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Abstract: P-11

Speed-up of halogens and sulfur automatic combustion analytical system and application to multi-elemental analysis (3): Reduction of carry over

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An automatic analyzer for organic halogens and sulfur has been developed by coupled combustion/ion chromatography (IC). The system is composed by combustion furnace, absorption unit, automatic sampler (Yanaco) and ion chromatograph (TOA-DKK). The reduction of carry over (blank after NAC-st4 analysis) was examined in this study. We have established a simultaneous micro-determination of organic halogens (F, Cl, Br, I) and sulfur (S), based on conductivity detection after decomposition in this speed-up automatic system using clean air.

1. Introduction

CHN (O) analysis, which is the mainstream for micro organic elemental analysis, can be measured CHN simultaneously and rapidly. On the other, in hetero elements such as halogens (F, Cl, Br, I) and sulfur (S), it has not achieved as simultaneous and high speed analysis for multi-elements. For instance, in case of combustion/ion chromatograph (IC), it is possible case that “element required oxidation” and “element required reduction” are co-existed.

Also in view of the measurement facet, even though the combustion time is shortened, high speed measurement is not attainable if longer chromatogram development time is required. Moreover, in case of continuous analysis for a lot of samples, it is concerned that previously analyzed samples' portion is remained in the phase (so-called “carry-over”).

Thus far, we have realized that efficiency of oxidation/reduction reaction by utilizing oxidation/reduction absorption solutions¹⁾, also high speed analysis method²⁾ as well as ultra-micro analysis method³⁾ for 5 or 6 samples containing 4 halogens and sulfur per hour were established.

As investigation so far is continued, we have considered reduction of carry-over, which is one of the most important subjects being overcome.

Generated gas from the sample, which is produced during combustion process in the combustion system, is adhered at the tube path close to exhaustion outlet of the combustion furnace at downstream side; thus it may cause carry-over. Consequently, it may cause conspicuous disordering of the baseline and its reason is specifically determined. By introducing considerable amount of clean air from the outside of the combustion tube, gas adsorption can be eliminated and carry-over is reduced drastically. This countermeasure enables to implement accurate analysis, even the samples having huge concentration range are analyzed one by one.

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2. Experiment

The system of halogens/sulfur analysis is composed of combustion furnace (HNS-15), absorption unit (HNS-15), auto-sampler (THA-25), manufactured collaboratively by Yanaco LID Company, and ion chromatograph (IC). Overall view of the system is illustrated in [Fig. 1](#), while the measuring conditions are described in [Table 1](#).

Table 1 Measuring conditions

Column :	Shodex IC SI-90 4E (4.0 i.d. x 250mm) by Showa Denko, at 35°C
Moving phase :	3.0mM Na ₂ CO ₃ / 2.0mM NaHCO ₃
Flow rate :	1.2mL/min
Injection amount :	50μL
Detector :	Electric conductivity detector
Carrier gas :	Clean air, 2.0L/min
Moving furnace :	400 to 950°C
Fixed furnace :	1,000°C
Absorption solution :	25mL + 15mL, total 40mL
Absorption solution - ① :	dil. H ₂ O ₂ / NH ₂ NH ₂ , containing pure water
Absorption solution - ② :	dil. H ₂ O ₂ / NH ₂ NH ₂ , containing moving phase

As the specific feature in the system, high consideration for functionality as well as safety conditions are taken into account, by using the open-type combustion tube that the sample introduction part is opened. As for the carrier gas, clean air is applied for in place of gas cylinders (Ar, O₂), so that drastic cost reduction is attainable. For the sample amounts, 2 step measurements can be realized both for micro analysis (1 to 10mg) and for ultra-micro analysis (0.1 to 1.0mg)

As for the IC, ICA-2000 (TOA-DKK) is used, and for sample's weighing, ultra-microelectronic balance, UMX-2 (Mettler) is used. For the combustion standard sample, standard sample for organic elemental analysis (Kishida Chemical) is used, as well as multi-element containing standard sample (NAC-st1, NAC-st2 and NAC-st4), that were collaboratively developed between "Tokyo Metropolitan Industrial Technology Research Institute" and "NAC Techno Service".

NAC-st1 (C₁₂H₈O₂NFCIBrS), NAC-st2 (C₁₂H₈O₂NFBrIS), NAC-st4 (C₁₂H₇O₂NFCIBrIS)
As for the absorption solution, 2 sorts of oxidation/reduction absorption solutions (①,②), shown in Table 1.

The system used in this study was developed in 2002, and due to its high durability, it can be contributing routine analyses of halogens/sulfur even now. Required analysis time sums up to 112 minutes per 10 samples, i.e., about 11 minutes per 1 sample.



Fig. 1 Overall view: Organic elemental analysis system
(Developed in 2002)

3. Experimental results and consideration

3-1. Separation condition for ion species

By adding tungsten oxide as combustion supportive agent, partial tungsten acid is produced during combustion process, and other ion's separation is affected by eluting close retention time. Therefore, effect of column temperature, which affects separation of anion ion species, has considered. (Fig. 2)

At 35°C as the column temperature, ions of SO_4^{2-} , I and WO_4^{2-} are separated in adequate interval.

All ion species are eluted within 10 minutes, and rapid separation was achievable even in addition of combustion supportive agent (WO_3).

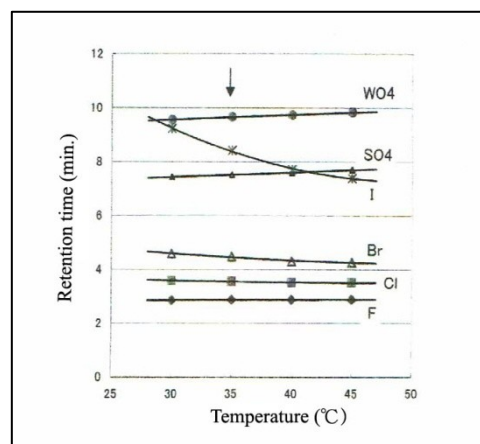


Fig. 2

Effect of column temperature to separation

3-2. Reduction of carry over

The point taking into consideration most in implementing speeding-up and ultra-micronization of CIC method, is contamination in the carrier gas and the influence by carry-over (previous sample is remained in the phase as residue). At upstream side, impurity in the carrier gas is absorbed and removed by washing with conventional washing bottles. Also combustion product is adhered at the tube path close to exhaustion outlet of the combustion furnace at downstream side, and it may cause conspicuous disordering of the baseline and its reason is specifically determined. Thus, in order to prevent adsorption to the combustion part, the method is adopted that considerable amount of clean air is introduced from the outside of the needle tube, too.⁴⁾

As one trial, standard reagent of NAC-st4 is used for simultaneous test for the carry-over. This method enables to obtain the carry-over values for total 5 elements of F, Cl, Br, I and S at just one measurement. Chromatograms of NAC-st4 are illustrated in Fig. 3, and test result of carry-over is shown in Table 2.

Sample	Element	Peak area	Carry-over (%)	
			the 1st blank	the 2nd blank
NAC-st4 (2.068mg)	F	36,988	<0.10	<0.10
	Cl	38,131	0.11	<0.10
	Br	39,716	0.15	<0.10
	I	40,684	<0.20	<0.20
	S	90,973	0.23	0.12

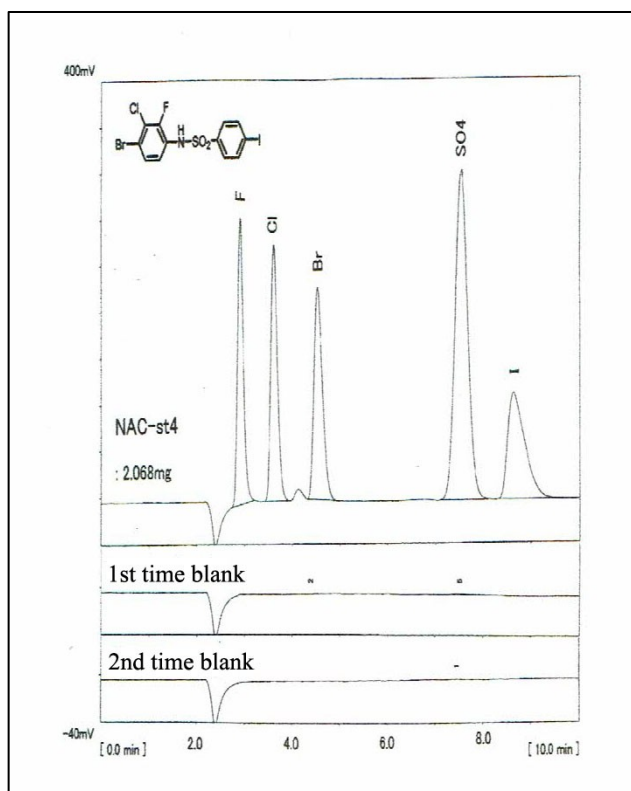


Fig. 3

Ion chromatogram of combustion solution obtained from NAC-st4

In this system, one time washing process by pure water is adopted in the phase of absorption, after sample combustion and injection. Whereas in this carry-over test, blank test is implemented after sample measurement, and detected amount as the blank is regarded as the 1st blank (carry-over). 1st blank (carry-over) values are; S is less than 0.25%, others are less than 0.20%. 2nd blank which is implemented continuously, values in all 5 elements are reduced under detection limit. Furthermore, even measurements are implemented as changing the standard sample amount of NAC-st4, conspicuous deviation of carry-over has not recognized.

3-3. Application example to the actual sample

By looking through the samples, that are submitted from the fields of recent electronics and fuel cell and so forth, various elements containing samples such as boron, phosphorus metal etc. are spread besides previous mentioned 5 elements.

As one example, analysis result of high fluorine compound containing boron and iodine is introduced. (FBI containing compound: $C_{40}H_{18}BF_{20}I$, mw = 1016.25)

Ion chromatograms of FBI containing compound and standard sample of 4-Fluorobenzoic acid are shown in Fig. 4, and analysis results are summarized in Table 3.

No peak of BF_4 ion's retention time (RT) is recognized at 4-Fluorobenzoic acid, while the peak of BF_4 ion is recognized at FBI compound. Hence, BF_4 ion generation is not related to external factor, but even fluorine/boron in the compound were decomposed in the combustion tube, it is presumed that they were reacted each other in the phase, and BF_4 ion was generated eventually.

In order to trap boron selectively before BF_4 generation, BF_4 's complete decomposition was attempted by adding absorption agent (WO_3) or increasing temperature of the combustion furnace, significant improvement was not recognized.

As well, from Table 3, for FBI compound, F analyzed value of 33.1% to F estimated value of 37.4%, while BF_4 analyzed value of 3.3% (as F) is indicated; even adding up these values, still 36.5% of lower value is resulted.

As for the fluorine analysis of organic samples that contain fluorine and boron together, it is remained as deeply considering subjects. On the other, in iodine analysis, analyzed value of 12.4% is obtained to the estimated value of 12.5%, even under high amount of fluorine existing environment.

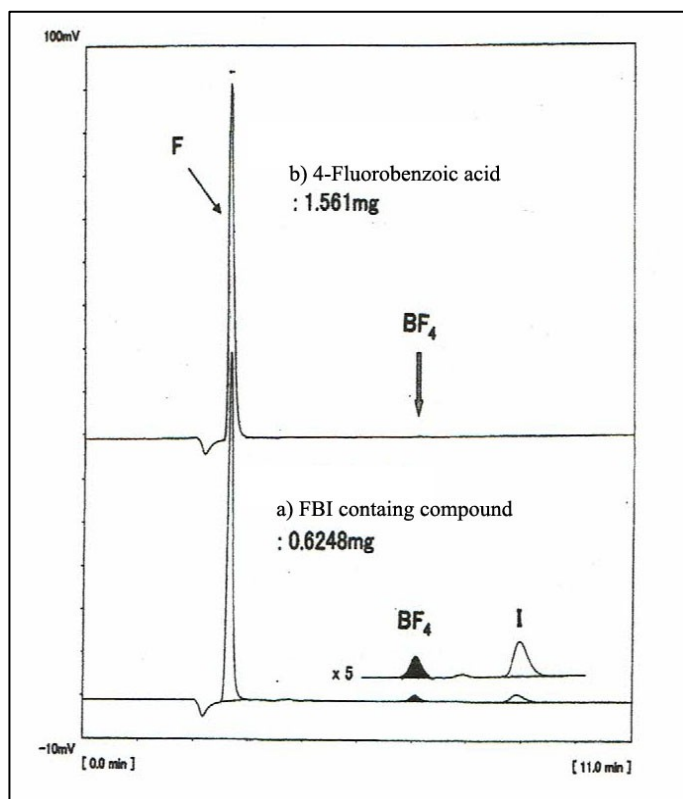


Fig. 4
Chromatogram of FBI containing compound

Table 3 Analysis example for high Fluorine compound containing Boron and Iodine

Compound	Element (Estimated value)	n=3	Sample (mg)	a) F analyzed (%)	b) BF ₄ analyzed (F %)	(a + b) (%)	Deviation (%)
C ₄₀ H ₁₈ BF ₂₀ I	F analysis (F: 37.4%)	1	0.6248	32.9	3.3	36.2	-1.2
		2	0.6055	33.2	3.4	36.6	-0.8
		3	0.6131	33.3	3.3	36.6	-0.8
		Average		33.1%	3.3%	36.5%	-0.9
	I analysis (I: 12.5%)	n=3	Sample (mg)	a) F analyzed (%)	Deviation (%)		
		1	0.6248	12.4	-0.1		
		2	0.6055	12.5	0		
	3	0.6131	12.3	-0.2			
	Average		12.40%	-0.10%			

4. Conclusion

We have been discussed and developed regarding high-speed measurement realization of automatic combustion analysis system for halogens/sulfur, as well as establishment for ultra-micro analysis method, under the title of “Speed-up of halogens and sulfur automatic combustion analytical system and application to multi-elemental analysis” in 3 years duration so far. In addition, we have discussed reduction of carry-over in this paper.

We have presumed multi-elemental analysis in hetero elements will be achievable in simultaneous, rapid and high cost performance way, as in the same way as mainstream CHN analysis in the near future.

Bibliography

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