

Determination of Fluorine, Chlorine, Bromine and Iodine by Barrier Discharge Radiofrequency Helium Plasma

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A determination method of fluorine (F), chlorine (Cl), bromine (Br) and iodine (I) by a barrier discharge radiofrequency helium plasma-atomic emission spectroscopy was developed. A borosilicate glass was wrapped by two copper film electrodes, one of which was earthed, and the other was supplied with a radiofrequency high voltage (98 kHz, 3.2 kV), resulting in a discharge inside of the tube. An optical emission from the discharge tube was introduced to a charge-coupled device (CCD)-spectrometer through an optical fiber, and was monitored in the wavelength range of 730 - 960 nm. The emission lines of F (733.2 nm, 739.9 nm), Cl (833.3 nm, 837.6 nm, 858.6 nm, 894.8 nm, 912.1 nm, *etc.*), Br (827.2 nm, 882.5 nm, 889.8 nm, 926.5 nm, *etc.*) and I (905.8 nm) were observed. The linearity of the calibration was determined for F and Cl over the range of 1 - 10 µg, and for Br of 0.1 - 1 µg. The relative emission intensity was in the order of Br > I > Cl > F.

The problem of organic chlorinated compounds, such as dioxins, discharged from combustion have been increasing. However, since the analysis of dioxins is very expensive and takes a significant time period, daily monitoring of them is practically impossible. Therefore, an effective dioxin-indicator of low cost and of rapid response is now needed. One of the proposed methods is to measure the total organic halogens (TOX).¹

Previously, workers have applied an aqueous adsorbable organic halogens (AOX) measurement technique to gas samples. However, the procedure was found to have some defects: possible contamination through handling and a considerable halogen blank in the activated carbon, itself. Consequently the sample volume should be larger than 1 m³. From a practical standpoint, a smaller sample size and a simpler procedure is desired.

In the conservative AOX measurement, halogens are detected by coulometry using a deposition reaction of silver ion and halogen ions; therefore, neither fluorine detection nor an element-selective determination is possible. However, spectroscopy is element-selective, besides being highly more sensitive than coulometry.

A helium (He) discharge provides a stronger exciting energy than an argon (Ar) plasma; hence, a He plasma has been applied as an atomic emission detector for organic elements in gas chromatography, being a commercially available microwave induced plasma (MIP).²

On the other hand, a radiofrequency discharge plasma was proposed by Rice *et al.*³ and was practically applied by Pedersen-Bjergaard *et al.*⁴ Those apparatuses involved a quartz tube supported by a metal nut screw and an electrode at the outlet of the tube, between which a radiofrequency discharge was maintained with He flow. The optical emission collected by the side-on mode was spectrally monitored for halogen emission lines in near-infrared (NIR) region, the advantage of which over the visible area was confirmed by Rodriguez *et al.*⁵ Lepkojus *et al.*⁶ developed a radiofrequency helium glow discharge plasma (RFP), enabling an end-on monitor by using a ring electrode at the outlet of the discharge tube.

However, the contact of sample gas to the electrode resulted in a deterioration of the electrode. Therefore, it is desired to be placed outside of the tube so as to have no contact with the sample gas. As a solution, we developed a barrier discharge RFP consisting of two copper film electrodes outside of the discharge tube, between which a He glow discharge was maintained by a radiofrequency high voltage. The optical emission was collected by a flexible optical fiber with an end-on alignment into and introduced a spectrometer equipped with charge-coupled device (CCD) (replacing the monochromator). The system enabled simultaneous spectrum observations.

Experimental

Barrier discharge radiofrequency helium plasma

The apparatus is described in Fig 1. A borosilicate glass (6 mm i.d.; 8 mm o.d.) was wrapped by two copper films; one functioned as an earth electrode (width 25 mm), and the other as a high voltage (with 20 mm); with an interval of 10 mm. The earth film was connected to the earthed optical bench frame (Spindler & Hoyer, Germany). A radiofrequency impulse high voltage (98 kHz, 3.2 kV, Haiden, Japan) was supplied to the

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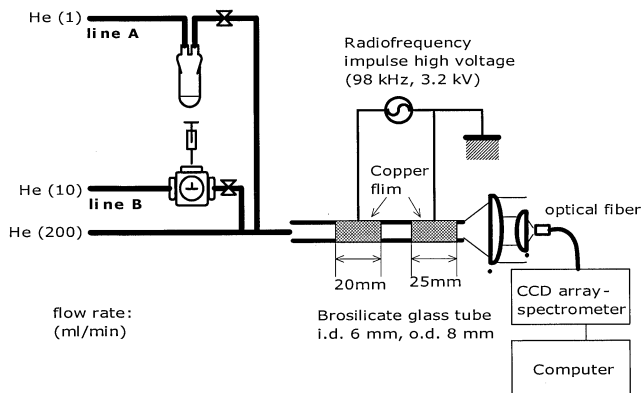


Fig. 1 Experimental apparatus. A gaseous sample was introduced either continuously (line A, vaporization) or by syringe injection (line B).

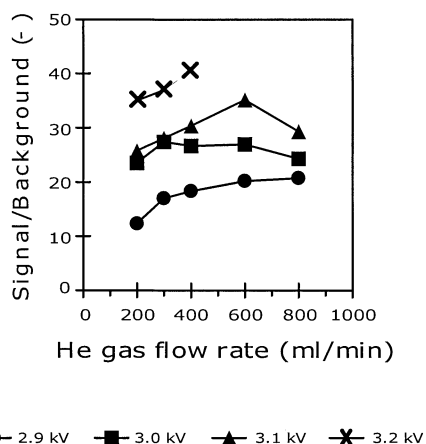


Fig. 2 Signal/background dependence on the high voltage and the He gas flow rate. As the Cl source, 1,1,1-trichloroethane diluted with ethanol was placed in an ice-cooled test tube (line A). The emission line of Cl at 837.6 nm was monitored as the signal, while a wavelength of 836.2 nm was used as the background. A voltage higher than 3.3 kV and more He flow at 3.2 kV caused the risk of a short circuit through the glass discharge tube; hence, 3.2 kV-200 ml/min was chosen for the sake of stability.

high-voltage film. Helium plasma gas (200 ml/min) was introduced from the high-voltage side and emitted out.

Sample introduction was carried out by either of two ways: continuous introduction (line A, sample gas flow 1 ml/min) or syringe injection (line B, 10 ml/min).

Optical system

As described in Fig. 1, the optical emission from the outlet of the discharge tube was collected by a collimator placed *ca.* 10 cm apart, and transferred through optical fiber to the CCD-spectrometer (Ocean Optics, S2000, spectral range 730–960 nm, FWHM 0.6 nm) connected to a PC.

Reagents

The reagents used were 1,1,1,3,3,3-hexafluoro-2-propanol for the fluorine (F) source, tetrachloromethane, dichloromethane, trichloromethane and 1,1,1-trichloroethane for chlorine (Cl), bromoethane for the bromine (Br) source and iodomethane for the iodine (I) source.

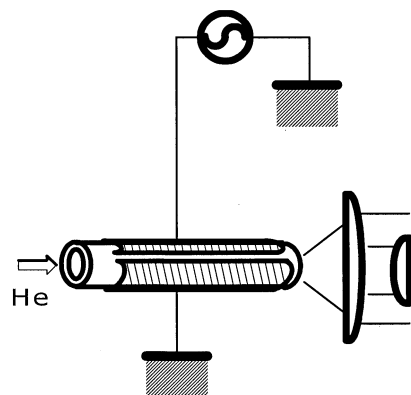


Fig. 3 Glow discharge emitting no chlorine line. This type of plasma easily maintained a glow discharge. However, it emitted no Cl line. Besides, the brightness was lower than the plasma shown in Fig. 1.

Procedure

Using line A. A volatile organic chlorinated compound was placed in a test tube (10 ml) immersed in an iced bath. While supplying 1 ml/min of He, the compound was constantly volatilized and introduced to the discharge tube.

Using line B. An organic halogenated compound was diluted in a gas mouse (100 ml) filled with helium, from which sample gas was drawn by a gas-tight syringe. For a calibration study, 3.6 μ l of 1,1,1,3,3,3-hexafluoro-2-propanol (MW = 168.0, density 1.62 g ml⁻¹) was diluted in the gas mouse, from which taking 25, 50, 125, and 250 μ l was equivalent to 1, 2, 5, 10 μ gF. The same procedure was applied to other reagents, while adjusting the mass range to meet the highest CCD response to 3000–4000 count s⁻¹.

Results and Discussion

Observation

By supplying He gas and a high voltage, a discharge was easily initiated. A homogeneous plasma was maintained between the film electrodes inside of the tube. The color of the plasma was dark blue-violet at 2.0–2.5 kV, light blue-violet at 2.5–3.0 kV, and pinkish blue-violet at 3.0–3.4 kV. The heat emission was so slight that the tube could be hand-touched just after ceasing of the discharge.

However, if the voltage was increased to as high as 3.5 kV, an orange-colored region was built in the discharge tube; moreover, the 10 min, the plasma resulted in a spark through borosilicate glass, making a pin hole (a safety circuit automatically shut down the power). The color was supposedly due to the sodium included in the borosilicate tube, or to the emission of neon as a trace impurity in He gas.

The signal/background ratio (*S/B*) was examined by varying the radiofrequency high voltage and He gas flow, supplying 1,1,1-trichloroethane through line A. The signal and background were the emission at wavelengths of 837.6 nm and 836.2 nm, respectively. The result is given in Fig. 2. By raising the discharge voltage from 2.9 kV to 3.2 kV, *S/B* was increased. However, both a higher voltage than 3.3 kV and a larger He gas flow than 400 ml min⁻¹ with 3.2 kV often resulted in the short circuit described above, after light-on had occurred for a while. Consequently, the condition of 3.2 kV and 200 ml min⁻¹ was chosen, while considering the stability.

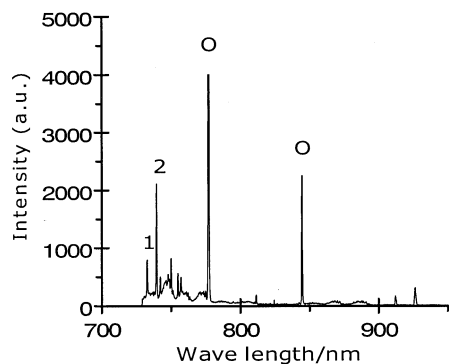


Fig. 4 Emission spectrum of fluorine. 1, 733.2 nm; 2, 739.9 nm. The lines at 777 and 845 nm are oxygen emission.

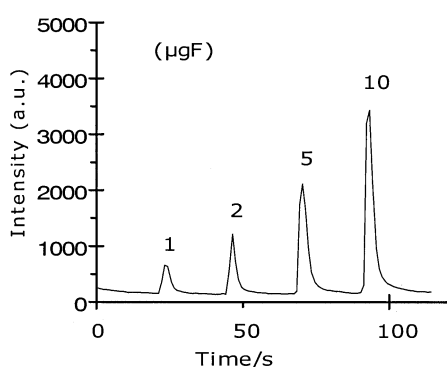


Fig. 5 Time series profile of the stepwise injection of fluorine, monitored at 739.9 nm. As the fluorine source, 1,1,1,3,3,3-hexafluoro-2-propanol was used.

It is noteworthy that all kinds of He glow plasma will not always emit the halogen line. For example, the discharge tube shown in Fig. 3 could initiate a glow discharge very easily; nevertheless, no chlorine emission line was observed. The color was different; the plasma shown in Fig. 1 was bright, whereas that in Fig. 3 was transparent light blue.

Spectrum and sensitivity

Organic halogenated compounds were sequentially introduced by syringe injection (line B). Figures 4 and 5 show the spectrum and time profile of the emission line of F (1,1,1,3,3,3-hexafluoro-2-propanol was used as the sample), respectively. Two fluorine emission lines (wavelengths of 733.2 and 739.9 nm) appeared; besides, good linearity of the calibration was obtained in the range of 1 - 10 μgF .

In our previous work using a ring electrode placed at the outlet of the discharge tube, a significant peak tailing appeared, which made the calibration linearity poor.⁶ It was considered to be due to a reaction between F and the discharge tube. In the present barrier discharge RFP, however, the reaction was suppressed due to the low temperature of the discharge tube.

In addition, two other known F emission lines (685.6 and 690.2 nm) were out of the spectral range of the used spectrometer.

Other halogen element lines were observed at the wavelengths listed in Table 1. Good linear calibration was obtained for Cl and Br by monitoring the lines indicated by * in Table 1. Poor linearity for I was supposed to be due to the adsorption of iodomethane to the transfer line.

Table 1 Emission lines of halogens

F	(685.6)	(690.2)	733.2	739.9*	
Cl	833.3	837.6*	858.6	894.8	912.1
Br	827.2*	882.5	889.8	926.5	
I	905.8*	(965.3)	(973.1)		

unit: nm.

The wavelength marked with * was monitored in a quantity-response study (using line B). The wavelength in parenthesis was out of the range of the used spectrometer.

Table 2 Response factor of different organic chlorinated compounds

Tetrachloromethane	CCl_4	1.00
Dichloromethane	CH_2Cl_2	1.04
Trichloromethane	CHCl_3	0.94
1,1,1-Trichloroethane	CH_3CCl_3	1.02

Based on the peak height by syringe injection (line B).

Response of various compounds

In order to check the response of various compounds, four Cl-containing reagents (tetrachloromethane, dichloromethane, trichloromethane and 1,1,1-trichloroethane) were injected through line B. Comparing the peak height, the responses of all compounds were the same (Table 2), namely, the response factors were 0.94 - 1.04 while taking tetrachloromethane as the unit. Consequently, the response was considered to be independent of the compound's structure.

Response of each halogen

The response of each halogen was different, affected by the excitation efficiency. The CCD counts number divided by the common element mole were calculated from the elemental signal (S) subtracted background signal (B) of 1 μg injection (Table 3). Comparing the highest line of each element, the CCD counts were in the order $\text{Br} > \text{I} > \text{Cl} > \text{F}$. Referring to the ionizing potential⁷ it was revealed that the smaller was the energy extracting the electron, the stronger was the emission, although the order of Br and I was reverse.

Conclusion

A low-cost and simple barrier discharge radiofrequency helium plasma (barrier discharge RFP) equipped with a CCD-spectrometer system was able to determine F, Cl, Br and I. Current additional work includes studying the property of the plasma and developing on exhaust gas TOX determination while adapting a thermal desorption tube.

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Table 3 Signal intensity of halogens

Element	Ionizing energy/eV	Elemental line/nm	S + B, counts	B, counts	S, counts	Signal from 10 ¹⁴ elements, counts
F	17.4	733.2	390	179	212	0.7
		739.9	823	185	638	2
Cl	13	833.3	78	26	52	0.3
		837.6	610	22	589	3.5
		858.6	140	33	107	0.6
		894.8	498	16	482	2.9
		912.1	1302	39	1263	7.5
Br	11.8	827.2	1432	28	1404	18.7
		882.5	1666	47	1619	21.6
		889.8	3034	68	2967	39.6
I	10.5	905.8	641	25	616	13.3

S, signal; B, background. The background was the average of counts of both neighbouring sides (*ca.* 1.5 nm apart from the elemental line).

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