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Abstract: O-03

Speed-up of halogens and sulfur auto-combustion analytical system and application to multi-elemental analysis: Analysis of rubber samples

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A multifunctional halogens and sulfur analytical system has been developed by coupled combustion/ion chromatography (CIC). In this study, the developed system was connected with efficient Ion chromatograph, IC-2010 (TOSOH), and the high speed analysis was achievable effectively. The multi-elements of F, Cl, Br, I and S were able to be analyzed 6 organic samples within 1 hour. This method was applied to the analysis of total sulfur in the rubber samples.

1. Introduction

In these 10 and few years duration, we have developed 3 kinds of halogens/sulfur automatic combustion analysis system such as:

1. For organic micro elemental analysis
2. For environmental samples conformed to JIS regulation
3. For inorganic/organic samples compatible high temperature type system

In organic micro elemental analysis, multi-elements (4 halogens and sulfur) simultaneous analysis has achieved as well as ultra-micro analysis method with ultra-micro amount of samples, furthermore, high speed realization of analysis operation including combustion time and chromatogram development, in order to approach effectively to mainstream CHN (O) analysis method [1)].

Recently, we had an opportunity to utilize high-performance ion chromatograph system of IC-2010, newly developed by TOSOH, which equipped high-speed and high-resolution column. IC-2010 was connected with our developed auto-combustion analysis system.

As a result, we confirmed that simultaneous determination for halogens (F, Cl, Br, I) and sulfur (S) were achievable, while 6 samples per hour were able to analyze continuously.

Since this attempt is newly considered, we have tried to obtain proper validation data for the analysis method establishment, as well as the CIC system was applied for the total sulfur analysis in rubber samples; this method was recently conformed as in JIS regulation (JIS K6233-2016).

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2. Experiment and Result

2-1. Automatic combustion analysis system

The system of halogens/sulfur analysis is composed of combustion furnace (HNS-15), absorption unit (HSU-15) and auto-sampler (THA-25), manufactured collaboratively by Yanaco LID Company, and ion chromatograph, manufactured by TOSOH.

Measuring conditions are described in Table 1. Samples were weighed on the platinum or ceramic boats as 1 to 20mg, and boats were set on the auto-sample (24 samples). Then whole processes of combustion, absorption and chromatogram development can be implemented automatically.

Quantitative analysis was executed by organic calibration curve method, with standard sample of NAC-st4 ($C_{12}H_7NO_2FClBrIS$, MW=490.51).

Table 1 Measuring Conditions

Ion Chromatograph (TOSOH IC-2010)
Column : TSKgel SuperIC-Anion HS (4.6mm x10cm)
Guardcolumn Anion HS (4.6mmx1.0cm)
Column temperature : 40℃
Moving phase : 3.0mM Na_2CO_3 — 3.8mM $NaHCO_3$
Flow rate : 1.2 ml/min Injection amount : 50μL
Detector : Electric conductivity detector
Combustion system
Fixed furnace temperature : 1,050℃
Carrier gas: Purified air 1.5～2.0 L/min
Absorption unit
Absorption solution : Pure water adding a small amount of H_2O_2 ,NH_2NH_2 (total 40ml)

2-2. Validation data

Verified data were obtained along with required items. Chromatogram by combusted NAC-st4 is shown in Fig.1. It clearly illustrates significantly sharp peak respectively, and all components were eluted within 8 minutes even including iodide elution.

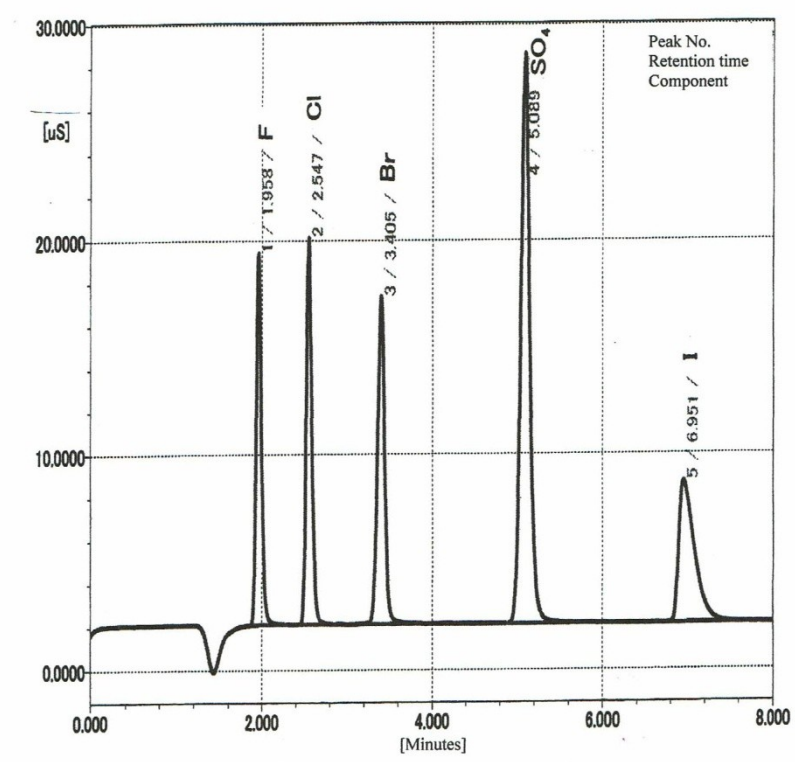

Fig. 1 Ion chromatogram; Combustion of NAC-st4

Theoretical plate numbers of 5 respective ions are summarized in Table 2.
Especially for SO_4 ion, quite high number around 11,000 is indicated.

Quadratic approximation formulas, which are necessary for calibration curve creation by IC's organic calibration curve method, are indicated in Table 3.
Good correlation coefficient (r^2) more than 0.999 had obtained in respective element (ion).

Table 2 Theoretical plates (N) for respective ion

NAC-st4	F	Cl	Br	SO_4	I
0.558mg	4,910	6,860	9,400	10,460	9,130
1.004mg	4,990	6,920	9,500	10,800	8,680
3.002mg	5,000	7,030	8,660	11,500	7,190

Table 3 Correlation between NAC-st4 sample quantity and respective ion peak

Generated ion	Quadratic approximation formula (n=5)	Correlation coefficient (r^2)
F	$y = 0.8825x^2 + 22.934x - 0.1085$	0.9999
Cl	$y = 2.2942x^2 + 21.463x + 0.9382$	0.9970
Br	$y = 1.4508x^2 + 24.519x + 0.4796$	0.9998
SO_4	$y = 4.2744x^2 + 53.558x + 0.0989$	0.9999
I	$y = 0.5970x^2 + 26.466x - 0.2577$	1.0000

y: peak area x: NAC-st4 (0.558 to 4.025mg, n=5)

3. Application for rubber samples

Quantitative determination method of total sulfur in rubber with IC was standardized as JIS regulation (JIS K6233) in accordance with technical contents and constitution from ISO-19242.

Targeting materials are raw rubber, un-vulcanized and vulcanized compounded rubber.

For the sample pre-treatment method, both of oxygen flask method and of tubular furnace combustion method are utilized. In case of measuring trace sulfur of total sulfur amount, less than 0.1%, also the rubber contains metals forming unsolved sulfates such as barium sulfate, it describes in the article that the tubular combustion method is much more suitable.

We have applied for the total sulfur analysis in the tire samples, and its 2 examples are shown in Table 4. Both examples illustrate constant analysis values are obtained, even heating temperature was changed from 900℃ to 1,100℃, and/or whether tungsten oxide as combustion supportive agent is added or not. This implies that there is no affection to total sulfur analysis even the tire sample contains metals, such as zinc, etc.

Now following for sulfur, determinations of total chloride and bromine in the tire samples are taking into account from ISO to JIS standardization process.

Table 4 Measuring example: Total sulfur in the tires

Tire sample	Combustion supportive agent (WO_3)	Heating temp. (℃)	Sample amount (mg)	Sulfur containing ratio	
				(%)	(WO_3 addition: 100%)
for bicycle (B company)	No addition	900	11.48	1.32	98.5
		950	11.88	1.35	100.7
		1,000	11.48	1.35	100.7
		1,050	11.13	1.34	100.0
		1,100	11.75	1.35	100.7
	Addition	1,100	11.63	1.34	100.0
for vehicle (S company)	No addition	900	12.30	1.42	99.3
		950	11.14	1.45	101.4
		1,000	11.96	14.44	100.7
		1,050	11.99	1.45	101.4
		1,100	11.62	1.42	99.3
	Addition	1,100	11.25	1.43	100.0

Bibliography

1) H. Nagashima, Y. Dewa, *Analytical Chemistry*, 66, 81 (2017)