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THE SPECTRUM OF FLUORINE

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By WILLIAM R. SMYTHE

In 1910 Kayser, in his *Handbuch der Spectroscopie*, made the statement, "Das Spectrum des Fluor ist noch so gut wie unbekannt." Before that time Böttger[1] (1864) and Liveing[2] (1878), working with calcium fluoride; Mitscherlich[3] (1864), Ditte[4] (1871) and Demarçay[5] (1895), working with hydrofluoric acid, Salet[6] (1875), Cramican[7] (1880) and Lunt[8] (1906), working with silicon tetrafluoride; Exner and Haschek[9] (1901), working with ammonium fluoride; and Moissan[10] (1889–91), working with fluorine, had described lines which they assigned to fluorine. The most reliable of these were Lunt, who worked in the violet, and Moissan, who worked in the red.

Since that time Exner and Haschek[11] (1912), working with potassium fluoride on charcoal, have assigned 69 lines to fluorine; and Porlezza[12] (1912), working with silicon tetrafluoride, has assigned 78 lines to fluorine. A comparison of their results shows only 19 lines in common, within one angstrom of each other.

It is evident that the spectrum of fluorine is not yet settled and further measurements are desirable. Apparently, since Moissan's time, no one has worked with the element itself, due probably

[1] *Jahrbuch für practische Chemie*, **65**, 392–94, 1862.

[2] *Proceedings Cambridge Philosophical Society* (3), **3**, 96–98, 1878.

[3] *Poggendorfs Annalen*, **121**, 459–88, 1864.

[4] *Comptes Rendus*, **73**, 738–42, 1871.

[5] *Spectres Electriques*, 1895.

[6] *Annales de Chimie et de Physique* (4), **28**, 34, 1873.

[7] *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften*, Wien (82), **2**, 425–57, 1880.

[8] *Annals of the Cape Observatory*, 10 (2), 5B, 1906; and *Proceedings of the Royal Society*, **75**, 118, 1905.

[9] *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften*, Wien (100), **20**, 964–87, 1901.

[10] *Comptes Rendus*, **109**, 937–40, 1889; and *Annales de Chimie et de Physique* (6), **35**, 125, 1891.

[11] *Die Spectren der Elemente bei normalem Druck*, **3**, 85.

[12] *Gazetta chimica Italiana*, **42**, 42, 1912.

to the great difficulty of preparing and keeping it. We are indebted to Dr. Mather and others of the Chemical Warfare Service for a practicable method for the preparation of fluorine.

The fluorine is generated by the electrolysis of fused potassium acid fluoride. A heavy copper vessel, on the outside of which is wound a nichrome heating coil, contains the electrolyte and serves as the cathode. Soldered to the base of this is a block of brass, having a hole in which a thermometer is inserted. The whole is insulated with asbestos to prevent loss of heat by radiation. The anode is of hard electrode carbon and is inclosed in a heavy

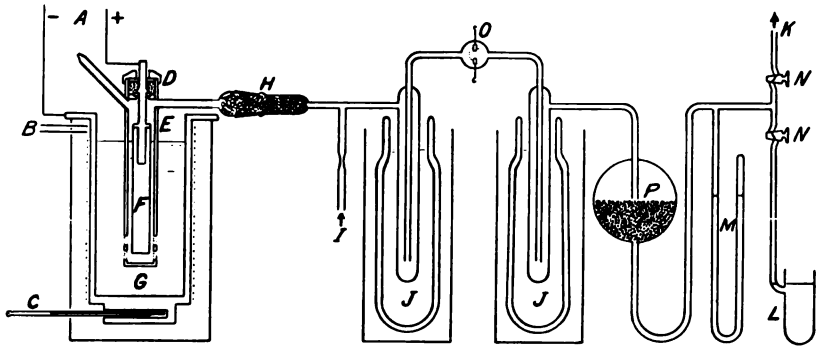

FIG 1

copper "bell" which collects the flourine. It is insulated from the bell and kept in position by powdered calcium fluoride packed between a fluorite and a glass washer, which is held in place by a brass cap.

A 5 mm copper tube on one side of the bell is open to the air and is annealed so that it can be pinched shut. A second copper tube supports the bell and carries off the fluorine, which passes through a copper-in-glass ground joint and a glass tube filled with sodium fluoride, into the purifying trap and discharge tube.

Potassium bifluoride is placed in the generator, melted at 230° C. and electrolyzed with about half an ampere for several hours to remove the last traces of water, while a current of nitrogen passes

from a tank through the apparatus and bell into the air. When fluorine is detected by its odor, the nitrogen is turned off, the copper tube leading to the air pinched shut, and the electrolyzing current increased to an ampere and a quarter. The fluorine stream now enters the apparatus.

Besides being mixed with oxygen and nitrogen, this fluorine contains hydrofluoric acid given off by the electrolyte. This is largely removed by sodium fluoride to protect the glass parts. Since fluorine combines with every element except oxygen, nitrogen, and the noble gases, and since most of these compounds are solid at the temperature of frozen alcohol, while fluorine itself is still gaseous, the obvious way to purify the gas was to place a trap surrounded by frozen alcohol on each side of the discharge tube. Fluorine does not affect clean, cool, dry glass; so by passing a stream through the discharge tube for several hours, all spectroscopic impurities except nitrogen will be removed.

To prevent corrosion of the pump and contamination of the air in the room, the fluorine passed from a second trap into a bulb half-filled with charcoal, with which it combined violently, forming carbon tetrafluoride. In this reaction the charcoal glowed, shot off sparks, and generated so much heat that it was necessary to keep the point of combustion away from the walls of the bulb, as shown in the diagram; otherwise the carbon tetrafluoride reacted with the glass, forming carbon dioxide and silicon tetrafluoride.

Three types of discharge tubes were used. All were provided with a fluorite window. We could find no cement which was not attacked by fluorine. Hence the window was put on in optical contact without cement. Mr. Pearson polished the fluorite plate and glass flange until the usual tests showed them to be flat within .00001 cm. They were then cleaned, placed in contact and pressed together until there was no light reflected from the junction surface. Tests showed that it required two weeks for the pressure in such a tube to rise from an X-ray vacuum to one millimeter. The outside of the joint was painted with shellac to prevent it from slipping and to stop inward leakage. Absolutely no trouble was experienced due to the negligible amount of fluorine which reached and attacked the shellac.

The first tube tried was of the electrodeless type shown in Figure 2. Working at a pressure of about 5 mm we could obtain only band spectra in this tube without heating it to the point where the fluorine attacked it. The charcoal used in this run flared back into the alcohol trap, thus contaminating the contents with carbon tetrafluoride. The photograph on the quartz spectrograph showed a continuous spectrum from 2400 A to 2900 A, nitrogen bands from 2900 A to 4400 A, a set of nine bands, sharp on the violet side, between 4500 A and 6500 A, and five of the fluorine lines. The bands are listed in Table III as carbon tetrafluoride bands.

The second tube, shown in Figure 3, contained electrodes of a gold-palladium alloy. The heavy metals, which resist fluorine,

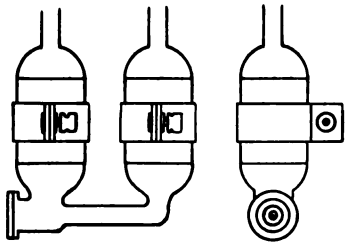

FIG. 2

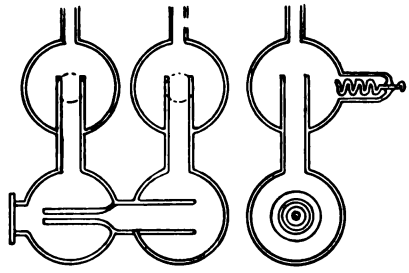

FIG. 3

sputter badly, so that a tube of ordinary pattern soon becomes short-circuited across the sputtered walls. The second tube was designed to avoid this, but, in so doing, its resistance was made so high that the energy required to operate it heated the capillary beyond the safety point. This resulted in the contamination of the spectrum by lines due to most of the elements in the glass, especially silicon. The pressure in the tube was about 5 mm. At lower pressures the fluorine disappeared rapidly; at higher pressures the resistance increased. The photographs of this tube show about 500 lines, including most of those due to fluorine.

The third tube, shown in Figure 4, was designed to operate with a steady stream of fluorine at atmospheric pressure. The electrodes are of gold on platinum wires. By avoiding self-induction and capacity it was found possible nearly to eliminate metal lines and to obtain the gas lines fairly narrow. A tube of distilled water

of 1 square cm cross-section and 60 cm long served as a resistance in the spark circuit. With this arrangement it was found possible to run the tube for eight hours without perceptibly heating it. The absence of a capillary reduced the action on the glass, and such impurities as were formed were carried out by the stream of fluorine at once. Spectra from this tube show only slight traces of silicon lines in the extreme ultraviolet, or none at all.

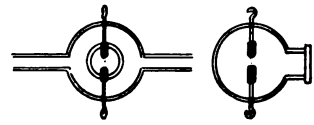

FIG. 4

A large transformer, operating on a 110-volt A.C. circuit, furnished the discharge current for the first two tubes. The third tube was operated by an induction coil giving a 6-inch spark on a 15-volt storage battery circuit.

Two spectroscopes were used. The first was an Adam Hilger quartz spectrograph of the standard type, and the second a grating instrument having a 4-inch concave grating of 50 cm focal length, with a dispersion of 24.88 A per mm. This grating, ruled for vacuum work in the extreme ultraviolet, throws practically all the light into the first order and is faster than any other grating in the laboratory. This is important, as the source of light is quite weak and the plates were slow in the red.

We used Wratten and Wainright Panchromatic Plates, treated with a solution of 3.5 cc NH_4OH in 100 cc H_2O to increase the speed and sensitiveness in the red. For the grating we used Wratten and Wainright Panchromatic Films, treated in the same way. The quartz exposure was two hours and the grating exposure six hours. All the lines in Table I except the longest were obtained on both instruments. The longest line appeared only on the quartz plate when heavily exposed. Its wave-length is computed by the Hartman interpolation formula and is accurate to about 1 A. The line at λ 6772.3 is very broad, perhaps double, and is accurate to about 5 A. The other lines are accurate to .1 A. The copper and zinc lines from a brass arc photographed on each side of the fluorine lines served for comparison. No lines whatever appeared in the violet, but weak lines might have been present and covered up by the nitrogen bands. The lines in the red follow in international units.

As previously mentioned, a set of bands shading towards the red and supposed to be due to carbon tetrafluoride was photographed

TABLE I

Porlezza		Smythe		Moissan	
	Int.		Int.		Int.
6239.75	10	6239.4	10	623	Strong
6348.73	10	6348.8	9	634	Strong
6413.95	10	6414.1	8	6405	Strong
6691 24	2	.		.	.
6775.38	6	6772.3d?	2	677	Strong
		6834.1	2	6835	Medium
		6855.3	6	6855	Medium
		6868.8	2	6875	Medium
		6901.6	2	.	.
		6909.1	1	691	Medium
		7034.	1	704	Medium

in the first tube. The approximate position of the heads of these bands is as follows:

TABLE II

	Int.		Int.
6525	10	5745	8
6500	5	5411	5
6209?	0	5105	3
6108	10	4829	1
5860	1		

In conclusion it may be said that fluorine has a characteristic spectrum in the red which is well established but that in the violet the situation is still confused. Apparently it has no spectrum in the green and yellow. Our plates, showing only fluorine and nitrogen, were blank in this region. It may be that a more powerful discharge than was possible with our tubes will bring out the violet lines.

Thanks are due Mr. Bowen and Dr. Aronberg, who assisted in manipulating the apparatus and in computing, and special thanks are due Dr. Gale, who supervised these investigations and whose suggestions have been invaluable.

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