Atmospheric Pressure Barrier Discharge Helium Plasma for Halogen Determination with Optical Emission

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An atmospheric pressure - barrier discharge helium plasma was built with a quartz tube wrapped with two copper film electrodes. Supplying the radiofrequency impulse high voltage (98 kHz, 3.4 kV) and helium gas flow (400 ml min^{-1}) to the tube, a glow discharge with no contact of sample gas and electrodes was maintained. Introducing organohalogencompounds to the plasma, emission lines of F (733.2 nm, 739.9 nm), Cl (833.3nm, 837.6nm, 858.6nm, 894.8nm, 912.1nm), Br (827.2 nm, 882.5 nm, 889.8 nm, 926.5 nm) and I (905.8 nm) were observed. The plasma is so robust as to accept more than 10 μg halogens, with a working calibration range of less than 0.1 ~ several μg. The relative Cl response of several aliphatic organochlorocompounds were the same.

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For the monitoring and controlling of possible pollution sources, group parameter *e.g.* organic halogen is very practical because of its inclusivity and quickness. So far, organic halogen group parameters has been determined by combustion - coulometry, which has nor elemental selectivity neither adequate sensitivity. One of the improving strategy is replacing the detection process by atomic spectroscopy[1,2].

Commercial plasma able to excite halogens was microwave induced plasma (MIP) for GC[3], however, the MIP was not enough robust for direct introduction of sample. At least, the detector for group parameter should endure μg amount of organics.

Helium glow plasma - OES has been introduced as halogen element selective detection for GC by several workers[4-6]. The advantage of those systems is the utilization of 700-1000 nm region, in which spectral interference is so few that a low resolution specrtometer (FWHM 1 nm) is applicable.

Those plasma were maintained in a quartz tube attached to metal electrodes. The metal surface might be damaged by contacting with sample gas and air in the long run. In that point those plasma might be inferior to MIP, the discharge of which is confined in a quartz tube with no contacting electrode. However, in the plasma industry, barrier discharge, inserting an nonconductor between gas and electrode, is currently utilized. Importing those technique to the analytical plasma, a helium glow discharge with no contact of gas and electrode can be build.

Experimental

Apparatus

The experimental instrument and the condition parameters are given in Fig. 1 and Table 1. The discharge tube and optical emission collimator were arranged on Spindler & Hoyer frame (Germany). A quartz tube (i.d. 6 mm and o.d. 8mm) wrapped with two copper film electrodes (width 25 mm, distance 10 mm, Nitto Denko, Japan) was used as a discharge tube. The discharge region of the quartz tube was narrowed to i. d. 2 mm. The discharge tube was placed with two silicon rubbers in the frame structure. Helium gas (99.99 %, normal grade, Osaka Sanso, Japan) of 400 ml min^{-1} was supplied to the discharge tube via a flow meter (Kofloc, Japan), after which a gas injection port made of three way PTFE valve, and a glass chamber (47 ml) were placed. Gas tube was made of PTFE and Viton®. A radiofrequency impulse high voltage (3.2 kV, 98 kHz, Haiden, Japan) was supplied to the copper electrode at the downstream side, while the other electrode was earthed.

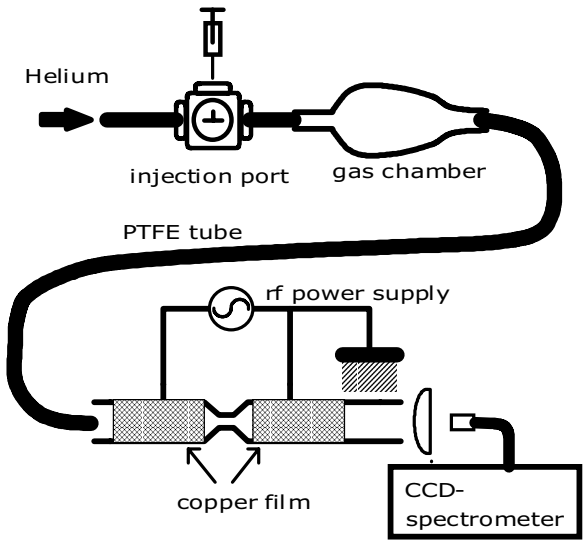

Fig. 1 Experimental instrument

The optical emission from the discharge tube was collected to an optical fiber (i.d. 400 μm, Ocean Optics, America), which is connected to a CCD-spectrometer (spectral range 520 - 940 nm, 0.9 nm resolution, USB2000, Ocean Optics, America).

Table 1 Constituents and parameters of the instrument

Constituents and parameters	Detail and values
Discharge tube/ mm	Quartz tube, 6 i.d. and 8 o.d.
Narrowed i.d. of the plasma region/ mm	2 (1, 6)
Electrodes/ mm	Copper films adhered to the outside of the tube, width 25, distance 10
Plasma gas	Helium, normal grade, 99.99%
Gas flow rate/ ml min^{-1}	400(200, 300, 600, 800)
Power supply	Haiden impulse – radiofrequency
Frequency/ kHz	98
Voltage/ kV	3.3 (2.7 - 3.4)
Spectrometer	USB 2000 (Ocean Optics)
Spectral range/ nm	520 – 940
Resolution(FWHM)/ nm	0.9

The studied parameters are in the parenthesis.

Reagents

All reagents used were of analytical reagent grade. 1,1,1,3,3,3-hexafluoro-2-propanol (Wako, Japan), bromoethane (Wako) and iodomethane (Wako) were utilized as fluorine, bromine and iodine source, respectively. As chlorinated compounds, dichloromethane (Wako, Japan), trichloromethane (chloroform, Ishizu, Japan), tetrachloromethane (carbon tetrachloride, Kishida, Japan), trichloroethylene (Supelco, America) and tetrachloroethylene (Supelco, America) were used.

The reagent was diluted in a volumetric gas mouse filled with helium, from which sample gas was drawn by a gas tight syringe (Terumo, Japan). example, 8.0 μl of 1,1,1,3,3,3-hexafluoro-2-propanol (MW= 168.0, 99 %, density 1.62 g ml^{-1}) was diluted in a 122.4 ml gas mouse, from which taking 100 μl is equivalent to 7.1 μg of fluorine atom.

Procedure

Providing the discharge tube with helium gas flow, the rf high voltage was supplied. The discharge started by self-ignition. The sample gas was injected from the injection port.

Results and Discussion

Emission Spectrum

In the background spectrum, the eminent observed emission lines were of He (667.8 nm, 706.5 nm, 728.1 nm), O (777.4 nm, 844.6 nm) and H (656.2 nm). The elements H and O were supposed to be the impurities in the normal grade helium gas (99.99 %).

The spectrum when bromoethane injected is given in Fig. 2.

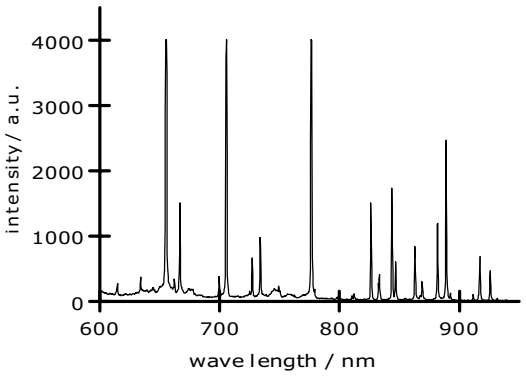

Fig. 2 Spectrum of the plasma (bromoethane was injected)

The CCD integration time was 100 msec. The bromine emission lines of 827.2 nm, 882.5 nm, 889.8 nm, 926.5 nm and others were observed. In the same way, F lines (685.6 nm, 733.2 nm, 739.9 nm), Cl lines (833.3nm, 837.6nm, 858.6nm, 894.8nm, 912.1nm) and I line (905.8 nm) were observed.

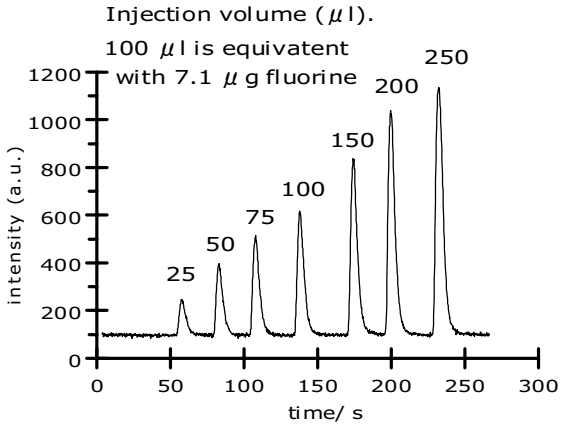

Fig. 3 Calibration injection of 1,1,1,3,3,3-hexafluoro-2-propanol (emission line of 739.9 nm was monitored)

The calibration injection of F is given in Fig. 3. A good linearity was obtained in the range of 2~ 20 μgF. Note that no tailing occurred, in contrast to our previous work[7]. The reason is the molecular temperature of the discharge tube was not so high that no chemical reaction with glass surface and fluorine atom occurred. Besides, the other advantage of this plasma was its robustness. Regardless of more than 20 μg of organic matter injected, no plasma interference was observed.

Property of the plasma

Material of discharge tube. In the beginning of this study, a borosilicate tube was used as a discharge tube. However, the discharge power in the borosilicate glass had increased along the time, even if no power adjustment was given. Namely, the background signal increased several minutes after the ignition, consequently an arc discharge penetrating the borosilicate glass occurred, making a small hole on the glass tube (The rf generator stopped by its safety circuit). The phenomena indicates that the electron in the borosilicate glass was driven by the rf high voltage and the vibration increased along the time, resulting in "electron rush".

Replacing the borosilicate glass by a quartz, the arcing problem was solved. The discharge voltage of quartz tube could be set higher than borosilicate tube for several hours, at least. The reason is supposed to be the bond energy of electron in quartz is larger than that in borosilicate.

Helium gas flow rate. The effect of the helium gas flow rate on the signal/background ratio of Cl emission line (837. 6nm) was studied. The result given in Fig. 4 indicated the constant range between 300 to 600 ml min^{-1}. Hence, 400 ml min^{-1} was selected.

Narrowment of the plasma region. It was attempted to constrict the plasma by making the discharge region narrow, expecting the excitation efficiency higher. Three types of the discharge tube: 1 mm, 2 mm and 6mm i.d. (straight tube) between the electrodes were examined with various voltage. The result is given in Fig. 5. The narrower the plasma region was, the higher S/B ratio was, at

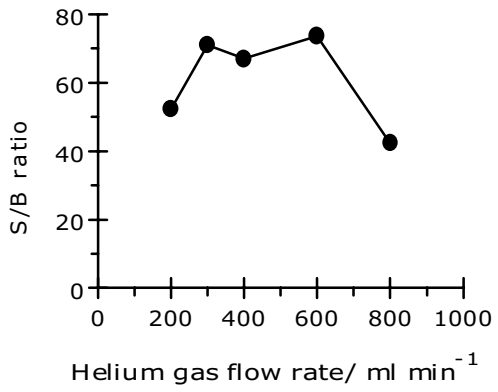

Fig. 4 Effect of helium gas flow rate on signal – background ratio

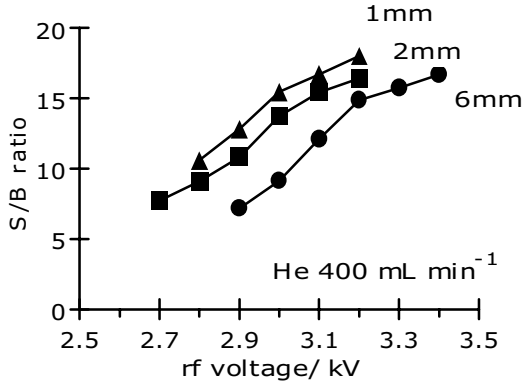

Fig. 5 Effect of narrowed part diameter on signal – background ratio

the same voltage. However, S/B ratio of all three tubes reached to the common ceiling.

Nevertheless, the narrowment of the plasma region brought a valuable result with regard to the heat on the electrodes. Namely, a narrowed tube could maintain a higher plasma density than a straight tube with a relative lower electric current. However, if that part was too narrow as 1 mm i.d., the self-ignition became difficult. Consequently, a quartz discharge tube of i.d. 6 mm and o.d. 8mm, the plasma region of which is narrowed to 2 mm i.d., was employed.

Table 2 Relative Cl response of various organic chlorinated compounds

Compound	relative Cl response
Dichloromethane	0.99
Trichloromethane	1.03
Tetrachloromethane	1.00
Trichloroethylene	0.91
Tetrachloroethylene	0.96

Low density plasma emitting no halogen line. Not all the helium barrier discharge emit halogen lines. In the beginning of this study, a plasma between two parallel film electrodes was examined, however, it resulted in no halogen line emission.

Response of various compounds. The response of different volatile organic chlorinated compounds were compared. Five reagents were diluted in each volumetric gas mouse and quantitatively injected to the injection port five times. The relative response per amount of Cl atom of the compounds are tabulated in Table 2. Setting the response of tetrachloromethane to be 1.00, the relative response of other five compounds ranged between 0.91 and 1.03. Consequently, volatile aliphatic chlorinated compounds are viewed to be the same response.

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