

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 [MI03].

9.2 Mathematical description of the problem

The problem is of the form

$$\frac{dy}{dt} = f(y), \quad y(0) = y_0,$$

with

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

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 $(1, 2, 3)^T$.

9.3 Origin of the problem

The OREGO problem originates from the celebrated Belousov–Zhabotinskii (BZ) reaction. When certain reactants, 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 rise 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	$0.100081487031852 \cdot 10^1$	$0.122817852154988 \cdot 10^4$	$0.132055494284651 \cdot 10^3$

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

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

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

hypobromous acid	$[\text{HBrO}_2] = X$	5.025×10^{-11}
bromide	$[\text{Br}^-] = Y$	3.0×10^{-7}
cerium - 4	$[\text{CE(IV)}] = Z$	2.412×10^{-8}
bromate	$[\text{BrO}_3^-] = A$	
all oxidizable organic species	$[\text{Org}] = B$	
	$[\text{HOBr}] = P$	

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

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

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 · 10-19`, `rtol = atol = h0 = 1.1 · 10-18`, `atol = h0 = 1.1 · 10-40`. For the work-precision diagrams, we used: `rtol = 10-(4+m/4)`, $m = 0, 1, \dots, 32$; `atol = rtol`; `h0 = 10-2 · rtol` for 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.

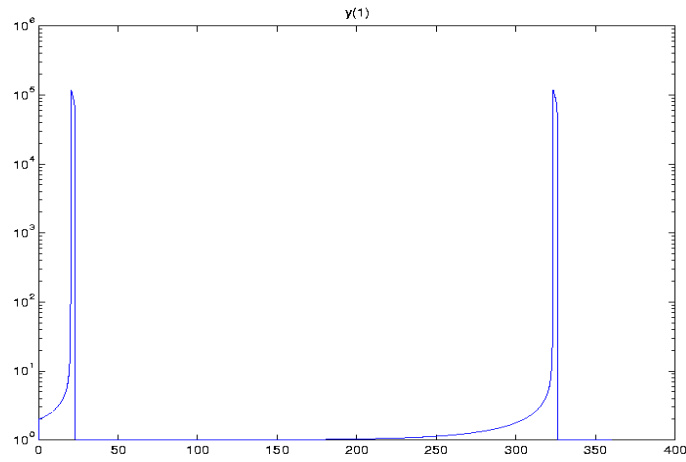


FIGURE II.9.1: Behavior of the solution component y_1 over the integration interval

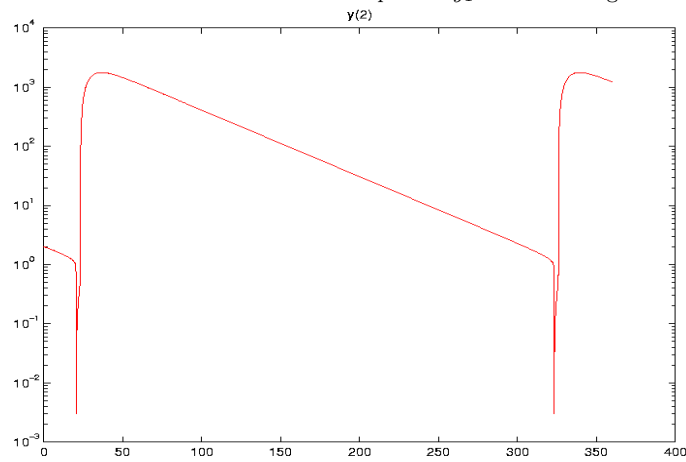


FIGURE II.9.2: Behavior of the solution component y_2 over the integration interval

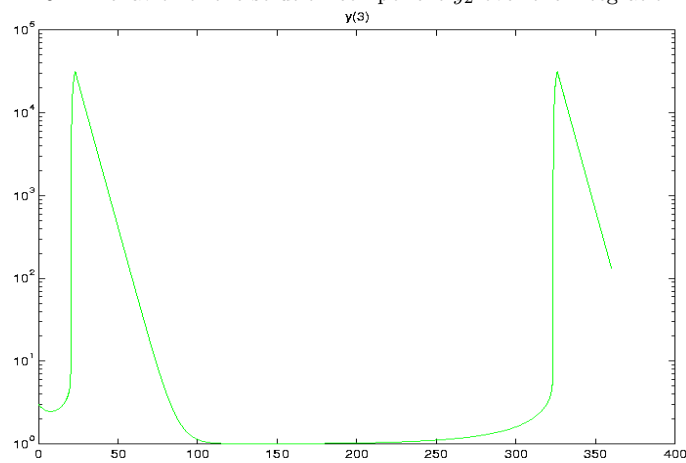


FIGURE II.9.3: Behavior of the solution component y_3 over the integration interval

TABLE II.9.3: Run characteristics.

solver	rtol	atol	h0	mescd	scd	steps	accept	#f	#Jac	#LU	CPU
DASSL	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}	3.72	3.71	219	163	8574	174	219	0.0088
	10^{-7}	10^{-7}	10^{-9}	7.02	7.02	248	203	16177	224	248	0.0176
	10^{-10}	10^{-10}	10^{-12}	9.44	9.44	288	268	21443	285	288	0.0234
MEBDFI	10^{-4}	10^{-4}	10^{-6}	3.34	3.33	733	687	2707	103	103	0.0059
	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	0.0224
PSIDE-1	10^{-4}	10^{-4}		4.74	4.73	221	178	4696	128	836	0.0068
	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	0.0117
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

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.
- [MI03] F. Mazzia and F. Iavernaro. *Test Set for Initial Value Problem Solvers*. Department of Mathematics, University of Bari, August 2003. Available at <http://www.dm.uniba.it/~testset>.

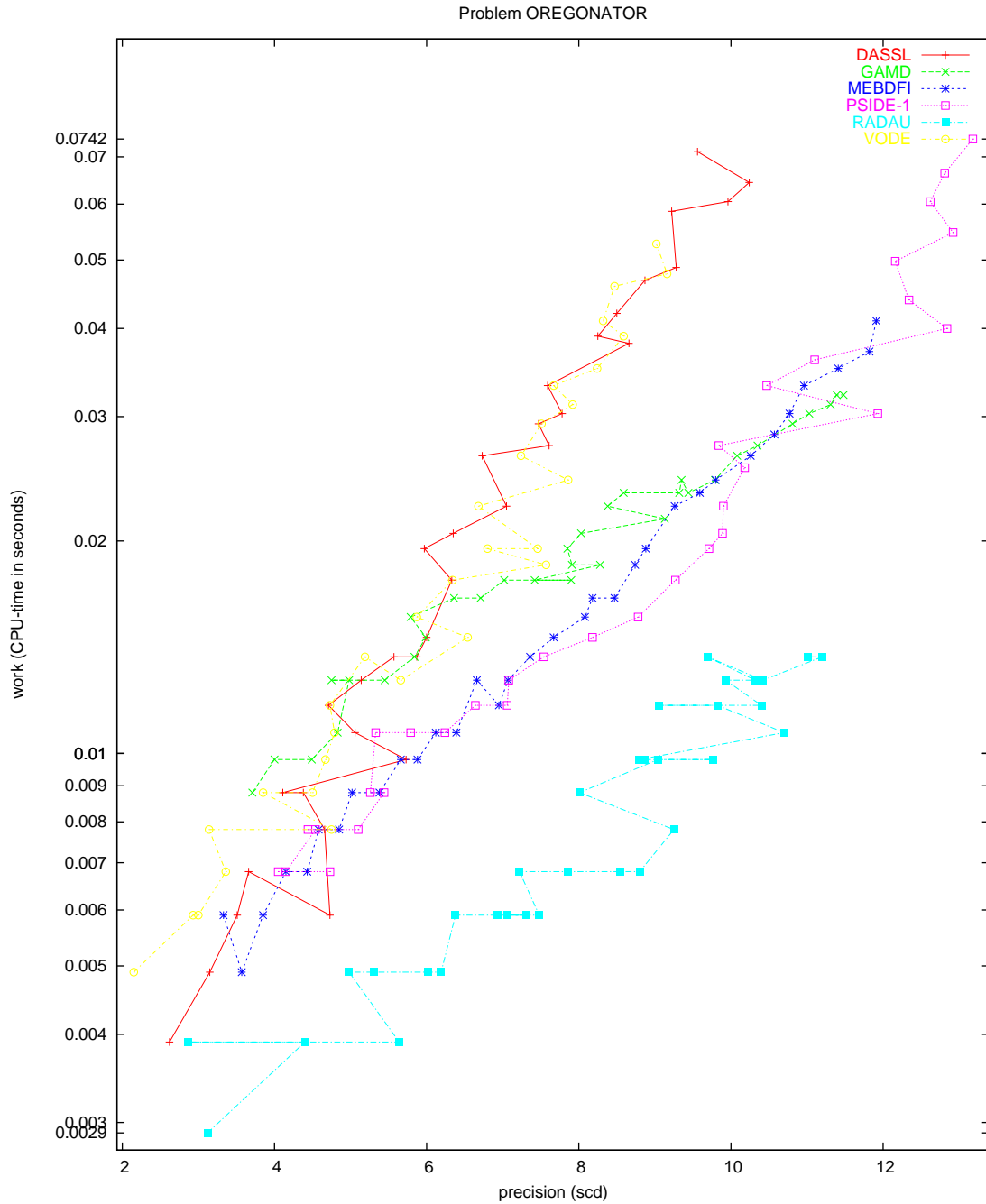


FIGURE II.9.4: Work-precision diagram (scd versus CPU-time).

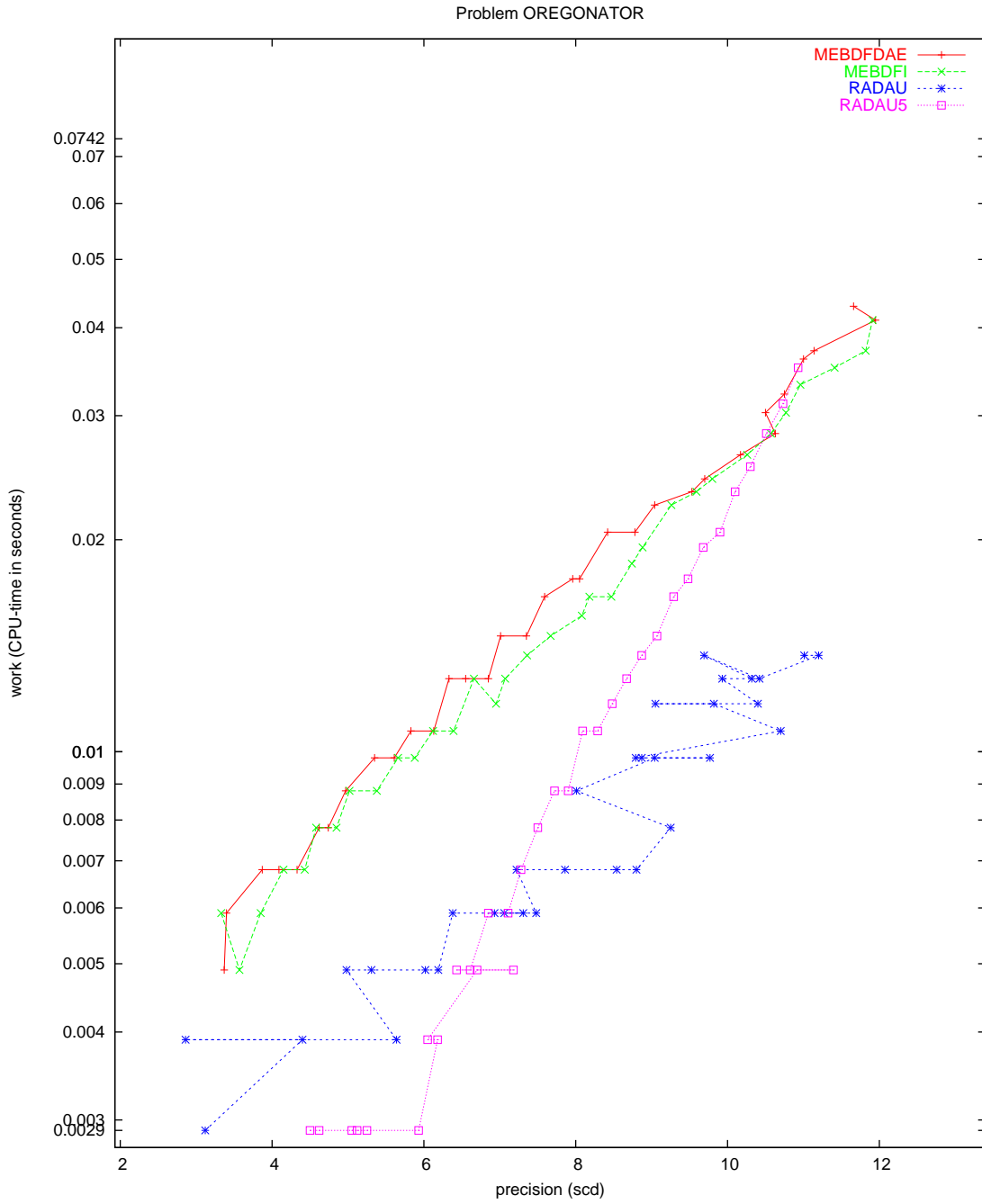


FIGURE II.9.5: Work-precision diagram (scd versus CPU-time).

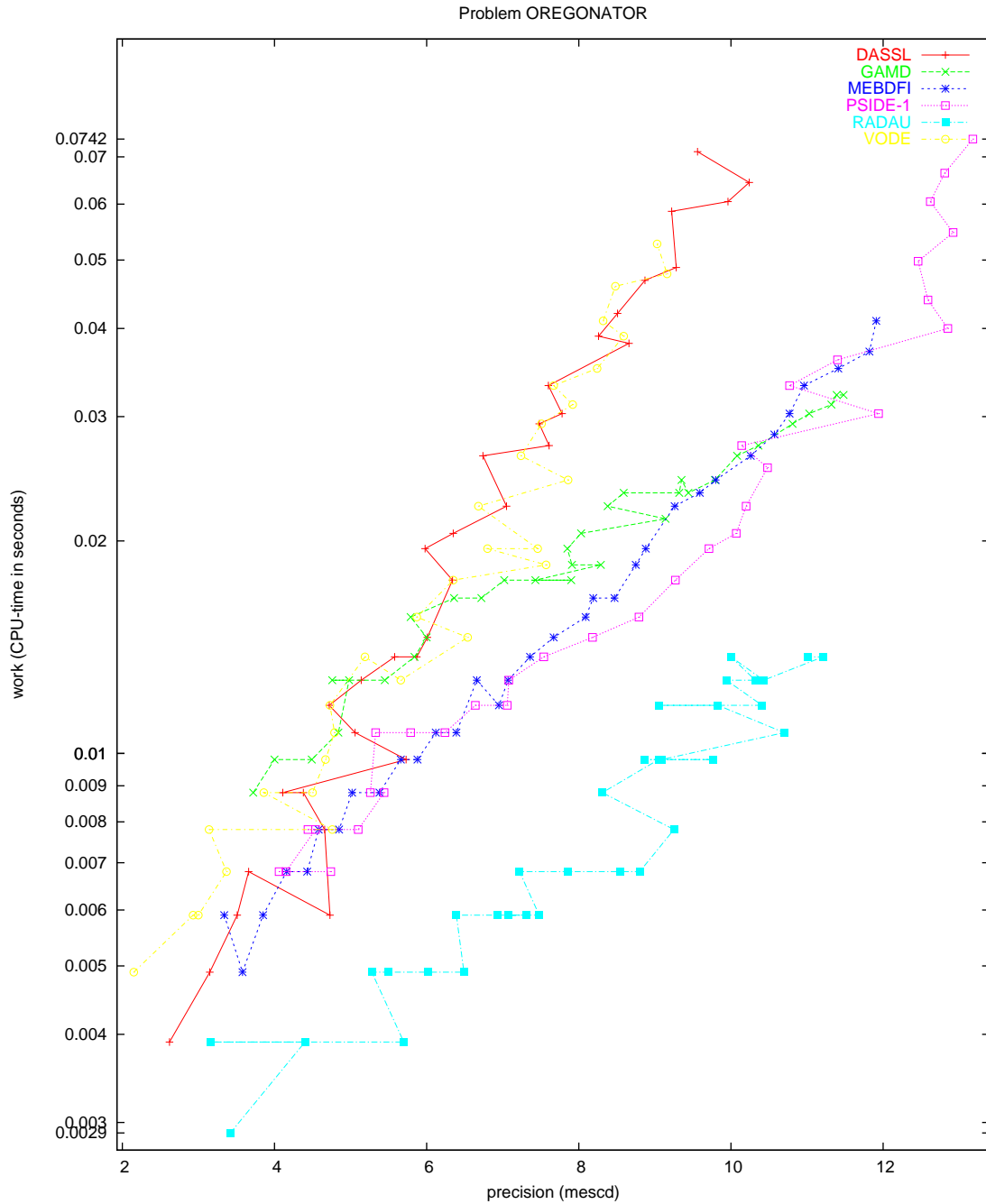


FIGURE II.9.6: Work-precision diagram (mescd versus CPU-time).

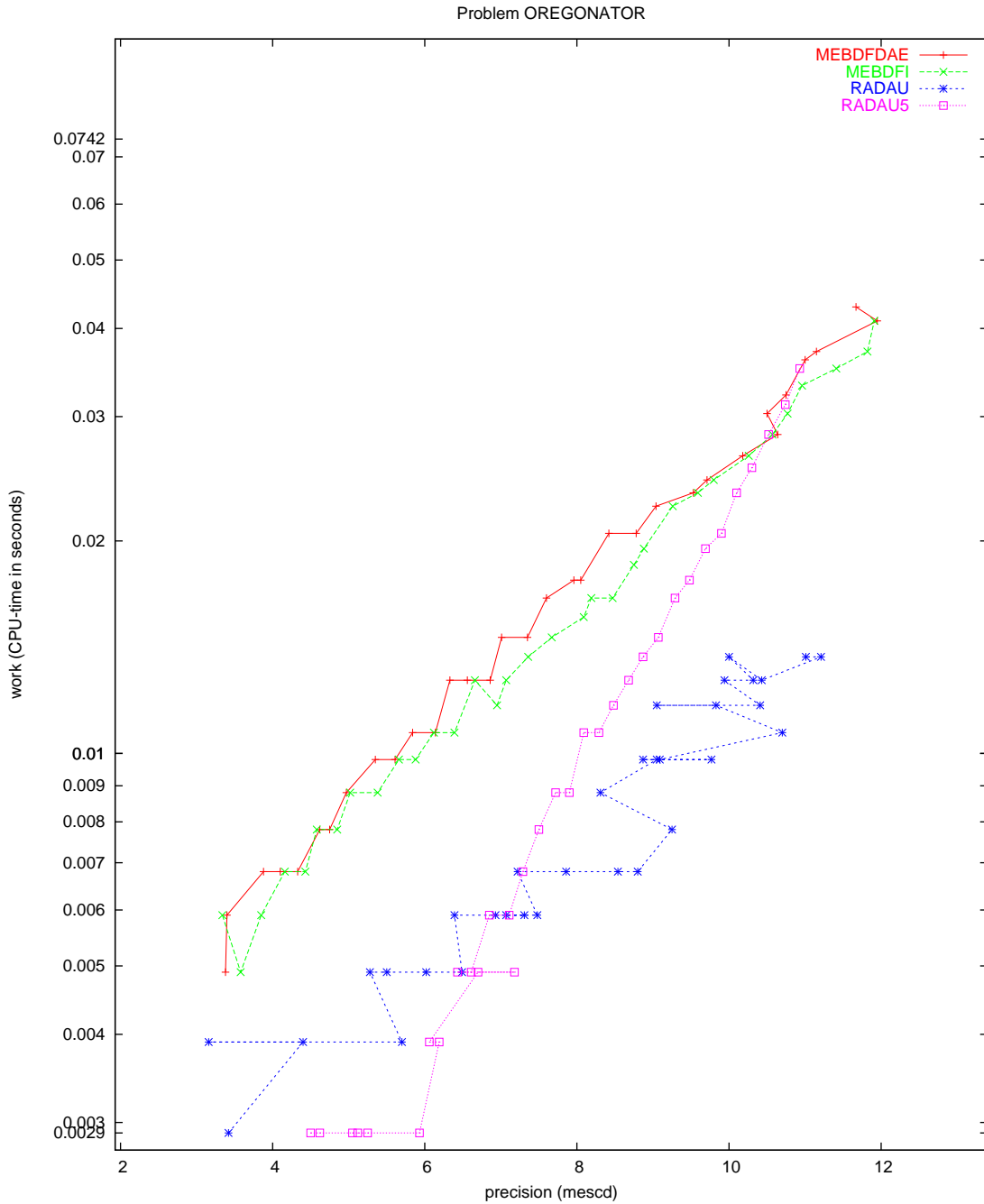


FIGURE II.9.7: Work-precision diagram (mescd versus CPU-time).