CHARACTERISTICS OF FLUORINE DETERMINATION BY BARRIER DISCHARGE ATOMIC EMISSION SPECTROMETRY

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Abstract

To control organic fluorinated compounds, the group parameter approach "total organic fluorine" is effective. Fluorine determination in gaseous sample can be carried out by barrier discharge radiofrequency helium plasma - atomic emission spectrometry with detection range of 10 ngF to several tens μgF. Some difficulties of F determination, compared with Cl and Br, were documented and overcome.

Introduction

Organic fluorinated compounds are widely used and detected in biological and environmental media, to which many analytical approaches are currently applied. In the same way with group parameter "total organic chlorine", measurement of total organic fluorine(F) can be a effective tool to monitor the destruction and to control the emission. One of the promising F determination technique is helium plasma - atomic emission spectrometry, because F excitation potential 17 eV can be exceeded by neither Ar(10 eV) nor Ne(16-17 eV), but by helium (20 eV). In this paper, the practical capability of this method is presented with some drawback properties.

Materials and Methods

Instrumentation

The instrumentation of the barrier helium discharge is in described in the previous paper[1]. The schematic illustration of the experiment with quantitative conditions is given in Fig 1. Briefly, helium gas introduced to a discharge tube(ceramic tube, id 4 mm x od 6 mm, SSA-S, Nikkatoh, Japan), which was equipped with two film electrodes outside of the tube, was turned plasma by radiofrequency high voltage (Haiden, Japan). The matching of the power supply and the discharge tube was adjusted by the manufacturer. Only the power consumption was controllable by laboratory users. The discharge tube was vertically placed instead of horizontally, in order to minimize the leak-in air.

The gas sample was introduced via the sample injection line with helium gas stream of 100 mL min^{-1}. The emission from the discharge tube was end-on monitored by collimate lens which was connected to spectrometer (HR 2000, Ocean Optics, USA), the resolution of which was 0.2 nm in the range of 700 - 870 nm. The data from the spectrometer was processed by software SpectraSuite(Ocean Optics). Three pixels were monitored as the elemental lines of F(739.9 nm),

Cl(837.6 nm) and Br(827.2 nm).

2,2,2-trifluoroethanol (Tokyo Kasei, Japan) was applied as the standard compound for fluorine. 16 μL of the reagent was injected into a gas mouse(522.3 mL) filled with helium gas. 20 μL of gas from the gas mouse is equivalent with 482 ngF. In the same manner, bromochloromethane(Tokyo Kasei, Japan) was utilized as Cl - and Br standard. 2 μL of bromochloromethane was diluted in the gas mouse(522.3 mL), resulting 40.5 ngCl and 91.3 ngBr in 20 μL gas, respectively.

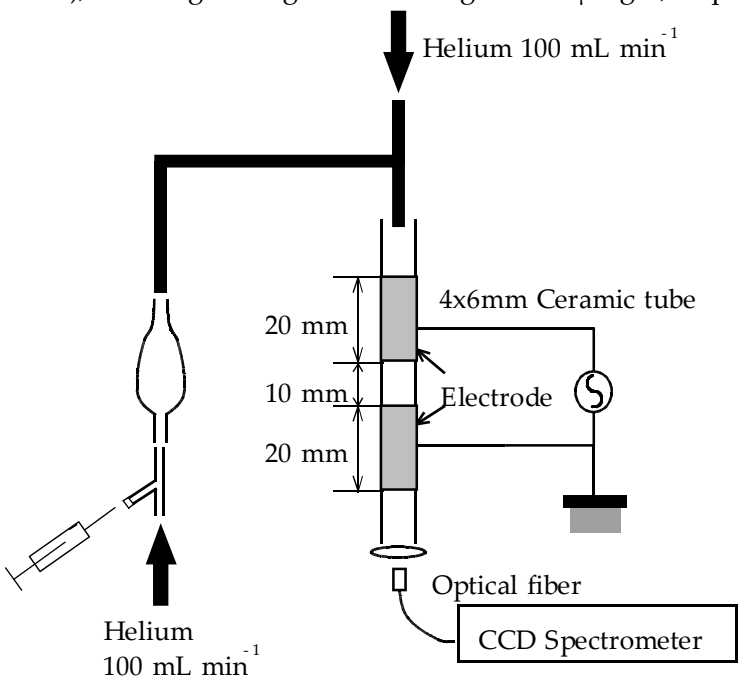

Fig 1 Barrier discharge radiofrequency helium plasma was maintained in a ceramic tube(SSA-S) supplied with 100 mL min^{-1} plasma gas(He) and 100 mL min^{-1} sample injection gas(He). The emission from the discharge was end-on monitored and itroduced to CCD-spectrometer. In order to minimize leak-in air from the outlet of the discharge tube, the tube was vertically placed.

Data evaluation

The monitored signal on the specific wave length was evaluated by intensity and detection limit. The evaluation concept is described in Fig 2. Intensity was expressed by the amount of F, Cl and Br equivalent to S/B value = 1, where "S" and "B" are the elemental and background signals, respectively. The smaller the amount of F, Cl and Br equivalent to S/B = 1 is , the higher the intensity is. The other evaluation aspect "detection limit" is expressed by the amount of F, Cl and Br equivalent to S/N value = 3, where "N" is mean noise.

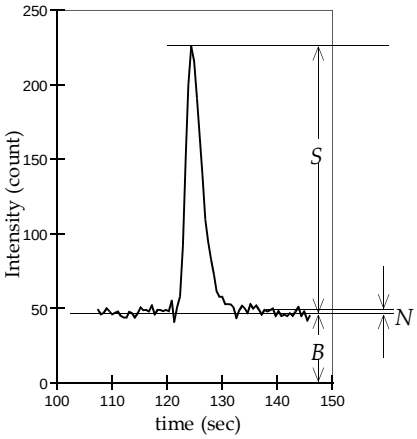

Fig 2 Detected peak was analyzed to signal(S), background(B) and noise(N). Comparing the achieved S/B value with the injected amount, the intensity was calculated as the amount of element equivalent to S/B = 1. The calculation scheme of detection limit (S/N=3) was similar.

Results and Discussion

Intensity and detection limit

The S/B study was summarized in Table 1. About 200 ngF, 10 ngCl and 5 ngBr gave the signal intensity equal to background(S/B = 1). The detection limit was 10 ngF, 2 ngCl and 1.5 ng Br, however, those value are drastically affected by the optical conditions. Recent report by Ohba[2] using DC-microplasma achieved detection limit of 10 pg region. Instead, practical applicable range is more important to actual application. The present discharge endured up to several tens of μgF, Cl and Br injection.

Table 1 Intensity of fluorine, chlorine and bromine in barrier discharge radiofrequency helium plasma - atomic emission spectrometry

	32 W	40 W	46 W
Fluorine	185	181	185
Chlorine	12.5	8.9	7.1
Bromine	6.5	5.2	4.7

ng amount at S/B=1

One of the reason of F determination difficulty compared to Cl and Br was that the elemental line 739.9 nm was neighbored by emission from leak-in air (Fig 3) via the outlet of the discharge tube opened to air. The problem was not true of Cl and Br, whose elemental lines monitored were in the range of 820-840 nm.

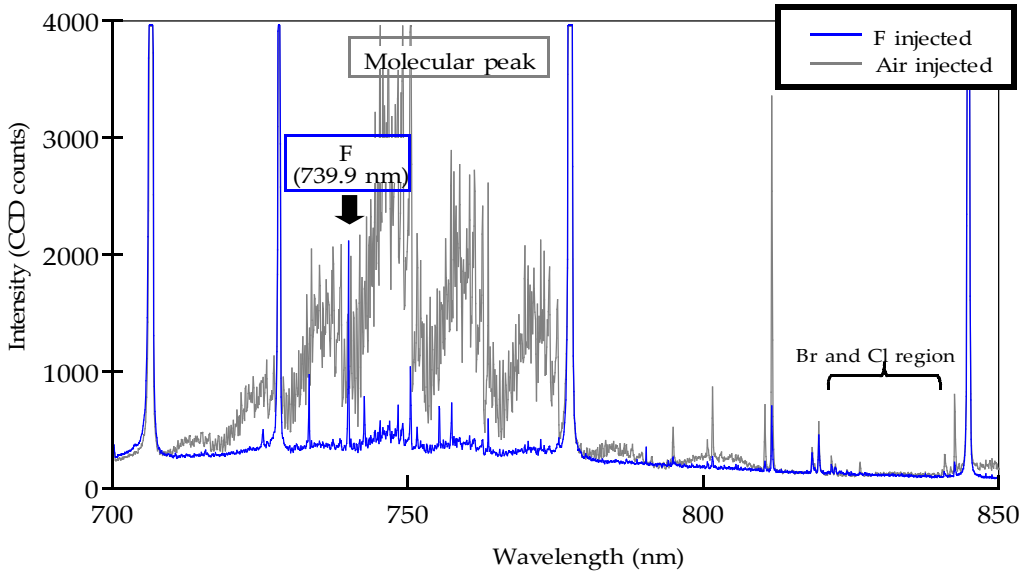

Fig 3 Fluorine line at 739.9 nm is selected as quantification line, however, air(40 μL) injection posed a big molecular emission at 700-800 nm. Namely, background of F determination is not stable. On the other hand, Cl(837.6 nm) and Br(827.2 nm) are not suffered from molecular peak from air.

Interaction with discharge tube
The remarkable characteristics was independence of F-sensitivity from the power consumption, while that of Cl and Br were affected by it. The difference between F and other two halogens were the reaction product with ceramic tube material. Although the ceramic tube SSA-S is very stable, partial reaction with elemental halogens can occur. While $AlCl_3$ and $AlBr_3$ are gaseous in 300 ºC, AlF_3 is in condensed phase. Namely the interaction enhanced by temperature elevation might reduce F in gas, although the plasma density was increased with the temperature.

In our first report about this type of plasma[3], only F peak gave rapid decrease while Cl- and Br peak had smooth decrease. In that instrumentation, the temperature of the discharge tube was as high as to soften the support screw made by Teflon. However, present work made smooth decrease on F-peak with a considerably efficient plasma emitting little heat. The temperature of the surface of the electrode was about 250 ºC, besides the support parts were as low as touchable after plasma extinguish.

In conclusion, barrier discharge radiofrequency helium plasma - atomic emission spectrometry could determine F with a detection limit of 10 ng, S/B = 1 intensity of 180 ngF and endured up to several tens μgF. Moderate power consumption was sufficient to achieve good F line signal. The interaction of F with the inner surface of discharge tube was minimized by low temperature.

References

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