A QUICK METHOD FOR ELEMENTAL ANALYSIS
BY THE COMBUSTION FLASK- ION CHROMATOGRAPHY

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Sulfur in fuels and chlorine, bromine and sulfur in biological samples were quickly determined with a satisfactory accuracy without complicated pretreatments by the combustion flask method coupled with ion chromatography.

INTRODUCTION

The combustion flask method is frequently used¹⁾²⁾ as an easy and quick method of complete decomposition of samples for the determination of halogens and sulfur in organic compounds, and titration or absorption spectrophotometry is used for determination of each element. Then procedures after decomposition of samples are complicated and time-consuming.

The authors applied ion chromatography (IC) to the combustion flask method. Time required for this method is less than 20 minutes after flask combustion.

EXPERIMENTAL

Apparatus

A Dionex Model 14 Ion Chromatograph was used which is equipped with anion separator and suppressor columns, a Perkin Elmer Sigma 10 data processor and an electric combustion flask supplied by Hamada Rika Co, LTD.

Reagents

Sodium carbonate (extra pure, Merck), Sodium hydroxide (GR, Merck), hydrazin hydrate (extra pure, Nakarai Kagaku), hydrogen peroxide (special grade, Mithubishi Gas Kagaku) were used together with standard reagents for elemental analysis, hexachlorocyclohexane, hexabromocyclohexane and sulfanilamide (standard reagent, all produced by Kishida Kagaku). All other reagents used were of analytical grade.

Sample preparation

A 300 ml electric combustion flask was used for the decomposition of samples, and the absorption solutions shown in Table 1 were taken in a flask. The sample and ashless filter paper (No.7 Toyo Roshi Co.) was weighed and placed in a platinum basket by folding the filter paper. Replacing air in the flask with oxygen, after combustion and absorption are complete, the sample solution was analyzed by IC.

Conditions of IC

Table 2 shows the conditions for determination of chlorine, bromine and sulfur

by IC. Fig.1 shows a typical chromatogram of the standard solution.

Table 1. Absorption solutions for the combustion flask

Element	Absorption solution
Cl	0.002M Na_2CO_3
Br	0.002M Na_2CO_3 + 5 drops of Hydrazine hydrate
S	0.002M Na_2CO_3 + 5 drops of 30% H_2O_2

Table 2. IC condition

Eluent	0.002M Na_2CO_3
Separator Column	3 x 750mm, Dionex low capacity anion exchange resin
Suppressor Column	6 x 250mm, Dowex high capacity cation exchange resin
Flow Rate	2.6ml/min
Sample Loop	100 μl
Detector	Conductivity

Fig.1. Typical chromatogram of the standard solution

RESULTS AND DISCUSSION

Selection of absorption solution

In general, water can be used as the absorption solution of the halide ions. But we found out that the use of 0.002M Na_2CO_3 solution as the absorption solution was better for the good reproducibility of chlorine on the ion chromatographic determination.

Bromine dose not convert to bromide ion completely by the 0.002M Na_2CO_3

solution alone. The recovery of bromide ion from organic bromide (hexabromocyclohexane) was about 65%, and almost 100% recovery of bromide ion was attained by the addition of 5 drops of 80% hydrazine hydrate.

For the absorption of sulfur, 2 to 5 drops of 30% $\text{H}_2\text{O}_2^{(3)}$ was added to the absorption solution as an oxidizing agent of sulfite to sulfate. By this procedure sulfur dioxide is completely oxidized to sulfate.

In the present experiment, the solutions shown in Table 1 were used for the absorption of each component.

Recovery of organic elemental analysis using standard reagents

The recoveries of elements from organic compounds : Chlorine from hexachlorocyclohexane (BHC), bromine from hexabromocyclohexane and sulfur from sulfanilamide are shown in Table 3. Excellent agreements between the experimental and theoretical values are seen for each element.

Table 3. Recoveries of elements from these becoming compounds

	Hexachlorocyclohexane		Hexabromocyclohexane		Sulfanilamide	
	Cl %		Br %		S %	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
1	73.18	73.14	85.88	85.99	19.08	18.62
2	72.84		86.07		18.81	
3	72.52		85.97		18.76	
$\bar{x}$	72.85		85.97		18.76	
C.V. (%)	0.45		0.11		0.91	

*C.V. : Coefficient of Variation

Applications to fuel and biological samples

1) Determination of sulfur in heavy oil and coke

The results of analysis of sulfur in the standard coke sample No.1 supplied by the Japan Fuel Association are shown in Table 4. The standard reference values of sulfur content determined by the Escheka and the combustion methods, both specified in JIS M 8813-1973 are 1.09% and 1.06%, respectively. The values measured by our procedure were 1.07% -1.08%, with an average of 1.077%, which agreed well with the standard reference values.

Table 5 shows the results of determination of sulfur content in a standard heavy oil sample supplied by the Japan Petroleum Institute (JPI). Sulfur content determined by the combustion tube method specified in JIS K 2541 was $1.05 \pm 0.01\%$, and sulfur content determined by our procedure was 1.02%, which also showed a satisfactory agreement with standard reference values.

Table 4. Sulfur content in standard coke sample No.1

	Found (%)	Standard value (%)	
		A	B
1	1.08	1.09	1.06
2	1.08		
3	1.07		
$\bar{X}$	1.077		
C.V.(%)	0.54		

A : Escheka method JIS M 8813

B : Combustion method JIS M 8813

Table 5. Sulfur content in standard heavy oil sample S-226

	Found (%)	Standard value* (%)
1	1.00	1.05 $\pm$ 0.01
2	1.02	
3	1.06	
$\bar{X}$	1.027	
C.V.(%)	2.9	

* "Test Method for Sulfur Content in Petroleum
Products by Combustion Tube" JIS K 2541

2) Determination of chlorine and sulfur in biological samples

Table 6 shows the results of analysis of chlorine and sulfur in rice flour, bamboo leaves and fish powder (salmon and shark). The values determined by IC were compared with those determined by the mercuric thiocyanate method in spectrophotometry (chlorine), and the turbidimetric method with barium sulfate (sulfur), and they agreed satisfactorily. Typical ion chromatograms of rice flour and fish powder are shown in Fig. 2.

Table 6. Analytical results of biological samples

Unit:mg/g									
Rice flour					Bamboo leaves				
Cl		S			Cl		S		
A	B	A	C		A	B	A	C	
1	5.7	5.9	1.2	1.5	1	10.0	11.5	4.6	5.0
2	5.6	6.0	1.3	1.5	2	11.1	11.0	4.6	5.0
3	5.9	5.5	1.1	1.0	3	11.5	11.0	4.8	5.5

Fish powder(salmon)					Fish powder(shark)				
Cl		S			Cl		S		
A	B	A	C		A	B	A	C	
1	22.5	23.0	5.0	4.5	1	34.6	35.0	4.6	4.5
2	27.4	27.0	5.4	5.5	2	33.5	34.0	4.6	4.5
3	25.3	25.0	5.1	5.0	3	35.7	35.0	4.8	5.0

A : Present method (IC)

B : The mercuric thiocyanate method

C : The barium sulfate method

Fig.2. Typical chromatograms of fish powder and rice flour

CONCLUSION

The results may be summarized as follows, the combustion flask-ion chromatographic method is applicable to fuels and biological samples with good accuracies for chlorine, bromine and sulfur. This method makes it possible to analyze samples within about 20 minutes after the flask combustion procedure.

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Keyword phrases

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