

Part V: Flame Spectra of Blue Color Compositions

ABSTRACT

We can see three different flame colors (i.e., blue, light green and reddish orange) when we insert a small copper piece into a flame of a burner. The blue color is caused by CuCl bands with the strongest lines between 4269–4560 Å. Our goal is to use this color for fireworks. Blue is produced by some copper salts or copper metal powder in the presence of chlorine or hydrogen chloride gas, but if the concentration of gas is small, the blue color is interfered with by the light green color, which seems to be caused by a continuous spectrum of other copper chloride bands (5263–5531 Å).

The flame spectra are examined under various conditions. For low temperature flames, ammonium perchlorate is the best oxidizer and produces an excellent bright blue. For high temperature flames it is necessary to decrease the percentage of magnesium powder, because the CuCl bands seem to dissociate with increasing magnesium.

1. Introduction

The purpose of this Part is to examine the spectra of the blue flames produced by fundamental compositions to explain the principle of making blue flames, considering the effects of various ingredients and ratios of the compositions, etc. This study will greatly help in developing good blue compositions.

2. Materials and Instruments for Experiments

Materials other than color agents were described in earlier Parts.

Blue color agents:

Copper sulfate, CuSO_4 : commercial reagent grade.

Cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: basic copper carbonate was gradually added to a 12 N hydrochloric acid solution. When the bubbling of CO_2 stopped, the solution was filtered, recrystallized three times, and dried at 60 °C to obtain the cupric chloride.

Cupric oxalate, CuC_2O_4 : Ammonium oxalate was added to a water solution of copper sulfate of commercial reagent grade, and the precipitate was separated by natural sedimentation from the liquid. The precipitate was washed four times with distilled water. The precipitate consisted of very fine particles, some of which passed through a filter paper. It was difficult to use ordinary filtrating methods; therefore, it was difficult to completely remove the ammonium salt, which was produced as a by-product.

Basic copper carbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$: Ammonium carbonate was added to a water solution of copper sulfate of commercial reagent grade, and the precipitate was washed with distilled water until the reaction of the Nessler reagent did not occur. Then it was dried at 60 °C in an oven. The carbonate produced by this method partially dissolves in the ammonium carbonate solution, which results in a decreased yield.

Paris green, $3\text{CuO} \cdot \text{As}_2\text{O}_3 + \text{Cu}(\text{CH}_3\text{COO})_2$: This was synthesized in the author's laboratory. It was analyzed as $\text{Cu}=22.5\%$.^[1]

Copper arsenite, CuHAsO_3 : This was synthesized in the author's laboratory.^[2]

Sample specimens and instruments were the same as described in Part III.

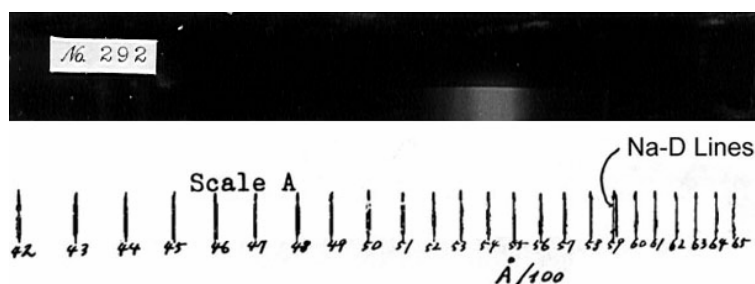


Photo 1. Copper chloride spectrum from a flame of a gasoline burner (2 hour exposure).

3.0 Preliminary Experiment: Observation of Flame Color and Flame Spectra from Copper

As the blue color agent, copper or copper compounds are used. Some formulations show mercury compounds; however, they are not commonly used at present. The color of the flame from copper compounds is fairly complex, and the blue color producing mechanism is quite different from the others, so this preliminary testing is important.

3.1 Observation of Flame Color by Copper and Its Spectra Using Copper Metal Wire

(1) A quantity of sodium chloride (reagent grade) was placed into a conical flask. A quantity of concentrated sulfuric acid was poured onto it and heated. From the flask, well dried HCl gas was produced. The HCl gas was introduced into another conical flask of 1 liter, which was used as a HCl gas reservoir that was closed by a piece of glass plate. Separately, a length of bare electric copper wire of about 2 mm in diameter was prepared. The copper wire was inserted into the HCl reservoir and after a while the surface of the copper wire was chemically covered with a copper chloride film; then the wire was inserted into an almost colorless flame of a gasoline burner. The flame above the wire was colored light green. The spectrum that was photographed is in Photo 1. It was a continuous spectrum of 5170–5510 Å.

(2) Initially the spectrum looked green, but a few seconds later it changed to red orange. This change of flame color was due to the va-

porizing of the copper chloride that was fixed on the surface of the copper wire. The spectrum of red orange flame could not be photographed even with two hours of exposure, because it was very weak.

(3) From the above described hydrogen chloride gas generator, HCl gas was blown into the gasoline flame through a nozzle. The partial mixing of the two gases, of the gasoline burner flame and of the hydrogen chloride gas, emitted a faint green light. Then, when a bare copper wire with no preliminary treatment was inserted above the mixing point of the flame, the flame was colored with a pretty blue. This spectrum was photographed as the upper spectrum S6 in Photo 2.

(4) When dried Cl₂ gas, instead of HCl gas, was blown into the flame, yellowish sparks were visible at the mixing point of the gases. When the copper wire was inserted above the mixing point of the flame, the same blue was observed; this spectrum is shown by S7 in Photo 2.

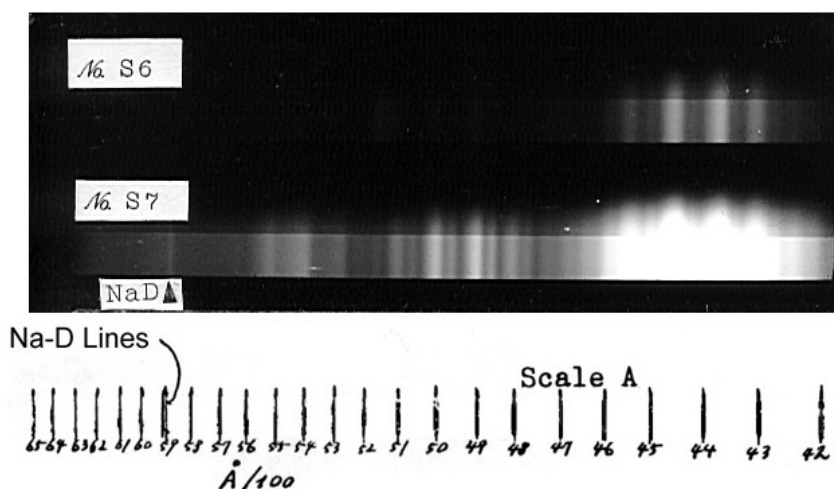


Photo 2. Flame spectra of copper chloride from gasoline burner.
 S6: by blowing HCl gas into the flame, 27 minutes exposure,
 S7: by blowing Cl₂ gas into the flame, 24 minute exposure.
 [Ed. Note: The Scales and Spectra are reversed in this Photo.]

3.2 Experiments with Firework Compositions

(1) A quantity of ammonium perchlorate was mixed with shellac in a weight ratio 5:1. This mixture was burned. A piece of copper wire with no preliminary treatment was inserted into this burning flame. The color was pretty blue; the same as that in (4) of Section 3.1. In this case the tip of the flame was colored with weak red orange. This color was the same as the red orange flame described in (1) of Section 3.1.

(2) A quantity of potassium perchlorate was mixed with shellac in a weight ratio 5:1 to which 10% basic copper carbonate was added. When it was burned, three different flame colors were observed, as shown in Figure 1 with blowing HCl gas into the flame through a nozzle.

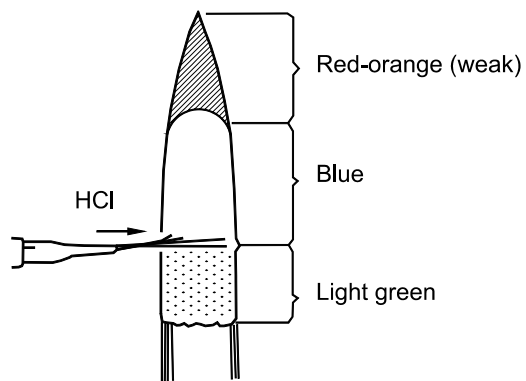


Figure 1. The flame colors observed from the potassium perchlorate composition that contained copper compound blowing into the flame with HCl gas.

3.3 Examination of the Effects

From the above experiments, it is understood that there are three kinds of flame color: blue, light green and red orange. For firework use only the blue is desired. From the above experiments we know that the light green disappears in the presence of HCl gas in the flame, and the blue appears most clearly under the same conditions. Also the red orange does not disappear, however, it is very weak, and from a distance it does not interfere with the blue.

It is well known that blue flames come from CuCl band spectra. However, where does the light green come from? Perhaps the emitter has a different structure from that of the blue. The red orange always appears at the tip of the flame. Therefore it may be caused by CuO due to oxygen in the air.

4. Examination of the CuCl Band Spectra

R. Ritschl already analyzed the CuCl band spectra.^[3] The structures are in Table 1:

Table 1. CuCl Band Spectra Analyzed by R. Ritschl in Å.

1	5380 (0,1)	5262 (0,0)	5152 (1,0)
2	4982 (0,1)	4882 (0,0)	4789 (1,0)
3	4946 (0,1)	4847 (0,0)	4756 (1,0)
4	4434 (0,0)	4354 (0,0)	4281 (1,0)
5	4412 (0,0)	4333 (0,0)	4259 (1,0)

Specifically, five types of transition between electronic states were proposed. However, the values of the wavelengths were somewhat different from the author's. And more intensive bands were omitted. The bands generally appeared with almost the same difference of the wave numbers, and from these results it is thought that there is another way of analyzing than the above.

The CuCl band spectra appeared between 4030–5640 Å. The main blue light source appeared as an intense band: 4210–4589 Å, followed by somewhat weak bands: 4580–5099 Å. The difference in wavelengths between the bands were regular. Thirty one bands were observed in the range of wavelengths shorter than the Na-D lines.

The wavelengths (or wave numbers) and roughly estimated intensities of the bands are shown in Table 2 and Figure 2, using the following symbols:

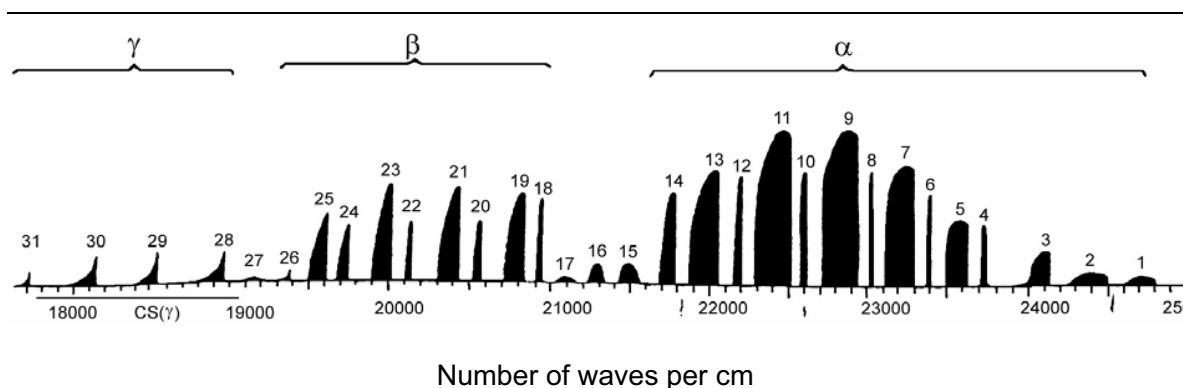


Figure 2. CuCl bands from the author's experiments.

Table 2. CuCl Spectra from the Author's Experiments.

		Bandwidth (Å)				Band width (Å)	
α band	1.	4026–4058		β band	18.	4769–4781* ³	
	2.	4071–4105			19.	4801–4838* ²	⊙
	3.	4123–4164			20.	4850–4863* ³	
	4.	4201–4219			21.	4888–4928* ²	⊙
	5.	4229–4252			22.	4950–4966* ³	
	6.	4269–4277* ⁵			23.	4989–5037* ²	⊙
	7.	4290–4323* ⁴	●		24.	5056–5074	
	8.	4340–4343* ⁵			25.	5092–5120	
	9.	4355–4399* ⁴	●		26.	5151–5169* ¹	
	10.	4417–4432* ⁵			27.	5190–5225	
	11.	4438–4481* ⁴	●	γ band	28.	5263–5304* ¹	
	12.	4496–4513			29.	5385–5429* ¹	
	13.	4526–4560	●		30.	5503–5531	
	14.	4590–4608		31.	5628		
	15.	4630–4658				Continuous spectrum 5263–5531	
	16.	4678–4698					
	17.	4724–4749					

Note: The continuous spectrum 5263–5531 Å appeared when the density of the HCl gas in the flame is low, for example with the flame from a potassium perchlorate composition.

●	strongest
⊙	middle class intensity
no symbol	weak and ineffective
*	band corresponding to those of R. Ritschl, (Table 1), with the unit of wavelength as Å

According to the classification in Table 2 and Figure 2, the characteristics of the bands are described as follows:

α band: Strongest band group, which contains four main bands, α_7 , α_9 , α_{11} , α_{13} , with weaker bands that alternately appear between the main bands. These are the main spectra for creating blue. In this paper the intensity of the α band is represented by the intensity of the α_9 band.

β band: Weaker than the α band; however, the band arrangement resembles that of the α band. The intensity of band is represented by that of β_{21} .

γ band: weak band elements appear with almost the same intervals. The intensity is represented by that of γ_{29} .

Table 3. The Effect of Oxidizer-Fuel Mixing Ratio.

Composition (71)	%
Ammonium perchlorate	<i>x</i>
Shellac	<i>y</i>
Basic copper carbonate	10

No.	<i>x</i> %	<i>y</i> %	ω	Δ	ν	<i>L</i>	<i>E</i>	α	β	γ	CS(D)	Oxygen Balance
229	50	40	23.6	1.06	1.40	30	257	2.0	weak	0	3.2	-0.674
230	60	30	24.3	1.11	2.20	50	259	2.8	weak	0	3.2	-0.402
231	70	20	25.9	1.15	2.53	50	195	4.7	1.8	weak	weak	-0.130
232	80	10	26.9	1.22	2.93	20	71.4	5.3	2.5	weak	weak	+0.142

Note: The oxygen balance is shown by the excess or lack of oxygen in grams per 1 gram of the composition.

5.0 Low Temperature Blue Flames

5.1 The Effect of Mixing Ratio of Oxidizer and Fuel

For the oxidizer, ammonium perchlorate, which produces HCl gas in the flame, was used.

In Table 3 the intensity of the α band becomes larger and larger with increasing values of *x/y*, and the intensity of the β or γ bands have

the same tendency as the δ band. On the other hand, the intensity of the continuous spectrum decreases with increasing *x/y*. Therefore, a clear blue flame can be obtained at a fairly high temperature with excess oxygen.

Table 4. The Effect of Color Agents with Ammonium Perchlorate Oxidizer.

Composition (72)	%
Ammonium perchlorate	75
Shellac	15
Color agent	10

No.	Color agent	Cu %	ω	Δ	ν	<i>L</i>	<i>E</i>	α	β	γ	CS
261	Basic copper carbonate	5.75	27.0	1.22	3.35	45	140	5.0	2.4	weak	0
262	Copper oxalate	5.91	27.0	1.23	?	?	—	3.9	weak	0	0
263	Copper chloride	3.73	27.0	1.23	1.16	9.0	80	5.8	3.5	weak	0
264	Copper sulfate	2.55	27.6	1.25	1.16	9.0	79.6	5.7	3.5	weak	0
265	Paris green	2.25	25.5	1.14	1.47	15.0	114	5.7	3.7	2.0	0
266	Copper arsenite	3.39	24.5	1.10	1.46	16.8	134	5.6	3.7	2.0	0
267	5% Copper powder	5.26	30.6	1.16	8.33	33.6	42.7	3.9	weak	0	0
268	10% Copper powder	10.00	26.7	1.19	3.61	44.8	133	5.8	3.9	2.5	0

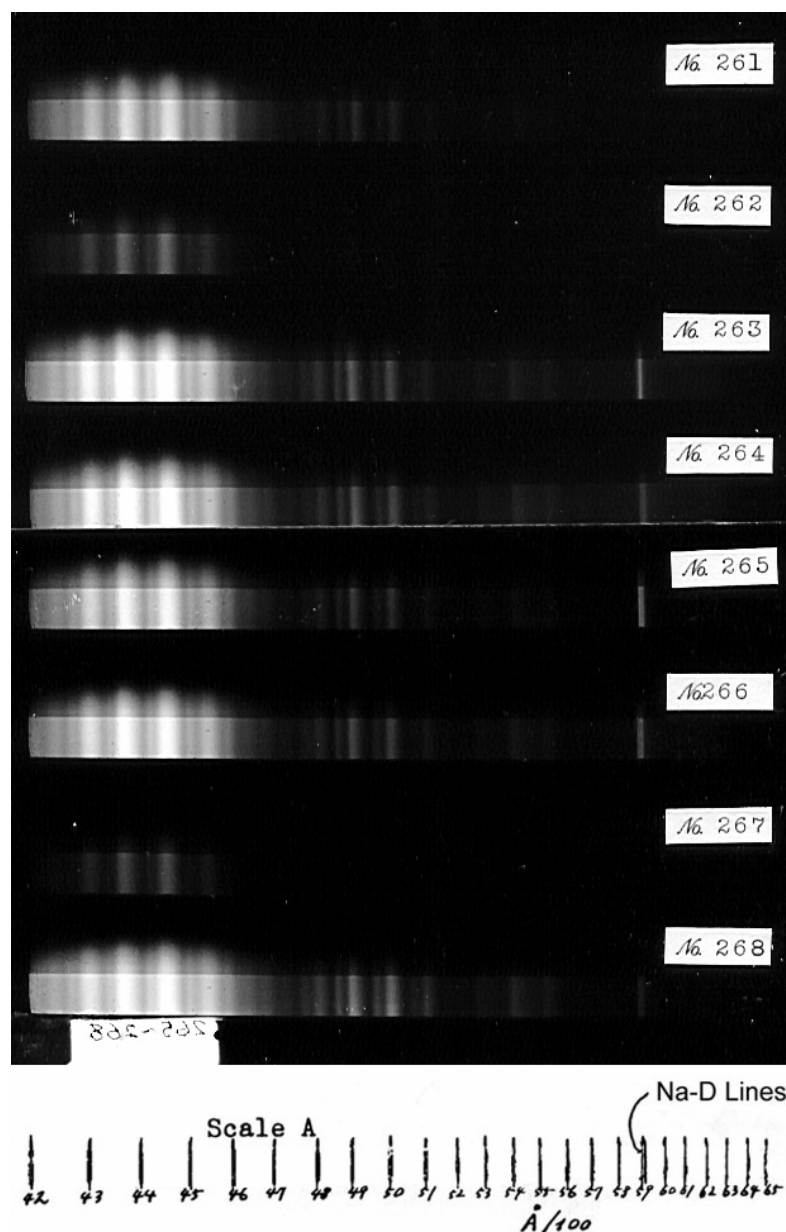


Photo. 3 Flame spectra when using ammonium perchlorate as the oxidizer. (These spectra correspond to the compositions in Table 4.)

5.2 The Effect of Various Color Agents and Oxidizers

The flame color of each composition in Table 4 was a pretty blue. In particular, the flames of Compositions Nos. 263 (copper chloride), 268 (10% copper), 264 (copper sulfate), and 265 (Paris green) were all similar and superior in producing blue. Compositions Nos. 262 (copper oxalate) and 267 (5% copper powder) burned

very irregularly and dangerously fast. All of its light was not introduced into the spectroscope.

As described above, the main part of each flame was colored blue, and only the tip was weak orange red.

Table 5. The Effect of Color Agents with Potassium Perchlorate Oxidizer.

Composition (73)	%
Potassium perchlorate	75
Colophony	15
Color agent	10

No.	Color agent	Cu %	ω	Δ	ν	L	E	α	β_{24}	β_{25}	γ	δ	CS(γ)	CS(K)
281	Basic copper carbonate	5.75	31.0	1.37	2.10	18.0	79.6	5.4	3.0	2.3	0	2.0	3.7	f.s.
282	Copper oxalate	5.91	30.8	1.40	1.29	36.0	254	5.4	2.6	2.6	0	2.4	3.8	f.s.
283	Copper chloride	3.73	29.3	1.30	1.52	23.0	149	4.8	w	w	0	w	3.0	w
284	Copper sulfate	2.55	30.8	1.36	1.70	20.0	110	4.8	w	s	0	w	2.6	w
285	Paris green	2.25	—	—	1.93	72.0	—	5.5	w	3.6	0	2.8	3.6	s
286	Copper arsenite	3.39	30.8	1.36	3.00	58.0	181	6.2	3.4	4.3	0	3.0	4.2	s
287	5% Copper powder	5.26	30.6	1.35	1.76	28.8	154	4.8	0	2.2	0	w	3.8	ss
288	10% Copper powder	10.00	31.2	1.38	1.89	50.4	246	5.0	0	2.8	0	w	3.8	ss

Note: Symbols: w = weak; ss = slightly strong; s = strong.

The flame spectra with potassium perchlorate compositions corresponding to Table 5 are shown in Photo 4.

When using potassium perchlorate as the oxidizer, the compositions with Paris green, copper arsenite and copper powder produced the prettiest blue flames in the range of experiments in Table 5. When comparing the effects of ammonium perchlorate, which produces HCl gas in the flame, and those of potassium perchlorate with no HCl gas, the latter was different from the former in the following points:

(1) The intensity of the α band was similar in both.

(2) New bands appeared at 6070 and 6150 Å, which were longer wavelength than the Na-D lines. In this study these are called the δ bands (Table 5).

(3) The γ band did not appear. In place of this band a green continuous band CS(γ) appeared with a high intensity.

(4) Generally, the bands were not as clear as with ammonium perchlorate and grew somewhat dim.

The above effects make the color of the flame whitish and greenish. From the preliminary experiments in Part III it is clear that this was caused from the lack of HCl in the flame.

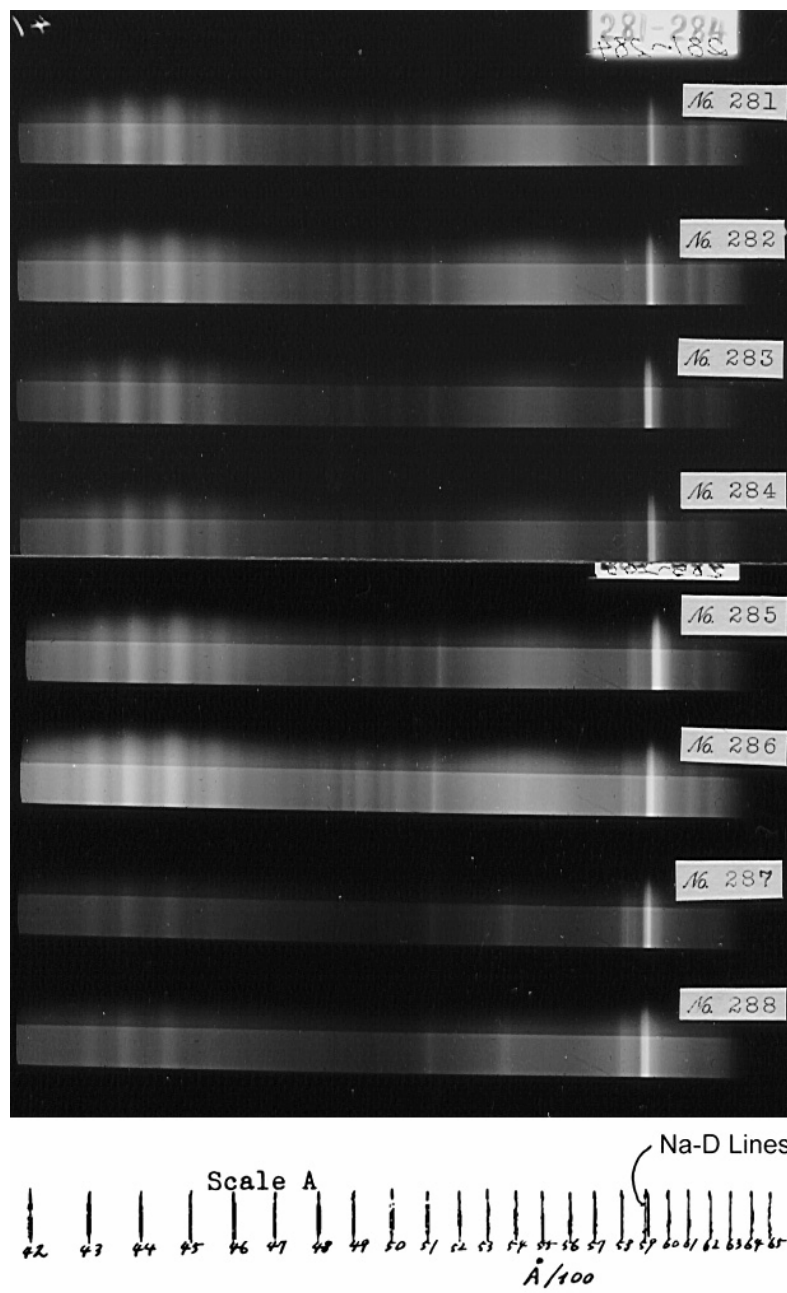


Photo 4. Flame spectra when using potassium perchlorate as the oxidizer. (These spectra correspond to the compositions in Table 5).

Table 6. The Effect of Various Fuels with Ammonium Perchlorate as the Oxidizer.

Composition (74)	%
Ammonium perchlorate	75
Fuel	15
Copper powder	10

No.	Fuel	ω	Δ	ν	L	E	α	β	γ	δ	CS(γ)
313	Shellac	30.2	1.34	3.20	72	215	4.9	3.1	weak	—	weak
314	Colophony	28.0	1.24	?	—	—	—	—	—	—	—
315	Pine root pitch	30.3	1.34	?	54	—	5.2	2.7	weak	—	weak
316	Coal pitch	28.8	1.27	?	—	—	—	—	—	—	—

Composition (75)	%
Ammonium perchlorate	80
Fuel	10
Copper powder	10

No.	Fuel	ω	Δ	ν	L	E	α	β
321	Shellac	31.5	1.48	4.84	43	76.5	—	—
322	Colophony	30.3	1.39	5.05	54	98.0	—	—
323	Pine root pitch	32.0	1.42	4.78	43	80.6	—	—
324	Coal pitch	31.7	1.44	0.00	—	—	—	—

5.3 The Effect of Various Fuels

It was difficult to obtain precise data from the tests in Table 6 because the samples generally burned in an unstable manner. Nos. 314, 316, and 321–324 burned irregularly and too fast to measure the intensity of the bands photographically. The tendency was enhanced by increasing the percentage of ammonium perchlorate. Shellac or pine root pitch was a relatively good fuel to create stable burning. The spectra in this case were similar to each other.

In Table 7, comparing Composition (76) with (77) the latter produced clearer, but somewhat weaker bands than the former.

The compositions that contained potassium perchlorate generally produced unclear bands. And in this case CS(γ) and δ other than α , β bands made the flame look quite blue green.

5.4 The Effect of Fuels That Contain Chlorine

Too much chlorine containing fuel decreases the flame temperature; so the quantity should be limited. Therefore 5% of this substance was tested.

In Table 8 the effects of the Cl or HCl producing substances was not very effective with such small quantities. However, if more is added, the flame temperatures will be decreased to obtain worthless effects. Therefore, for low temperature compositions, adding Cl or HCl producing substances is not expected to produce very good effects.

Table 7. The Effect of Various Fuels with Potassium Perchlorate as the Oxidizer.

Composition (76)	%
Potassium perchlorate	75
Fuel	15
Copper powder	10

No.	Fuel	ω	Δ	v	L	E	α	β_{24}	β_{25}	γ	δ	CS(K)
317	Shellac	31.8	1.41	1.80	29.0	146	5.7	3.8	5.2	5.2	4.6	strong
318	Colophony	30.2	1.34	1.96	36	175	5.3	3.5	4.3	5.0	3.8	strong
319	Pine root pitch	32.0	1.47	2.24	54	209	5.8	3.4	3.8	4.8	4.4	strong
320	Coal pitch	31.8	1.41	2.03	68	304	5.7	3.2	4.0	4.8	4.8	strong

Composition (77)	%
Potassium perchlorate	80
Fuel	10
Copper powder	10

No.	Fuel	ω	Δ	v	L	E	α	β_{24}	β_{25}	γ	δ	CS(K)
325	Shellac	32.0	1.61	1.71	7	31.7	5.1	weak	weak	3.4	2.1	weak
326	Colophony	31.9	1.49	1.37	18	64.9	4.7	weak	weak	3.4	2.6	weak
327	Pine root pitch	31.5	1.59	2.33	36	123	5.5	2.0	2.0	3.3	3.5	weak
328	Coal pitch	31.7	1.64	1.94	36	144	5.0	weak	2.0	3.9	3.5	weak

Table 8. The Effect of Various Chlorine Donors

Composition (78)	%
Potassium perchlorate	70
Colophony	10
Paris green	15
Cl or HCl producing substance (Cl donor)	5

No.	Cl donor	Cl %	HCl %	ω	Δ	v	L	E	α	β_{24}	β_{28}	δ	γ	CS(K)
237	—	—	—	30.5	1.53	2.71	77	237	6.7	3.6	3.9	4.5	3.9	strong
238	Polyvinyl chloride	—	2.92	31.6	1.45	2.45	83	296	5.9	3.7	3.7	4.3	3.5	strong
293	BHC	3.66	—	32.0	1.49	2.04	54	226	6.4	4.9	4.2	4.6	4.0	strong
294	Ammonium chloride	—	3.34	32.3	1.43	1.76	18	90	6.4	4.4	4.0	4.1	3.0	strong

Table 9. The Effect of Various Oxidizers to Fuel Mixing Ratios.

Composition (79)	%
Ammonium perchlorate	x
Magnesium	y
Polyvinyl chloride	10
Paris Green	10

No.	x%	y%	ω	Δ	α	β	γ	CS
418	60	20	8.4	5.4	2.7	weak	0	weak
419	40	40	8.3	5.4	2.7	0	0	slightly weak
420	20	60	7.9	4.1	weak	0	0	strong
421	20	60	7.3	0	0	0	0	strong

Composition (80)	%
Potassium perchlorate	x
Magnesium	y
Polyvinyl chloride	10
Paris Green	10

No.	x%	y%	ω	α	β	γ	δ	CS(K)
422	60	20	9.2	6.0	0	0	?	strong
423	40	40	8.8	6.0	0	0	?	strong
424	20	60	7.8	4.9	0	0	?	strong
425	20	60	7.6	0	0	0	?	strong

6.0 High Temperature Blue Flames

The color producing mechanism of the high temperature blue flames using CuCl band spectra is quite different from that of high temperature red flames using strontium bands or green flame using barium bands.

6.1 The Effect of Mixing Ratios of Oxidizers and Fuels

In Table 9 Nos. 421 and 425 were blank tests; they did not contain Paris green. The photographs related to Table 9 are shown in Photo 5.

In Table 9 the intensity of CuCl band spectra was very much decreased when the ratio of oxidizer to magnesium decreased (Photo 5). This is a central characteristics to SrO or BaCl band spectra. The emitter CuCl may be dissociated at

high temperatures to build MgCl molecules consuming Cl atoms in the flame. Therefore, at high flame temperatures, bright blue light can not be obtained when we use the CuCl band.

Using potassium perchlorate as the oxidizer produced a strong continuous spectra CS(K) that interferes with blue light.

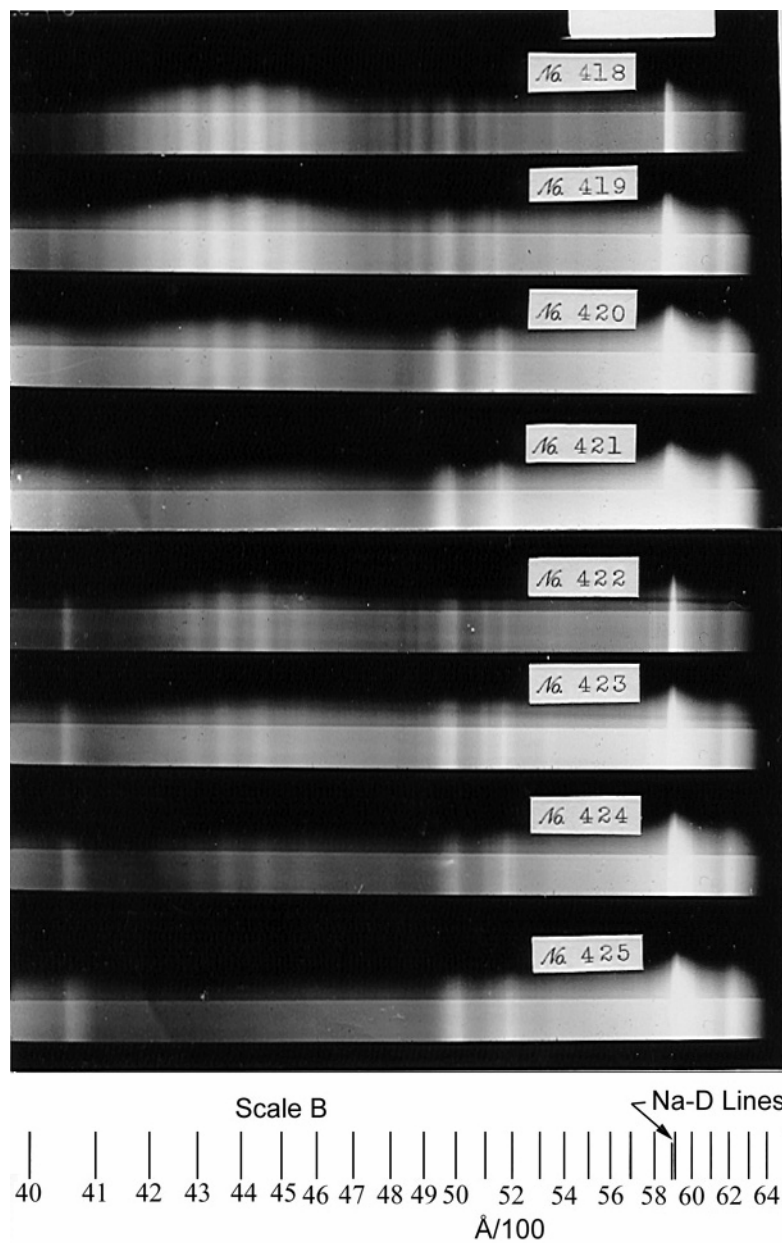


Photo 5. Effects of the mixing ratio of oxidizer to magnesium on the CuCl band spectra.

Table 10. The Effect of Various Copper Salts.

Composition (81)	%
Potassium nitrate	50
Magnesium	30
Copper salt	20

No.	Copper salt	ω	Δ	ν	L	E	α	β	γ	δ	CS(K)
207	Basic copper carbonate	10.2	1.49	2.91	800	2740	0	0	0	0	4.1
208	Copper chloride	9.7	1.30	4.04	800	1980	0	0	0	0	3.4

In Table 10, Composition No. 207 did not contain chlorine and no band related to chlorine appeared. This, as a matter of course, confirms the already described fact that the Cu bands came from copper chloride. The fact that no Cl band appeared, even when using copper chloride, may be due to the Cl being consumed to form MgCl.

6.2 The Effect of Various Color Agents

In Table 11, Composition (82), 10% copper powder was the most effective in producing color, followed by Paris green and copper arsenite.

Table 11. The Effect of Various Color Agents.

Composition (82)	%
Potassium perchlorate	60
Magnesium	10
Polyvinyl chloride	10
Color agent	20

No.	Color agent	Cu %	ω	Δ	ν	L	E	α	β	γ	δ	CS(K)
185	Basic copper carbonate	11.49	10.2	1.55	1.28	300	2532	weak	0	0	0	0
186	Copper oxalate	11.82	10.6	1.57	1.22	30	246	weak	0	0	0	0
187	Copper chloride	7.45	9.8	1.29	1.07	10	93	slight	0	0	0	0
188	Copper sulfate	5.09	10.3	1.38	1.03	10	97	0	0	0	0	0
189	Paris green	4.50	10.5	1.52	2.26	150	663	3.6	0	0	0	0
190	Copper arsenite	6.78	10.5	1.39	2.04	100	490	3.4	slight	0	0	0
191	5% Copper powder	5.88	9.0	1.45	2.65	200	765	2.9	slight	0	0	0
192	10% Copper powder	11.11	9.5	1.32	3.65	320	876	4.0	weak	0	0	0

6.3 The Effect of Using a Non-Chlorine Oxidizer with a Chlorine Producing Agent (Chlorine Donor)

Table 12. The Effect of Using a Chlorine Donor with a Non-Chlorine Containing Oxidizer.

Composition (83)	%
Potassium nitrate	40
Magnesium	60
Copper powder	additional 10
Polyvinyl chloride	additional x

When Composition (83) was tested with values for PVC of $x=20$ and 30 , the CuCl band did not appear. Perhaps this might be caused by the chlorine being consumed by magnesium to produce MgCl gas as in the case of No. 187.

7. Conclusion

To obtain good blue flames it is important to consider the following conditions.

(1) For low temperature flames: the existence of HCl (or Cl₂) gas in the flame is important to create the CuCl- α band, which is the main factor in blue light. When using an oxidizer that cannot produce HCl (or Cl₂) gas in the flame, the intensity of the δ band decreases. Ammonium perchlorate works well to produce blue flame compositions. Potassium perchlorate does not work well. It produces green continuous spectra CS(γ), and the flame becomes green white.

(2) For high temperature flames: it is difficult to obtain good blue flames at high temperatures. When the weight ratio of magnesium to oxidizer increases, the blue of the flame gradually decreases with the increasing consumption of HCl or Cl₂ gas by magnesium vapor to produce MgCl compound in the flame.

Literature cited

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- 2) Ditto, p 37.
- 3) V. Nishizawa, *Studies on Fireworks* (in Japanese) (1938) p 157.
- 4) J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry III* (1923) p 48.
- 5) Borenstein, *Physikalische Chemische Tabellen II*, p 862.

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

(Continued from page 56)

In November 1934 all officers of Artillery and Engineers of my contemporary came back from the regiments and entered the Military Artillery and Engineer Academy. We were taught mathematics, physics, chemistry, metallurgy, electrical engineering, ballistics, etc. So many things were stuffed into our heads by the cramming system of the Academy. After the regular course of one year and the higher course of one year, I was selected to learn more at Tokyo University.

In April 1937 I entered the School of Explosives at Tokyo University. In my class five other students from regular high schools gathered. Professor Nishimatsu, who was the highest authority of the day on manufacturing explosives, was chief. Professor Dr. N. Yamaga, who was a rear admiral in the Navy, lectured on interior ballistics. Assistant Professor S. Yamamoto lectured on manufacturing explosives. Their speaking was terrible and the students suffered to note their lectures. I felt most of the lectures in the School of Explosives were not of much interest. Therefore, I often visited the School of Chemistry, where Assistant Dr. Morino was studying the Raman Effect. I learned quantum mechanics with the help of Professor Dr. K. Higashi, who was an authority in the chemical structure of molecules. Dr. Higashi gave me a book, *FUYU NO HANA* which means “Winter Flowers” in English, by Professor Nakaya (1902-1962). It gave me a deep impression that I knew how to do experiments without any noble instruments of high cost, but using only the human head with excellent success. I named such a method “Terada’s Style”. The late Dr. Terada (1875-1935) was a famous professor in the Faculty of Physics at Tokyo University. Dr. Nakaya was a student under Dr. Terada and had most faithfully succeeded Terada’s school.

rada’s school. Although I had no personal acquaintance with Dr. Nakaya nor Dr. Terada, I decided to succeed Terada’s school in my future life. Therefore I thank Dr. Higashi who gave me such a direction until today.

In April 1940 I graduated from Tokyo University and arrived at my post at Ohji Factory of Explosives of the Tokyo Second Military Ordnance. I worked there as the section chief of manufacturing nitric and sulfuric acids. There stood a nitric acid plant producing 20 tons per day. Large absorption towers of 18-8 nickel-chrome steel were in use at that time. There were other sections for manufacturing TNT, picric acid, nitrocellulose, and tetryl and about a thousand people worked at the factory. I learned the controlling method of a chemical plant that moves continuously—day and night—with few people. Lieutenant Abe and Mr. Kojima, who had a special sense on chemical plants, helped me. Thus I started with this very interesting work as a chemical engineer. I feel it was the most happy days of my life.

After the daytime duty in the factory was over, I studied in my home at Saginomiya in the western part of Tokyo. I read papers of philosophy by professors Dr. Nishida and Dr. Tanabe of Kyoto University. They founded what was called the “Kyoto School”. I learned the dialectics. I also learned Buddhism and the Old and New Testaments by translations in Japanese. I intended further to read them in originals and began to study Sanskrit, Pall, Hebrew, and Greek. I thought the principle of Buddhism might be:

“All things change with time and go in the worse direction when making no human effort.”

(Continued on page 106)

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

(Continued from page 102)

In 1941 World War II broke out. I was in the ballistic section of the Institute of Explosives of the Second Tokyo Ordnance. All the officers in the ordnance felt uneasy because Japan was already fatigued by the long war in China. However, our work proceeded with no confusion. Everyone knew that battle is very foolish work for human beings, which are not different from animals. Men made many inventions in the war; however, there had been no invention that decreased the pain in their lives.

In 1942 I had an additional post as teacher at the Artillery and Engineer Academy, where I gave lectures on interior ballistics to the young officers in the higher course. My students returned from the battlefields. I completely rewrote the textbook, which had been a direct translation from a French one. I discovered a similarity rule to obtain velocity, pressure, and time, as functions of four parameters. When the war was over in 1945, I was a lieutenant colonel and the leader of the ballistic section of the Institute of Explosives. My military life was over with the defeat of Japan.

I had lost my spirit to survive; however, I had to live to support my wife and two children. I decided not to make explosives any more and selected to live in my birthplace, the village of Takamata. My parents were already dead and my junior brother was killed in battle in the Philippines. Few relatives supported me. I bought farm fields of two and a half acres from which I could obtain rice and vegetables for one year living. I built a small house of my own, a shack, without any help of a carpenter.

The house faced the south. There was a hill of Japanese Cedar behind the house. After a walk of ten minutes going up through cedars I would see a vast wild field. Before my house there were rice fields and eleven houses. The village was surrounded by copse hills through which a road and a stream passed outside. In

the daytime my wife and I labored in the rice and vegetable fields and at night I read sutras of Buddha under the light of an oil lamp while my wife and children were sleeping in bed. In spring and summer I enjoyed the twitters of birds. In the autumn my garden was full of flowers of cosmos. In winter it snowed deeply, and I heard the voices of hunted rabbits while I was weaving charcoal containers around the fire. I became very idle in writing letters and I acted rudely to people in acquaintance against my will. No radio or newspaper was in the house, and I could escape from troubles among people. The most terrible times were the rain storms and blizzards in the night. When attacking, I protected my family against the rain or snow by binding the doors and pushing them from the inside, however, it came into the rooms and fell onto the beds through the roof of cryptmeria barks. At last I fell into financial difficulties and had to sell books from my library with the help of my friend, Professor Namba of Tokyo University. One day I suddenly lost my eyesight. I thought I could not work anymore, fortunately I recovered in about a month. My wife fell ill, perhaps it came from an unbalanced diet. She had to go to her father living in Osaka, so I had to bring up my children by myself.

One day in the autumn of 1951, when the sun was shining in the blue sky, I received a letter from Professor S. Yamamoto of the School of Explosives at Tokyo University. Dr. Yamamoto recommended Hanabi, fireworks, to me. I did not know anything about fireworks, but felt it might be very interesting, and I accepted Dr. Yamamoto's request. Dr. Yamamoto was the only one who was concerned with fireworks at that time as a scholar in Japan. Dr. Yamamoto asked me to suppress accidents in this field and to make the traditional technique more scientific.

(Continued on page 120)

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

(Continued from page 106)

In November 1951 I obtained a position at Hosoyo Fireworks Co. in Tokyo through the introduction of Dr. Yamamoto. I had two duties there; to learn the manufacturing of fireworks from the President, Masao Hosoya, and to modernize the factory in business and technique. Mr. Hosoya very kindly taught his secrets in the technique called the “Machida School”. I analyzed the technique of Japanese chrysanthemum shells, and Dr. Yamamoto recommended that I submit the paper as a thesis for a degree. In 1958 I was granted the degree of Doctor of Engineering with the paper “The Design Conditions of Chrysanthemum Shells”.

My senior, A. Kawai, who was a friend of Dr. Yamamoto, asked me to help with his work, the manufacturing of rocket propellants at the plant of Dainippon Celluloid Co. in Kochi village in Hyogo-ken. Therefore, I often visited the plant and helped Mr. Kawai in designing rocket propellant. In the plant there were not many people, but two very superior assistants, Matsumoto and Matsuda.

In 1963 I changed my position to the Perfect Liberty Religion Order in Osaka, accepting the offer from the founder, T. Mild, who planned to build a new factory and an institute of fireworks. However, the plan was not realized because of financial reasons. I was very disappointed. Dr. Yamamoto had passed away that same year, and I lost my largest prop and stay in fireworks. I had plenty of time every day and decided to learn languages from the NHK Broadcasting. I had a secret desire to live in some foreign country and to build a fireworks factory. I learned English, German, French, Spanish, Russian, Chinese,

and by books, Italian and Arabic. I used to walk from my house to the PL fireworks office memorizing Arabic letters. I was often interrupted by the kind PL teachers who offered to bring me by car.

In 1967 I got my present position in the factory of Koa Fireworks. The factory was built by my old friend, the late N. Mizogami, who built a small laboratory for me. The factory was mainly producing maritime distress signals. I continued the study of fireworks finding time intervals at the work until today following the request of my old teacher Dr. Yamamoto. Therefore, very often, even on holidays, I am not working at home, but in my laboratory at the factory, which is fifteen kilometers distant from my house.

In the past some friends from overseas countries stayed overnight in my home in Kawagoe-shi, which is thirty five kilometers northwest of Tokyo: Miss Sigrid Wied, Dr. F-W Wasmann, W. Zink from Germany, Pierre-Alain Hubert from France, and Mrs. Pettit from the USA. Recently my wife fractured a vertebra and I can not invite guests to my home any more. My work room has been recently confused. The bookshelves are full of books and the residual books are scattered on the tables and floor. On the shelves there stand the complete works of philosophy by the late Dr. Nishida, and the same of the late Dr. Tanabe and of the late Kenji Miyazawa on his poets, the Testaments in various languages, books concerning Buddhism plus technical books, etc. They are covered in dust and will sleep until I have more time.