BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 693—695 (1969)

Emission Spectrographic Analysis of Metal Solid Samples with Plasma Jet Flame. I. Application of Nitrogen Plasma Flame*1

Kichinosuke Hirokawa and Hidehiro Gotô

The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai

(Received June 20, 1968)

A small plasma jet burner for direct excitation of metal solid samples was developed. The optimum operating conditions are as follows; d.c. arc current about 15 A, flow rate of nitrogen tangentially introduced gas about 1.5—2 *l*/min, and that of atomizer gas about 3.5—4 *l*/min. The limit of detection of some elements were determined with solution samples. Satisfactory calibration curves were also obtained for analyses of alloying elements in some solid form alloys.

For the plasma jet flame of emission spectroscopic source,1) argon or helium gas are used as plasma gas, and a high current of approximately one to a few hundred amperes are employed to excite solution samples. They can be also excited by wall stabilized d. c. arc plasma. Further in usual solution methods, the preparation of standard samples is not necessary. For the solution method, however, the effects of water (solvent), acid, alkali and impurities in the solution on the property of plasma flame must be considered. Therefore, sometimes, the direct excitation of solid sample is desired, and a plasma burner for solid samples was assembled. The small burner developed in our laboratory works with the usual power supply for spectrographic d. c. arc. Nitrogen was employed as tangentially introduced gas and as atomizer gas, so that temperature of plasma flame becomes considerable low, and spectra of low back ground and sharp atom lines are obtained. After the limit of detection for some elements had been studied with solution samples, application of this plasma flame to the analyses of solid metal samples was tried.

Experimental and Results

Instruments. The spectrograph was Shimadzu's Fastie-Ebert type spectrograph GE-340 with a grating of 3000 Å blased. The excitation source was the d. c. arc power supply of Shimadzu High

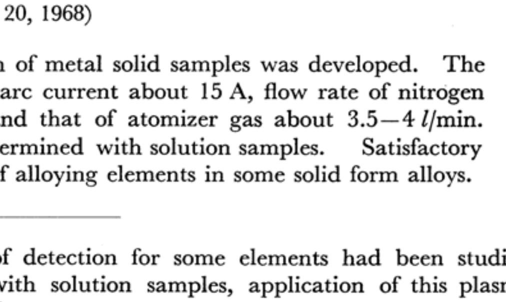

Fig. 1. Cross sectional drawings of plasma burner used.

---

*1 This paper was read at the 21th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

1) E. Kranz, "XII Colloquium Spectroscopicum Internationale, Exeter," Hilger & Watt, London (1965), p. 574.

Precision Source Unit. The cross sectional drawing of the burner is given in Fig. 1 and photographs of its before and after assembling are shown in Fig. 2.

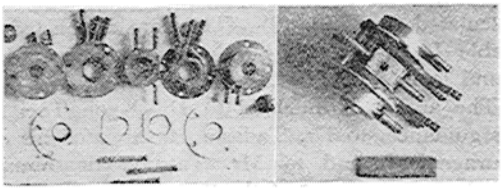

Fig. 2. Plasma burner before and after assembling.

Characteristics of the Plasma Burner and Tests with Solution Sample. The optimum operating conditions of the nitrogen plasma burner must be strictly controlled. An example of good condition is shown in Table 1. With tangentially introduced gas flow rate of about 2 *l*/min, condenser voltage of about 230 V and arc current of 15 A, a stable flame as Fig. 3 was obtained. With a flow rate of below about 1 *l*/min, however, a small flame as Fig. 4 and with a flow rate of over 2.5 *l*/min, a turbulent flame as Fig. 5 was obtained. Then the properties of plasma flame obtained with

TABLE 1. AN EXAMPLE OF OPERATING CONDITION OF PLASMA JET BURNER*

Flow rate of tangentially introduced gas (*l*/min)	Condenser voltage (V)	Arc current (A)	Arc voltage (V)	*Cf.*
1.0	215	16	65	Fig. 4
1.3	215	15	65	
1.5	220	15	74	Fig. 3
1.9	230	15	80	
2.3	228	14	110	Fig. 5

* Primary voltage: 200 V
Flow rate of atomizer gas: 3.5 *l*/min.

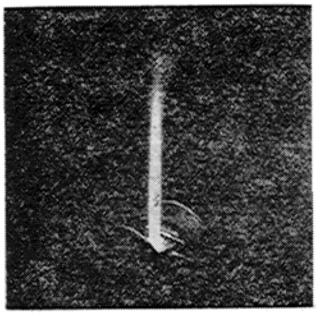

Fig. 3. Plasma flame obtained with an optimum condition.

Fig. 4. Short plasma flame obtained with small flow rate of tangentially introduced gas.

Fig. 5. Turbulent plasma flame obtained with large flow rate of tangentially introduced gas.

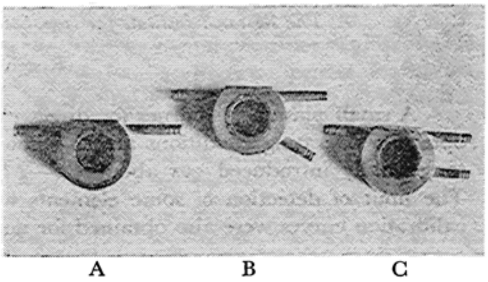

Fig. 6. Three types of center parts of plasma burner examined.

TABLE 2. DETECTION LIMIT OF SOME ELEMENTS IN μg/m*l*

Center part of burner used	A	B	C
Mode of sample charging	Vertically to the axis of plasma flame	Into center part of plasma core	Into the same direction of tangentially introduced gas.
Flow rate of tangentially introduced gas (*l*/min)	1.9	1.5	1.5
Flow rate of atomizer gas (*l*/min)	2.0	4.0	4.0
Al I 3961.5 Å	18	1.4	1.1
Mn I 4031 Å	4.5	1.3	1.2
Fe I 3581 Å	6.7	1.0	1.4
Fe I 3720 Å	2.7	0.95	1.1
Co I 3453.5 Å	4.4	0.92	1.1
Ni I 3414.8 Å	4.5	1.3	1.5
Pb I 4057 Å	11.0	—	1.2

three modes of sample charging (*cf.* Fig. 6 and Table 2) were tested. One tenth normal nitric acid solution of each element in Table 2 was introduced into the plasma flame with an ultrasonic nebulizer, and limits of detection[2] of the elements were studied under optimum conditions as shown in Table 2 in each case. The measurements were carried out by photographic method with slit width of 50 μ and exposure time of 90 sec. Fuji spectrographic photoplates were developed with F.D. 131 at 20°C for 4 min. The discharge conditions were as follows; primary excitation voltage 200 V, condenser voltage 230—240 V, arc current 13—14 A. The coefficient of variation for iron of 0.8 mg/m*l* with Fe I 3720 Å was about 5 per cent. When the solution was introduced into the flame, the flame temperature, measured with the two line method, was around 5500°K.

Application to Metal Solid Samples. In the present experiment, pin-form metal samples were employed as anodes (*cf.* Fig. 1). The operating conditions were the same as the case of c in Table 2, but the flow rate of atomizer gas was 3.5 *l*/min. The time-intensity curve for chromium in chromium steel was obtained as given in Fig. 7-a, and those for chromium, niobium and molybdenum in S-816 alloy (Mn: 1.5, Cr: 20.0, Ni: 20,0, Co: 43.0, Mo: 4.0, W: 4.0, Nb: 4.0, Fe: 3%) were as in Fig. 7-b. After 30 sec pre-discharge, a nearly constant spectral line intensity ratio was obtained in each case. The calibration curve for chromium in chromium steel was prepared under the following conditions: sample 15 mm in length, 5 mm in diameter, polarity anode, excitation 230 V and 15 A, tangentially introduced gas flow rate 1.5 *l*/min, atomizer gas flow rate 3.5 *l*/min, slit width of the spectrograph 30 μ, pre-discharge time 30 sec and exposure time 10 sec. A calibration curve with good linearity was obtained in a wide concentration range of chromium in steel (Fig. 8).

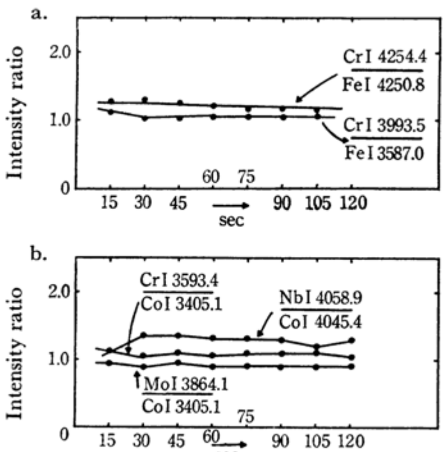

Fig. 7. Time-intensity curve for Cr in Cr-steel (a) and of some elements in S-816 alloy (b).

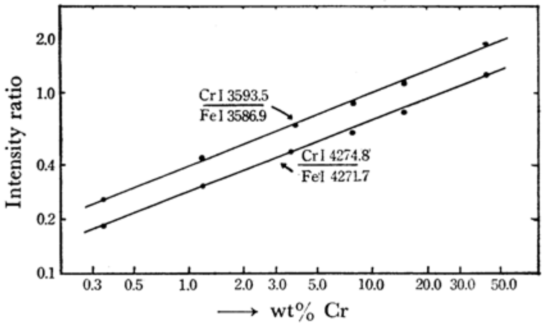

Fig. 8. Calibration curve for Cr in Cr-steel.

In this case the plasma temperature was about 6100°K. For the small amounts of elements in aluminum alloys, time-intensity curves were given as shown in Fig. 9 and the calibration curve for iron in aluminum alloy was given as in Fig. 10.

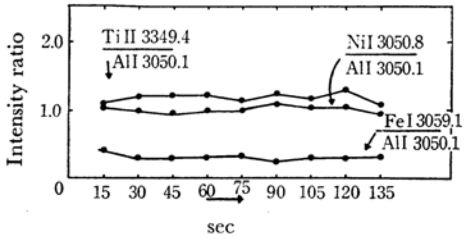

Fig. 9. Time-intensity curve for Ti, Ni and Fe in Al.

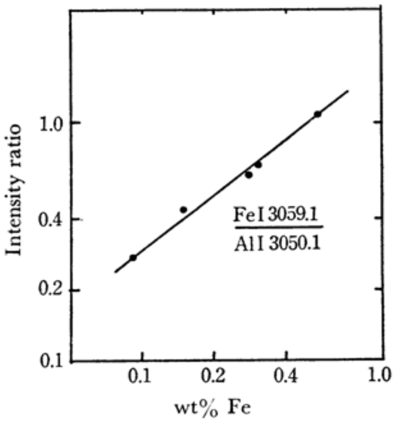

Fig. 10. Calibration curve for Fe in Al.

In this case, however, the operating conditions were the same except the exposure time of 15 sec. In the analyses of aluminum alloys with this nitrogen plasma flame, aluminum reacts with nitrogen and sputters as aluminum nitride, so that the precision for the determination of alloying elements in aluminum alloys is not satisfactory.

---

[2] H. Kaiser, *Spectrochim. Acta*, **3**, 40 (1947).