Appl. Phys. B 37, 151–157 (1985)

Applied Physics B Photophysics and Laser Chemistry

Laser Dye Stability, Part 10. Effects of DABCO on Flashlamp Pumping of Coumarin Dyes

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Received 3 December 1984/Accepted 17 February 1985

Abstract. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was tested as a flashlamp-pumped laser lifetime-extender with a variety of coumarin dyes and solvents under both air and argon. In a few cases, DABCO could be considered to have extended the lifetime as much as threefold; however, the selection of the appropriate cover gas and/or solvent could often yield a much greater improvement in the absence of DABCO. In general, DABCO was not found to be very valuable as a lifetime-extender. Furthermore, under some conditions DABCO was found to markedly reduce the laser lifetime and output.

PACS: 78,60, 61.8, 82.50

Von Trebra and Koch [1, 2] have reported that the compound 1,4-diazabicyclo[2.2.2]octane (DABCO) increases the laser lifetime of a variety of coumarin dyes. They hypothesized that since DABCO has been shown to be an efficient electron transfer quencher of singlet oxygen, it might be effective in increasing the laser lifetime in dye solutions that were in equilibrium with air. However, since they found that DABCO was also effective, to a lesser extent, in stabilizing oxygen degassed dye solutions, they also hypothesized that DABCO quenched a reactive excited state of coumarin (most likely the triplet state). Table 1 shows a matrix of the conditions in [1] which were reported using coumarin dyes.

For the laser-pumped work, Von Trebra and Koch used dye solutions at 5×10^{-3} M; for the flashlamp results they used 1.6×10^{-4} M [1]. They reported that DABCO at 0.01 M made little effect upon the magnitude of the laser output and did not affect the spectral line width or the laser pulse width [1]. The improvements in lifetime that they reported was threefold for the laser output above 90% of the initial value.

In a separate study, the rate of photobleaching of oxazole dyes using 366 nm radiation has been reported to be reduced by the presence of 0.05 M DABCO under air equilibrated conditions [3]. Photobleaching is an important consideration to the usefulness of laser dyes, but it is not of primary concern; the absorption of photoproducts that absorb at wavelengths of lasing are much more critical [4, 5]. If photobleaching was all that occurred, it would be a simple matter to add more dye to a spent solution and resume laser action [6].

The total amount of pump energy to the flashlamp of a laser for a given volume of dye solution, *T*, can be

Table 1. Conditions previously reported for lifetime effects of DABCO [1]

Dye	Solvent	Under air	Under argon	N_2 Laser pumped	Flashlamp pumped
Coumarin 1	Ethanol	✓	✓	✓	
Coumarin 120	Ethanol	✓		✓	
Coumarin 311	Ethanol	✓		✓	
Coumarin 314	Methanol/water	✓			✓

related to a decreasing laser output, ϕ, by the relationship [7],

$$T=\sum_{1}^{n} I/V=\frac{D}{c}\frac{(I-t_0)}{[I(1-D)+Dt_0]} \quad [\mathrm{Jdm}^{-3}], \tag{1}$$

where n is the number of flashes of the lamp, I is the electrical input energy per flash to the flashlamp in Joules, V is the volume of circulating dye solution in dm^3, t_0 is the initial lasing threshold in Joules, $1/c$ is the lifetime constant in Jdm^{-3}, and D is the fraction of degradation of the laser output, ϕ, from its initial value ϕ_0, i.e.,

$$D=(\phi_0-\phi)/\phi_0 . \tag{2}$$

From (1) it can be seen that the initial threshold of lasing, t_0, is also crucial to the number of laser pulses that can be obtained before the laser output has dropped a specific amount. Unfortunately, Von Trebra and Koch did not report lasing threshold values in [1, 2] and only made qualitative evaluations of lifetimes.

1. Experimental

1.1. Equipment and Materials

A Cary Model 14 was used to determine the absorbance of new and spent dye solutions. A wavelength and intensity corrected linear flashlamp and triaxial dye laser were used to degrade the dye solution as reported in [8]. The only changes in this equipment was the use of circulating $1\,\mathrm{g\,dm}^{-3}$ of caffeine in distilled water (and a quartz tube) in the triaxial dye laser as a uv filter instead of pyrex [9]. The linear degradation lamp continues to use pyrex as a uv cut-off filter. DABCO was obtained from Aldrich Chemical Co. and was sublimed at 25 Torr and 100–110 °C. Except for traces of water, different samples of DABCO showed the same NMR spectrum. The dyes were laser grade from Exciton Chemical Co., Eastman Kodak Co., or prepared in this laboratory (AC3F) [10]. Mixtures of alcohol and water (Milli-Q grade) were prepared 50:50 by volume. Unless noted otherwise, the dye solutions were continuously pumped through a 0.5 µm Fluoropore filter before going through the heat exchangers and the laser head. The volume of solution used was $0.55\,\mathrm{dm}^3$.

1.2. Results

Table 2 compares the values of the lifetime constants $1/c$ with and without DABCO for all of the dyes examined except Exciton Coumarin 504 (Eastman Kodak 314). Table 3 compares Coumarin 504 in a variety of alcohol/water solvents with and without DABCO. Table 4 presents lifetime data for Coumarin 504 in the alcohols alone. Also determined in Tables 2 through 4 are the number of laser flashes that would be 90% or higher of the original value (D = 0.1) for one liter of dye solution using a 40-J input flash as

Table 2. Effect of 0.01 M DABCO on dye laser lifetime constants

Dye	Solvent	Cover gas	Without DABCO			With DABCO		
			$1/c$ [MJdm^{-3}]	t_0 [J]	$N\times10^{-3}$, [dm^{-3}] ($I=40$ J)[a]	$1/c$ [MJdm^{-3}]	t_0 [J]	$N\times10^{-3}$, [dm^{-3}] ($I=40$ J)[a]
Coum 120	Ethanol	Air	0.4	35.0	0.1	1.2	35.0	0.4
Coum 120	Ethanol	Argon	10.0	34.0	3.8	5.5	25.0	5.4
Coum 339	Ethanol/water	Air	–	–	–	4.3	21.0	5.4
Coum 339	Ethanol/water	Air	2.3[b]	26.0	2.1	3.2[b]	28.0	2.5
Coum 339	Ethanol/water	Argon	6.6[b]	28.0	5.1	3.6[b]	29.0	2.5
Coum 339	Ethanol	Air	0.5	32.0	0.3	0.8	33.0	0.4
Coum 339	Ethanol	Argon	15.0	30.0	9.6	13.0	30.0	8.3
Coum 1	Ethanol	Air	1.6	33.0	0.7	1.8	31.0	1.0
Coum 1	Ethanol	Argon	51.0	37.0	9.6	56.0	31.0	32.2
Coum 311	Ethanol	Air	1.9	37.0	0.4	1.8	31.0	1.0
Coum 311	Ethanol	Argon	35.0	36.0	8.8	36.0	28.0	27.8
LD490	Ethanol	Air	4.3	23.0	4.7	4.0	22.0	4.7
AC3F	Ethanol	Air	65.0	24.0	67.7	69.0	27.0	58.0
AC3F	Toluene[c]	Air	1.8	30.0	1.2	0.6	38.0	0.1
AC3F	Toluene[c]	Argon	11.8	26.0	10.6	17.3	32.0	8.8

[a] N is the number of laser pulses until a 10% drop in initial output calculated from (1) for an input energy of 40 J

[b] Using Millipore filter rather than Fluoropore

[c] Lases 452–480 nm

Table 3. Effect on lifetime constants of Coumarin 504 at 1×10^{-4} M by 0.01 M DABCO and cover gases using 50:50 by volume of alcohol/water as a solvent

Without DABCO			With DABCO		
$1/c$ [MJdm^{-3}]	t_0 [J]	$N \times 10^{-3}$, [dm^{-3}] ($I = 40$ J)	$1/c$ [MJdm^{-3}]	t_0 [J]	$N \times 10^{-3}$, [dm^{-3}] ($I = 40$ J)
Methanol/water under air					
26.0^{a}	21.8	30.1	1.9^{a}	20.4	2.4
19.0^{a}	18.5	27.0	1.9^{a}	21.0	2.4
25.0	20.0	32.9	19.0	19.9	25.1
–	–	–	27.0^{b}	20.3	35.0
Methanol/water under argon					
11.0^{a}	21.6	13.3	18.0^{a}	22.1	21.0
9.3^{a}	19.3	12.7	19.0^{a}	22.6	21.6
15.0	19.2	20.6	23.0	19.6	30.9
Ethanol/water under air					
31.0^{a}	21.6	37.4	21.0^{a}	19.8	27.9
Ethanol/water under argon					
9.8	21.2	12.1	–	–	–

[a] Using Millipore filter rather than Fluoropore
[b] Using 0.02 M DABCO

Table 4. Lifetime constants of Coumarin 504 at 1×10^{-4} M in alcohols

Solvent	Cover gas	$1/c$ [MJdm^{-3}]	t_0 [J]	$N \times 10^{-3}$, [dm^{-3}] ($I = 40$ J)
Ethanol	Air	2.8	19.8	3.7
Ethanol	Argon	1.6	17.3	2.4
Methanol^{a}	Air	2.9	19.9	3.8
Methanol^{a}	Argon	2.2	17.8	3.2
Methanol	Air	4.0	19.3	5.4

[a] Coumarin 504 at 2×10^{-4} M

calculated from (1). The number of laser pulses for a 10% degradation were calculated since this was the criterion selected by Von Trebra and Koch [1, 2].

2. Discussion

2.1. *Laser-Pumped Versus Flashlamp-Pumped*

To add a chemical to a dye solution so as to increase the lifetime of the laser operation without decreasing the laser output is an exciting goal. A dependence upon the experimental conditions would be expected for such a chemical improvement in laser lifetime. For example, the high concentrations of dye required for laser pumping has been suggested as a factor limiting the anticipated increase in dye solution lifetime where radical chain transfer agents are used to extend dye solution lifetimes [11]. Where the long-lived triplet-state molecules play an important factor in laser dye stability, the short nanosecond-long pulses provided by nitrogen and excimer lasers would be expected to lead to different chemical lifetime effects than would the microsecond-long pulses provided by flashlamps. Thus, only the single flashlamp-pumped run for Coumarin 504 in methanol/water under air by Von Trebra and Koch could be considered as evidence for an increase in flashlamp-pumped laser lifetime [1]. Their data for other dyes would be of interest, but might not be applicable for the lower concentrations and longer pumping pulses used in flashlamp applications.

2.2. *Exciton Coumarin 504 (Eastman Coumarin 314)*

In 50:50 alcohol/water, the single test shown by Von Trebra and Koch for increased lifetime of Coumarin 504 with DABCO in 50:50 methanol/water shows a nontypical rise in laser output starting from a low initial output compared to the results with no DABCO present, i.e., the presence of DABCO shows a 43% reduction in the initial laser output. The failure to have monotonically decreasing dye laser outputs have been noted previously [5]. Fig. 1 and 2 show Coumarin 504 without and with DABCO at four different input energies (I = 20, 25, 30, 35 J). We also find a reduction in laser output for Coumarin 504 in the presence of DABCO, but our slope efficiency is only 4% less (the lasing thresholds are about the same) rather than the 43% reduction shown by Von Trebra and Koch [1, 2]. Instead of causing an improvement in lifetime, how-

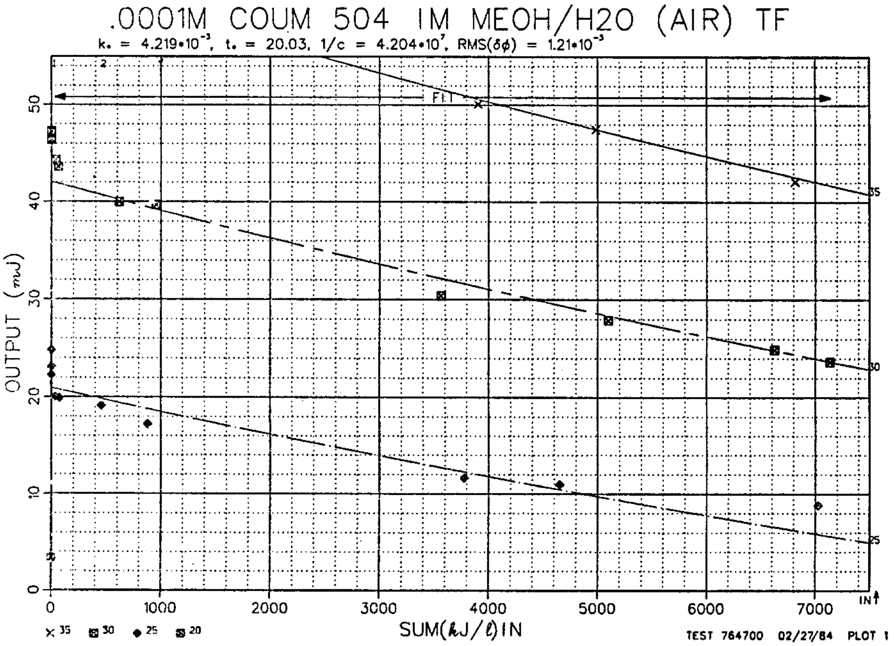

Fig. 1. Laser test of Coumarin 504 without DABCO. Test 7647 using Fluoropore filters

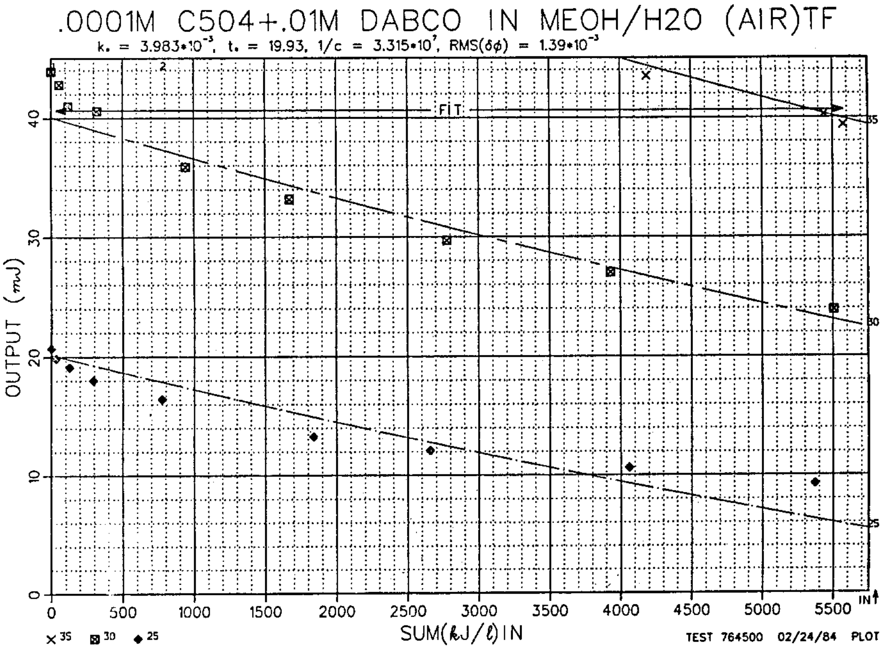

Fig. 2. Laser test of Coumarin 504 with 0.01 M DABCO. Test 7645 using Fluoropore filters

ever, as reported by Von Tebra and Koch, the data, as shown in Table 3 and Figs. 1 and 2, indicates that the presence of DABCO causes a 40% reduction of dye laser lifetime.

The results shown in Fig. 3 were obtained after doubling the DABCO concentration to 0.02 M [12]. The lifetime is increased over that found for 0.01 M, but is still only comparable to that found for no DABCO (Table 3). It should be noted that the lifetime constants $1/c$ found in Figs. 1–3 should be multiplied by 0.58, the optical factor, in order to agree with the results shown in Table 3. The optical factor compensates for variation in the output of the degradation flashlamp [8].

Some of the results in Table 3 were obtained using Millipore filters which are composed of mixed cellulose esters of acetate and nitrate. In methanol/water, in the presence of DABCO under air, these filters were observably physically degraded by the end of the test. The lifetime constants reflect this physical degradation in that they are only 1/10th as large as the values

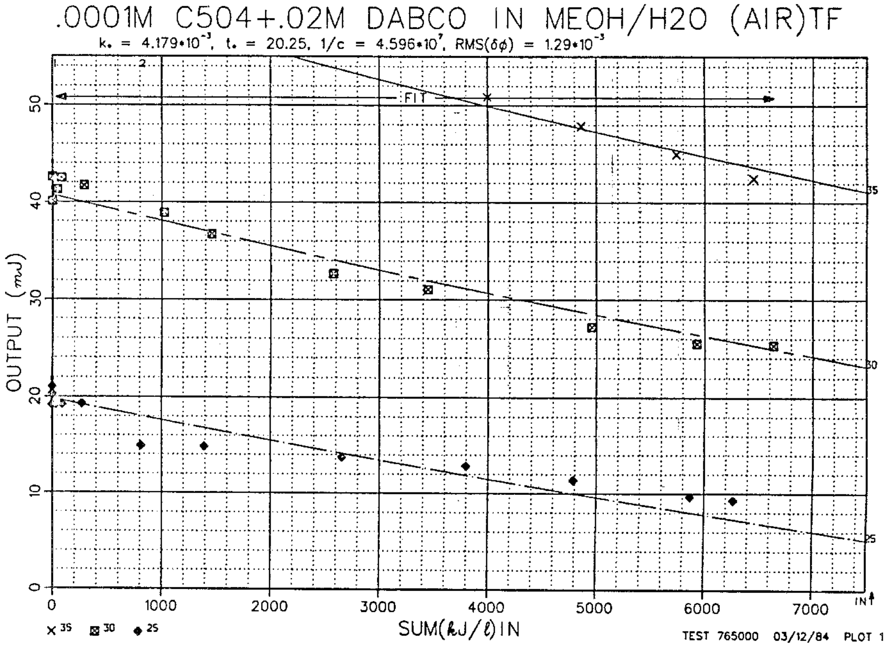

Fig. 3. Laser test of Coumarin 504 with 0.02 M DABCO. Test 7650 using Fluoropore filters

obtained using Fluoropore filters. Tests on Coumarin 504 using the Millipore composition with methanol/water under argon with DABCO, on the other hand, or using ethanol/water under air or argon with DABCO, did not appear to have the same level of filter and laser lifetime degradation as found for methanol/water with DABCO under air.

The results for the lifetime of Coumarin 504 under argon does show a twofold increase due to the effects of DABCO. However, the lifetime under argon without DABCO is about half that observed under air. Thus, there is no advantage in using DABCO under argon as compared to using the simpler system of Coumarin 504 under air without DABCO. A few measurements were also made using ethanol/water rather than methanol/water. Again, the effects of argon were found to reduce the laser lifetime and DABCO, if anything, reduced the laser lifetime under air.

2.3. *Exciton Coumarin 504 in Alcohol*

We did not test Coumarin 504 with DABCO in methanol or ethanol since Von Trebra and Koch had not done so, and our tests with other dyes had shown little effects due to DABCO. We show in Table 4 the results of using methanol, ethanol, air and argon. We also tested Coumarin 504 in methanol at double the concentration in the other tests. We again find that air yields longer lifetimes than does argon as was observed in alcohol/water mixtures. We also see a slight decrease in lifetime by using the higher concentration of Coumarin 504. The more interesting observation is the reduced lifetime using either methanol or ethanol as compared to the water mixtures. We have observed this alcohol/water improvement for other dyes [13, 14]. The addition of water reduces both the cost and the flammability of the solvent (it also often causes a red shift of the lasing wavelength) as well as yielding as much as a tenfold increase in dye lifetime. This seems to us to be a more viable improvement in dye laser lifetime than the small improvements that we *sometimes* see with the use of DABCO.

2.4. *Other Coumarin Dyes*

Table 2 shows the lasing characteristics of all of the laser-pumped dyes other than Coumarin 504 reported by Von Trebra and Koch in [1] as well as the dyes Coumarin 339, LD490, and AC3F. Time did not permit us to test all of the combinations of methanol and ethanol with and without water, Millipore versus Fluoropore filters, other solvents, and tests with and without argon.

We did not observe a two- to threefold increase in laser lifetime for the dyes Coumarin 1, 120, and 311 tested by Von Trebra and Koch using laser pumping when consideration is given to the effects of the changes in the initial lasing threshold upon the laser lifetime. The effects of a Millipore filter again appears to reduce the lifetime of a dye (Coumarin 339) in the presence of air and DABCO. Furthermore, the dyes Coumarin 339, LD490 and AC3F in ethanol did not show positive results to the effects of DABCO. The dye AC3F in toluene under air showed a marked decrease in laser lifetime and output due to the effects of DABCO. Under argon, DABCO also caused a reduction in laser lifetime and output but the decrease was less pronounced for AC3F in toluene compared to the results in air.

The more striking improvement for a number of the dyes shown in Table 2 is the effect of argon (or rather the absence of oxygen). A 31-fold improvement in the lifetime constant is seen for the dye Coumarin 1 for the removal of air. DABCO under argon produced an even greater improvement over the value of the lifetime constant observed using air without DABCO – a 35-fold improvement. The improvement in the number of laser pulses is somewhat less and would decrease even more if the laser were operated at a higher input energy [7].

2.5. *Effects of Time and* DABCO *on Coumarin 504*

Von Trebra and Koch noted that DABCO is a strong base and could affect some of the dye solutions. In test 7647 of Table 5, we see that when Coumarin 504 was flashed under air in 50:50 methanol/water (results shown in Fig. 1), it has its $S_1 \leftarrow S_0$ absorbance band, A, at about 446 to 447 nm, and that the photobleaching caused its absorbance cm^{-1} to reduce from 5.09 to 4.66. Similar results were obtained in test 7648 which was performed under argon. These absorbances were tested about a month after the solutions were prepared and laser tested. Test 7645 (which contained DABCO and whose laser results are shown in Fig. 2) shows that a solution of Coumarin 504 in methanol/water was tested for absorbance the day that it was prepared. It also had an initial absorbance of about 5.0 cm^{-1} at 447 nm. After lasing, the absorbance of the solution containing DABCO still peaked near 446 nm 2 days later and had been bleached about the same as had tests 7647 and 7648 that had not contained DABCO. The striking change is what happened to the solution of Coumarin 504 with 0.01 M DABCO upon standing for more than just a few days. The unlased stock solution of Coumarin 504 and 0.01 M DABCO in test 7645 in methanol/water was found to have an absorbance wavelength shift from 447 to 437 nm and have its absorbance decrease from 5.0 to 3.6 cm^{-1} after standing 1 month. A second test, 7646, performed under argon starting at the same concentration (but whose absorbance was not measured on the day of preparation), also had an absorbance near 3.7 cm^{-1} and a wavelength shift to 438 nm.

A fifth test, 7650, whose laser results are shown in Fig. 3, had a DABCO concentration of 0.02 M. Its dye absorbance was measured about 2 weeks after preparation and showed a decreased absorbance that was intermediate to those of the previous tests with DABCO after 1 month and the fresh value of 5.0 cm^{-1}. Whether this intermediate value was due to the shorter period of time for hydrolysis or because of the higher concentration of DABCO is not known. However, since test 7647 without DABCO and test 7650 with 0.02 M DABCO have both had about the same amount of bleaching and total input energy from the flashlamps (Table 5), and since test 7650 shows a decrease in the initial absorbance as would be expected from the hydrolysis of the dye as seen in tests 7645 and 7646, the DABCO could be considered as decreasing the photobleaching of the Coumarin 504 in test 7650, i.e., the value of the after lasing absorbance in test 7650 should be much lower than the unflashed solutions as found in tests 7645, 7646, 7647, and 7648. Thus 0.02 M DABCO could be reducing the rate of photobleaching as compared to the results obtained with 0.01 M DABCO. The laser lifetime results reported in Table 2 with DABCO, however, showed results comparable to those without DABCO.

Acknowledgement. The authors wish to thank Howard Lessoff and the Electronic Materials Program (Naval Research Laboratory) for interest and financial support of this work.

Table 5. Absorbance measurements on 0.0001 M Coumarin 504 in 50:50 by volume methanol:water

Test	Date(s) flashed	Date soln prepared	DABCO conc., M	Cover gas when lasing	Absorbance						Total input energy [MJ]
					Before lasing			After lasing			
					Date tested	A [cm^{-1}]	Max [nm]	Date tested	A [cm^{-1}]	Max [nm]	
7645	Feb. 15	Feb. 15	0.01	Air	Feb. 15	5.000	447	Feb. 17	4.431	446	3.11
					Mar. 16	3.618	437				
7646	Feb. 16, 17	Feb. 16	0.01	Argon	Mar. 16	3.700	438	Mar. 16	2.622	434	4.34
7647	Feb. 22	Feb. 22	0.00	Air	Mar. 20	5.089	447	Mar. 20	4.659	446	3.95
7648	Feb. 22, 23	Feb. 22	0.00	Argon	Mar. 20	5.089	447	Mar. 20	4.397	446	3.50
7650	Mar. 2	Mar. 2	0.02	Air	Mar. 19	4.481	445	Mar. 19	4.414	445	3.21

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