9 Problem OREGO

9.1 General information

The problem consists of a stiff system of 3 non-linear Ordinary Differential Equations. The name Orego was given by Hairer & Wanner [HW96] and refers to the Oregonator model which is described by this ODE. The Oregonator model takes its name from the University of Oregon where in the 1972 Field, Körös & Noyes [FKN72] proposed this model for the Belousov–Zhabotinskii reaction. The INdAM-Bari Test Set group contributed this problem to the test set. The software part of the problem is in the file orego.f available at [MM08].

9.2 Mathematical description of the problem

The problem is of the form

$$\frac{\mathrm{d}y}{\mathrm{d}t} = f(y), \quad y(0) = y_0,$$

with

$$y \in \mathcal{R}^3, \quad 0 \le t \le 360.$$

The function f is defined by

$$f(y) = \begin{pmatrix} s(y_2 - y_1 y_2 + y_1 - q y_1^2) \\ \frac{1}{s}(-y_2 - y_1 y_2 + y_3) \\ w(y_1 - y_3) \end{pmatrix}.$$

The values of the parameters s, q and w are

$$\begin{aligned} s &= 77.27 \\ w &= 0.161 \\ q &= 8.375 \cdot 10^{-6}. \end{aligned}$$

The initial vector y_0 is given by $(1, 2, 3)^{\mathrm{T}}$.

9.3 Origin of the problem

The OREGO problem originates from the celebrated Belousov–Zhabotinskii (BZ) reaction. When certain reactans, like bromous acid, bromide ion and cerium ion, are combined, they exhibit a chemical reaction which, after an induction period of inactivity, oscillates with change in structure and in color, from red to blue and viceversa.

The color changes are caused by alternating oxidation–reductions in which the cerium switches its oxidation state from Ce(III) to Ce(IV).

Field, Körös and Noyes formulated the following model for the most important parts of the kinetic mechanism that gives rice to oscillation in the BZ reaction. This mechanism can be summarized as three concurrent processes [Gra02]:

- the reduction of bromate (BrO_3^-) to bromine (Br) via the reducing agent bromide (Br^-). Bromomalonic acid (BrMA) is produced;
- the increase of hypobromous acid ($HBrO_2$) at an accelerating rate and the production of Ce(IV). Here we have a sudden change in color from red to blue;
- the reduction of Cerium catalyst Ce(IV) to Ce(III). Here we have a gradual change in color from blue to red.

TABLE II.9.1: Reference solution at the end of the integration interval.

t	X $= y_1$	Y $= y_2$	Z $= y_3$
360	$0.1000814870318523 \cdot 10^1$	$0.1228178521549917 \cdot 10^4$	$0.1320554942846706 \cdot 10^3$

TABLE II.9.2: *Failed runs.*

solver	m	reason
VODE	2,4	error test failed repeatedly

Then, from this mechanism the following Oregonator scheme is obtained

A+Y$\rightarrow$ X+P	r=k_3AY
X+Y$\rightarrow$ 2P	r=k_2XY
A+X$\rightarrow$ 2X+2Z	r=k_5AX
2X$\rightarrow$ A+P	r=k_4X^2
B+Z$\rightarrow$ $\frac{1}{2}f$Y	r=k_cBZ

Here using the conventional notation as in [FKN72] the assignments and the effective concentration are

hypobromous acid	$[\mathrm{HBrO_2}] = X$	5.025×10^{-11}
bromide	$[\mathrm{Br}^-] = Y$	3.0×10^{-7}
cerium − 4	$[\mathrm{CE(IV)}] = Z$	2.412×10^{-8}
bromate	$[\mathrm{BrO_3^-}] = A$	
all oxidizable organic species	$[\mathrm{Org}] = B$	
	$[\mathrm{HOBr}] = P$	.

The reaction rate equations for the intermediate species X, Y, and Z are

$$
\begin{aligned}
\frac{dX}{dt} &= s\left(Y - XY + X - qX^2\right) \\
\frac{dY}{dt} &= \frac{1}{s}\left(-Y - XY + fZ\right) \\
\frac{dZ}{dt} &= w\left(X - Z\right).
\end{aligned}
$$

with $f = 1$, and s, w, and q as in the previous subsection.

9.4 Numerical solution of the problem

Tables II.9.1, II.9.3 and Figures **II.9.1–II.9.7** present the reference solution at the end of the integration interval, the run characteristics, the behavior of the solution over the integration interval and the work-precision diagrams, respectively. The reference solution was computed by RADAU on an Alphaserver DS20E, with a 667 MHz EV67 processor, using double precision `work(1) = uround` `=` $1.01 \cdot 10^{-19}$, `rtol = atol = h0 =` $1.1 \cdot 10^{-18}$, `atol = h0 =` $1.1 \cdot 10^{-40}$. For the work-precision diagrams, we used: rtol $= 10^{-(4+m/4)}$, $m = 0, 1, \ldots, 32$; atol = rtol; `h0` $= 10^{-2} \cdot$ rtol for BIMD, GAMD, MEBDFDAE, MEBDFI, RADAU and RADAU5. The failed runs are in Table II.9.2; listed are the name of the solver that failed, for which values of m this happened, and the reason for failing.

TABLE II.9.3: *Run characteristics.*

solver	rtol	atol	h0	mescd	scd	steps	accept	#f	#Jac	#LU	CPU
BIMD	10^{-4}	10^{-4}	10^{-6}	3.85	3.85	235	224	4393	215	235	0.0049
	10^{-7}	10^{-7}	10^{-9}	7.87	7.86	347	339	9629	334	347	0.0107
	10^{-10}	10^{-10}	10^{-12}	11.29	11.29	373	367	16863	359	373	0.0176
DDASSL	10^{-4}	10^{-4}		2.62	2.62	889	813	1505	124		0.0039
	10^{-7}	10^{-7}		5.58	5.57	2725	2671	4210	189		0.0137
	10^{-10}	10^{-10}		8.66	8.66	8192	8098	11119	274		0.0381
GAMD	10^{-4}	10^{-4}	10^{-6}	3.61	3.61	219	162	8510	163	219	0.0088
	10^{-7}	10^{-7}	10^{-9}	6.90	6.89	251	205	16050	208	251	0.0176
	10^{-10}	10^{-10}	10^{-12}	9.50	9.50	291	268	22034	270	291	0.0234
MEBDFI	10^{-4}	10^{-4}	10^{-6}	3.34	3.33	733	687	2707	103	103	0.0049
	10^{-7}	10^{-7}	10^{-9}	6.39	6.39	1586	1529	5399	174	174	0.0107
	10^{-10}	10^{-10}	10^{-12}	9.59	9.59	3248	3232	10754	345	345	0.0205
PSIDE-1	10^{-4}	10^{-4}		4.74	4.73	221	178	4696	128	836	0.0059
	10^{-7}	10^{-7}		7.06	7.06	441	407	9235	148	1164	0.0117
	10^{-10}	10^{-10}		10.77	10.47	1450	1412	26255	219	1788	0.0332
RADAU	10^{-4}	10^{-4}	10^{-6}	3.42	3.12	268	222	3416	200	267	0.0029
	10^{-7}	10^{-7}	10^{-9}	7.48	7.48	267	216	6859	192	265	0.0059
	10^{-10}	10^{-10}	10^{-12}	9.83	9.82	261	202	12917	176	257	0.0098
VODE	10^{-4}	10^{-4}		2.15	2.15	1196	1101	1820	38	236	0.0049
	10^{-7}	10^{-7}		4.73	4.73	3083	2858	4348	64	454	0.0117
	10^{-10}	10^{-10}		7.51	7.51	7890	7430	9903	133	970	0.0293

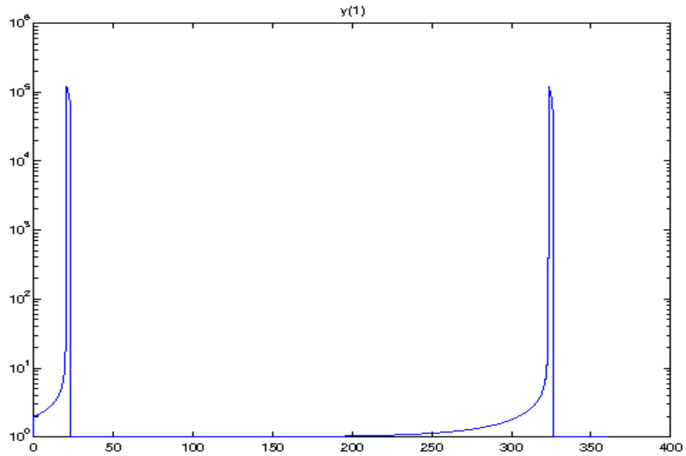

FIGURE II.9.1: Behavior of the solution component y_1 over the integration interval

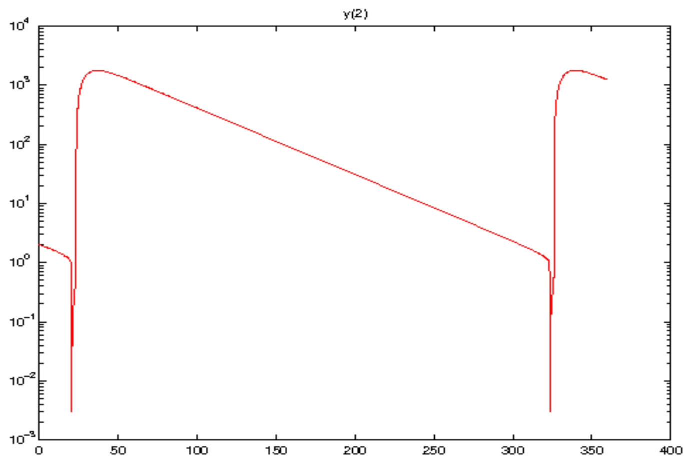

FIGURE II.9.2: Behavior of the solution component y_2 over the integration interval

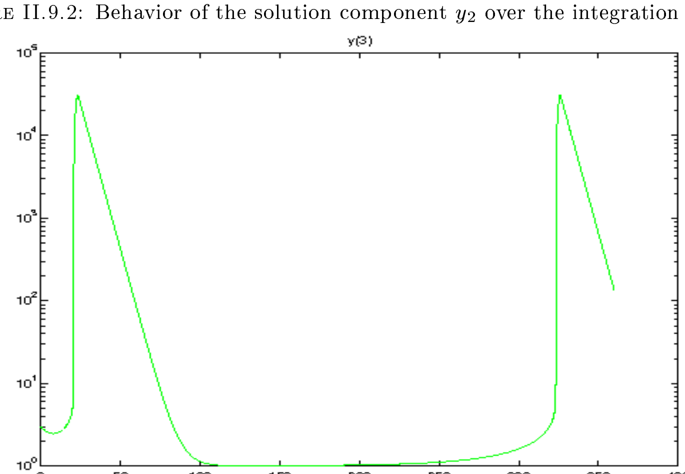

FIGURE II.9.3: Behavior of the solution component y_3 over the integration interval

References

[FKN72] R. J. Field, E. Körös, and R.M Noyes. Oscillation in chemical systems, part. 2. thorough analysis of temporal oscillations in the bromate–cerium–malonic acid system. *Journal of the American Society*, 94:8649–8664, 1972.

[Gra02] C. Gray. An analysis of the Belousov-Zhabotinskii reaction. *Rose-Hulman Undergraduate Mathematics Journal*, 3(1), 2002. http://www.rose-hulman.edu/mathjournal/.

[HW96] E. Hairer and G. Wanner. *Solving Ordinary Differential Equations II: Stiff and Differential-algebraic Problems*. Springer-Verlag, second revised edition, 1996.

[MM08] F. Mazzia and C. Magherini. *Test Set for Initial Value Problem Solvers, release 2.4*. Department of Mathematics, University of Bari and INdAM, Research Unit of Bari, February 2008. Available at http://www.dm.uniba.it/~testset.

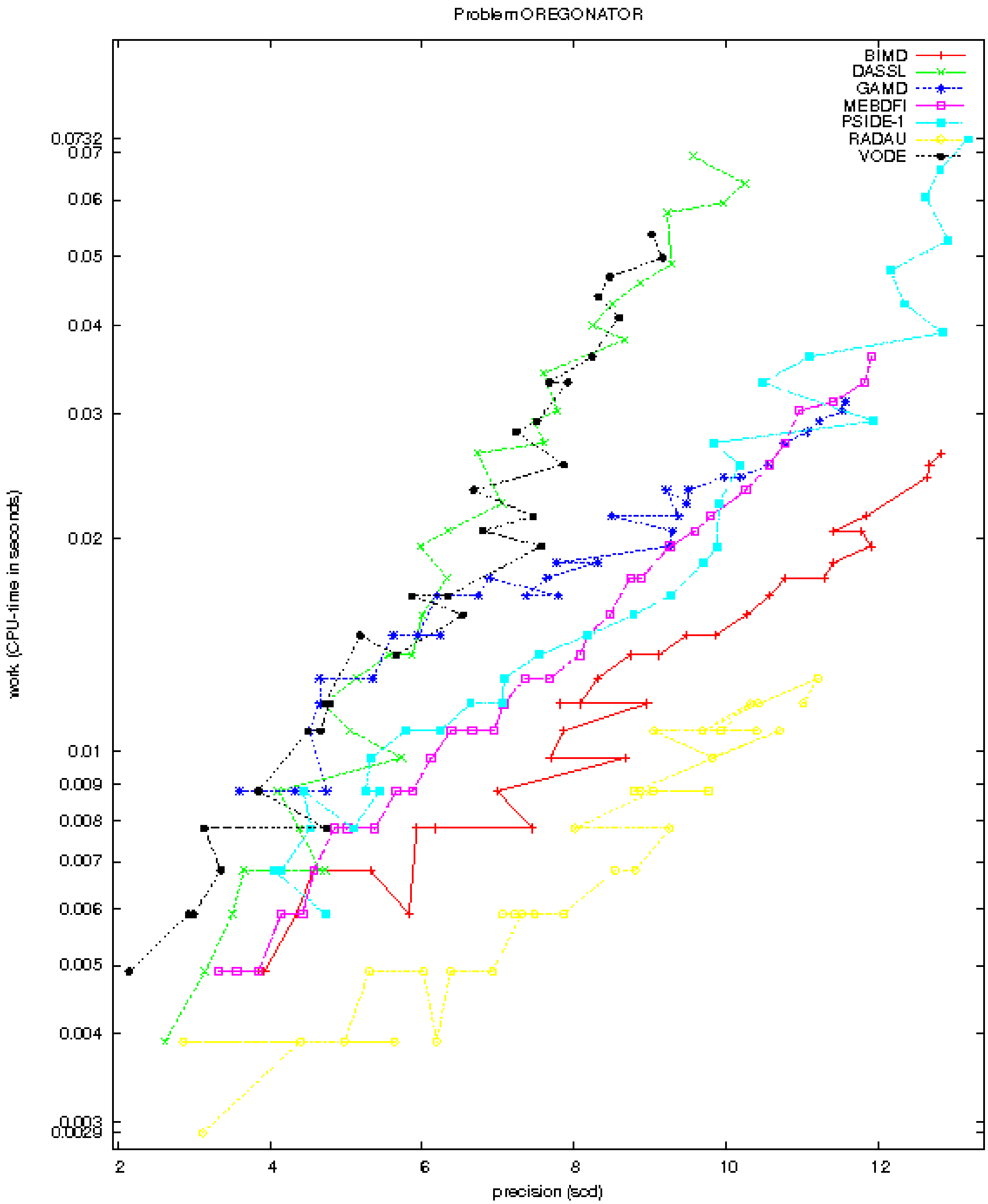

FIGURE II.9.4: *Work-precision diagram (scd versus CPU-time).*

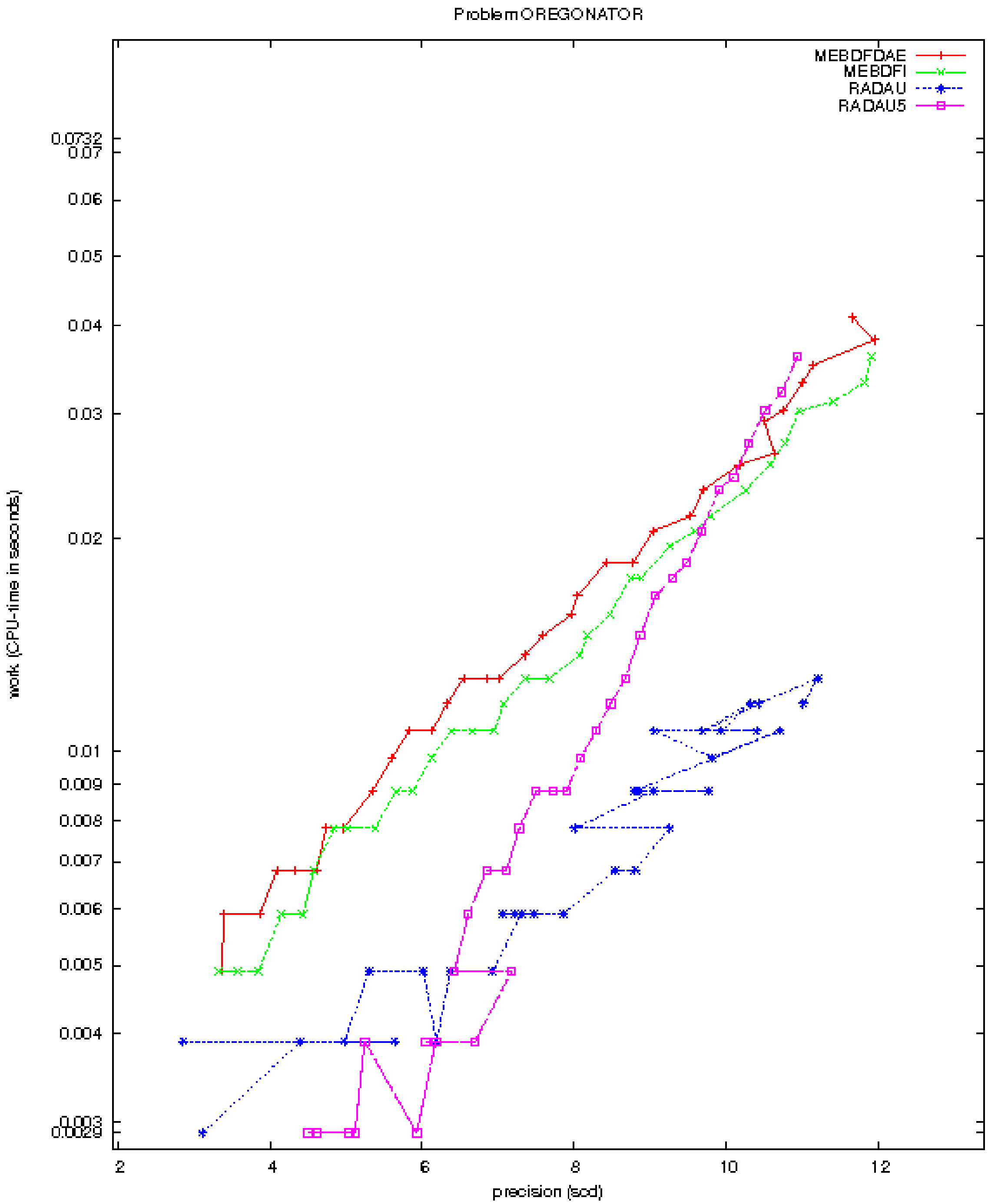

FIGURE II.9.5: *Work-precision diagram (scd versus CPU-time).*

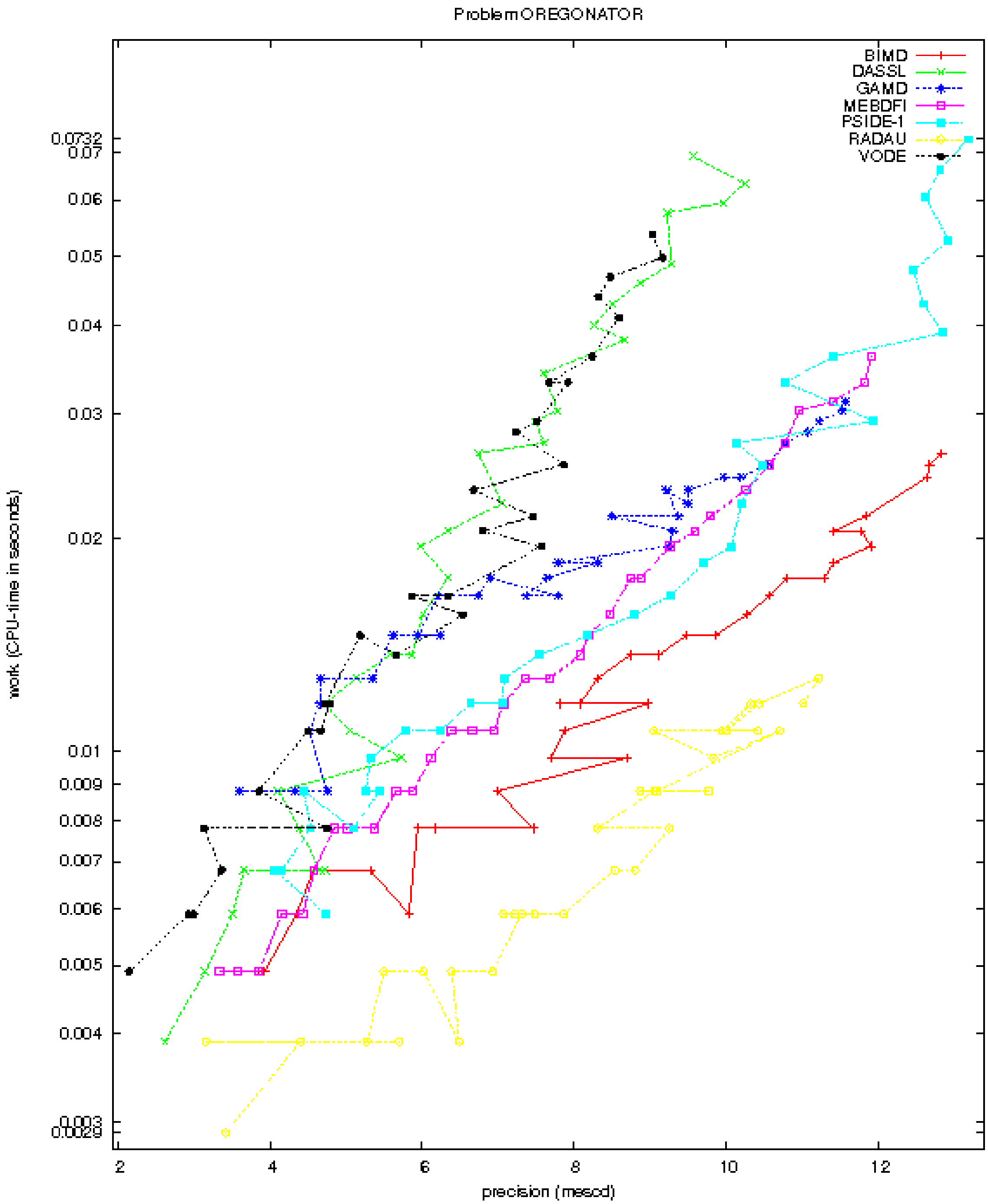

FIGURE II.9.6: *Work-precision diagram (mescd versus CPU-time).*

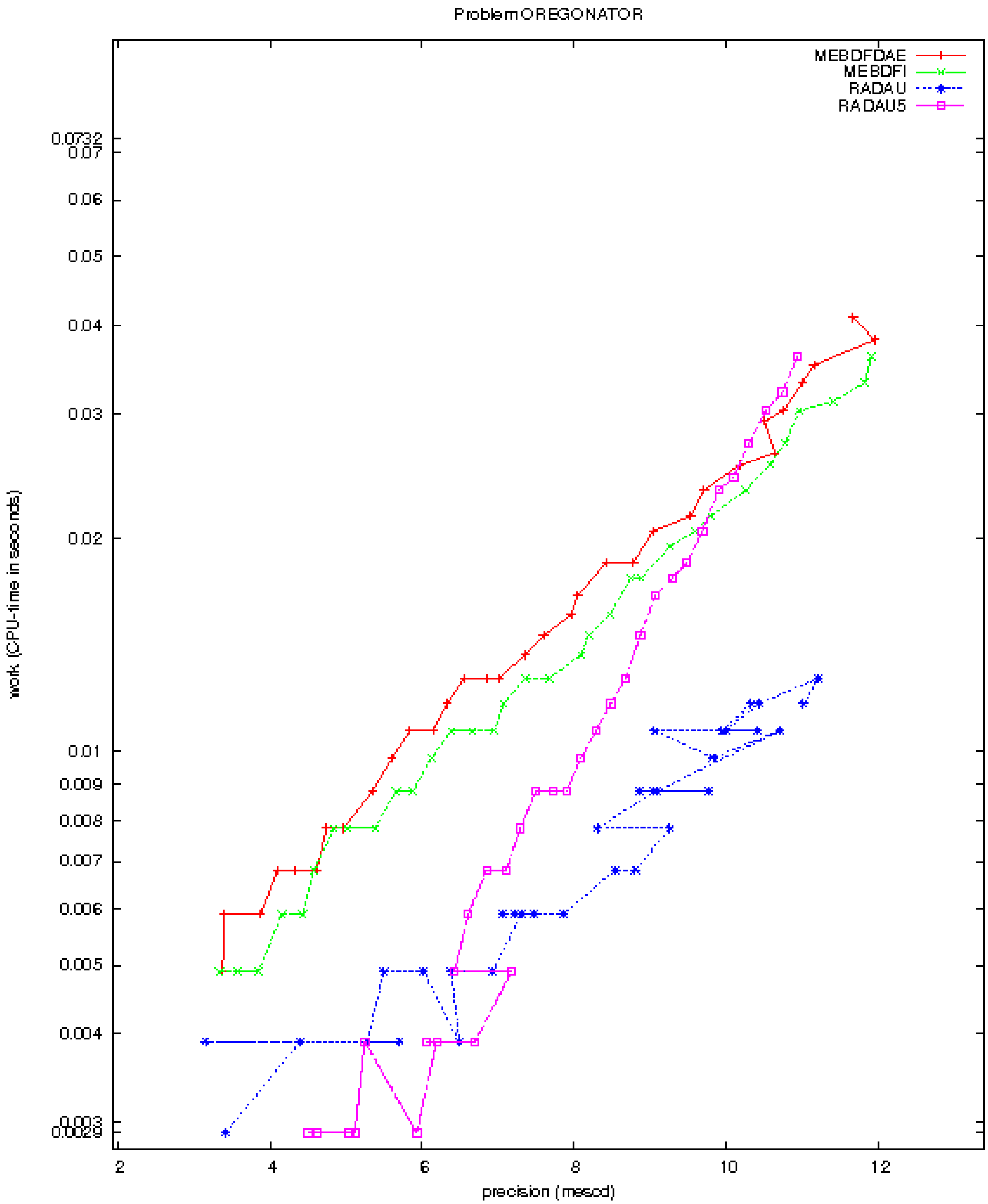

FIGURE II.9.7: *Work-precision diagram (mescd versus CPU-time).*