallel computers. *Atmospheric Environment* **28,** 1679–1687.

Enright W. H., Hull T. E. and Lindberg B. (1975) Comparing numerical methods for stiff systems of ODEs. *BIT* **15,** 10–48.

Gear C. W. (1971) *Numerical Initial Value Problems in Ordinary Differential Equations.* Prentice-Hall, Englewood Cliffs, New Jersey, U.S.A.

Hairer E. (1984) *Solving Ordinary Differential Equations.* Springer, New York, U.S.A.

Harley R. A., Russell A. G., McRae G. J., Cass G. R. and Seinfeld J. H. (1993) Photochemical modeling of the Southern California air quality study. *Environ. Sci. Technol.* **27,** 378–388.

Hesstvedt E., Hov Ø. and Isaksen I. S. A. (1978) Quasi-steady-state approximations in air pollution modeling: comparison of two numerical schemes for oxidant prediction. *Int. J. chem. Kinetics* **10,** 971–994.

Hindmarsh A. C. (1980) LSODE and LSODI, two new initial value ordinary differential equation solvers. *ACM-SIGNUM* **15**(4), 10–11.

Hov Ø., Zlatev Z., Berkowicz R., Eliassen A. and Prahm L. P. (1989) Comparison of numerical techniques for use in air pollution models with nonlinear chemical reactions. *Atmospheric Environment* **23,** 967–983.

Lapidus L. and Seinfeld J. H. (1971) *Numerical Solution of Ordinary Differential Equations.* Academic Press, New York, U.S.A.

Lurmann F. W., Carter W. P. L. and Coyner L. A. (1987) A surrogate species chemical reaction mechanism for urban-scale air quality simulation models. EPA No. 68-02-4104.

Morris R. E. and Myers T. C. (1990) User's guide for the Urban Airshed Model—Vol. I. User's manual for UAM (CB-IV). U.S. Environmental Protection Agency (EPA-450/4-90-007a).

Odman M. T., Kumar N. and Russell A. G. (1992) A comparison of fast chemical kinetic solvers for air-quality modeling. *Atmospheric Environment* **26,** 1783–1789.

Saylor R. D. and Fernandes R. I. (1993) On the parallelization of a comprehensive regional-scale air quality model. *Atmospheric Environment* **27A,** 625–631.

Shin W. C. and Carmichael G. R. (1992) Comprehensive air pollution modeling on a multiprocessor system. *Comput. chem. Engng* **16,** 805–815.

Stockwell W. R., Middlenton P., Chang J. S. and Tang X. (1990) The second generation regional acid deposition model chemical mechanism for regional air quality modeling. *J. geophys. Res.* **95,** 16,343–16,368.

Stoer J. and Burlisch R. (1980) *Introduction to Numerical Analysis.* Springer, New York, U.S.A.

Young T. R. and Boris J. P. (1977) A numerical technique for solving stiff ordinary differential equations associated with the chemical kinetics of reactive-flow problems. *J. phys. Chem.* **81,** 2424–2427.