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Abstract: O-01

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

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A multifunctional halogens and sulfur analytical system has been developed by coupled combustion/ion chromatography (CIC). The system is composed by combustion furnace, absorption unit. Auto-sampler and ion chromatograph. In this study, we have established a simultaneous determination for inorganic halogens (F, Cl, Br, I) and sulfur (S), based upon conductivity detection after decomposition in this automatic system using clean air. The method can be applied to the determination of mineral samples that mainly composed of the analysis of sulfur

1. Introduction

In recent years, the tendency of the movement for strengthening diffusion restriction of hazardous materials to the environment is focused on world-widely. As for the representative environment restriction method, RoHS[(a)]/WEEE[(b)] Directives in EU countries and REACH[(c)] are defined, and they are described that detrimental substances have to be restricted in their products or materials. In order to comply with this strong tendency, analysis of halogens (F, Cl, Br, I) and sulfur (S) that are contained in various products and raw materials, are becoming significantly necessary. However, halogens/sulfur containing in the products and raw materials are derived not only from organic compounds, but from inorganic compounds that elements' determination is quite difficult by the conventional methods. Here, by applying for combustion at high temperature (1,400℃), the analysis compatible system for halogens/sulfur elements was developed, that can comply with both of organic and of inorganic samples. We have previously considered analysis method for fluorine in cement and steel slug, and recently demand for especially sulfur analysis is increasing, with this high temperature type combustion system. In applying for sulfur analysis in mineral sample, we examined change of combustion temperature and adding/no adding of decomposition accelerator, and some knowledge were obtained and hence reported here.

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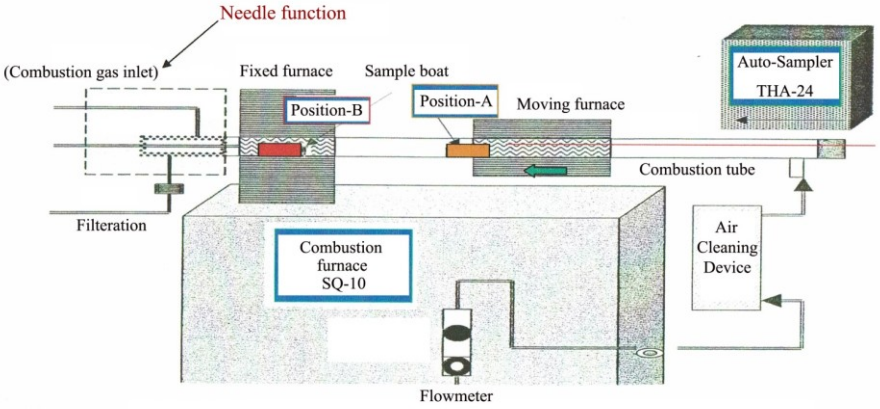
(a) Restriction of the use of certain hazardous substances in electrical and electronic equipment
(b) Waste electrical and electronic equipment Directive
(c) Registration, evaluation, authorization and restriction of chemicals

2. Experiment

Automatic combustion analysis system of halogens/sulfur in this measurement is composed of combustion furnace (SQ-10), absorption unit (HSU-35), auto-sampler (THA-24), manufactured by Yanaco LID Company, and ion chromatograph. Sample is weighed on the magnetic boat and is introduced into ceramic-made combustion tube. Then sample is combusted in the moving furnace, and thermal decomposition of the sample is progressed in the fixed furnace subsequently, such as the method of double-step insertion (Fig. 1). Halogen and sulfurous acid gases by combustion are collected into the absorption solution, and gases are analyzed along with the measuring condition shown in Table 1.

Fig. 1

Combustion pre-treatment of the sample by double-step insertion method



Organic sample: Position-A (300℃ → 950℃, 10 to 20 min)

Inorganic sample: Position-A (300℃ → 950℃, 5 to 10 min)

Position-B (1,100 to 1,350℃, 5 to 10 min)

Table 1 Operating conditions for CIC system

Ion chromatograph		
Column	:	Shodex IC SI-90 4E (4.6mm x 250mm)
Thermostat	:	35℃ (Cell 40℃)
Moving phase	:	3.0mM Na_2CO_3 --- 2.0mM $NaHCO_3$
Flow rate	:	1.2mL/min
Injection amount	:	5o or 100μL
Detector	:	Electric conductivity detector
Combustion system		
Moving furnace temp.	:	400 to 950℃
Fixed furnace temp.	:	950 to 1,350℃
Absorption unit		
Absorption solution	:	Pure water adding a small amount of H_2O_2, NH_2NH_2 (40mL)

3. Result and consideration

Temperature of fixed furnace in this system is increased sequentially in the range from 950℃ to 1,350℃, and analyses of sulfur quantity in several kinds of samples are determined, and thermal hydrolysis behaviors are examined. In addition, at the same temperature condition, decomposition accelerator (WO3) is added in the absorption solution, and its effect is searched.

1) Analysis of hardly decomposable inorganic reagents

In inorganic reagents that are commercially available to obtain, we have selected $CaSO_4$ and $BaSO_4$, that are hardly decomposable sulfates, and their thermal decomposition behavior are examined. These results are shown in Fig. 2.

In either case, nearly 100% yield is attained at more than 1,100℃ as well as WO_3 addition. In $CaSO_4$, quantitatively good yield is indicated from about 1,200℃, even WO_3 is not added. Conversely, in $BaSO_4$ with no WO_3 addition, yield remains at around 10% in wide temperature range.

2) Analysis of authentic samples

In EU authentic samples, BCR-681 was analyzed. This sample is containing multiple heavy metals and trace amount of Cl, Br and SO_4, in polyethylene substrate, and is used as an indicator for evaluation of device and combustion condition. Results are shown in Table 2, and every result corresponds with displayed value.

Especially in Br, high effectiveness is recognized by hydrazine-hydrate-added absorption solution ($Br_2 \rightarrow Br^-$).

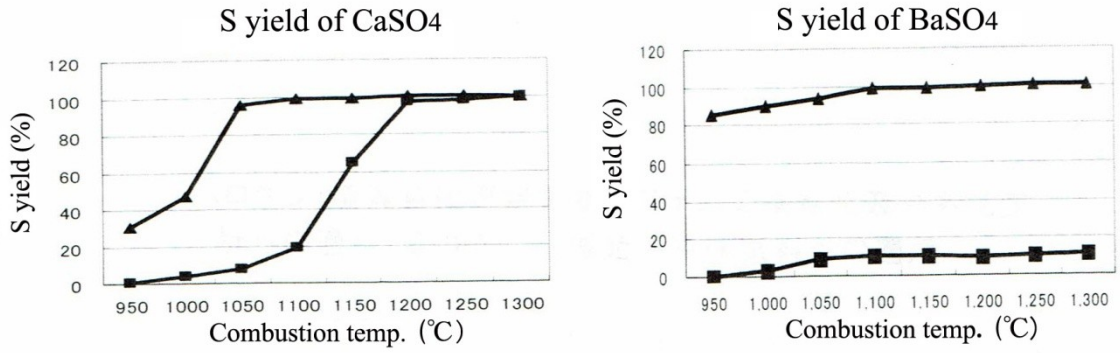


Fig. 2 Thermal hydrolysis behavior of hardly decomposable sulfates

Sample amount: 1mg, (-▲-) WO3 added (50mg), (-■-) WO3 on added

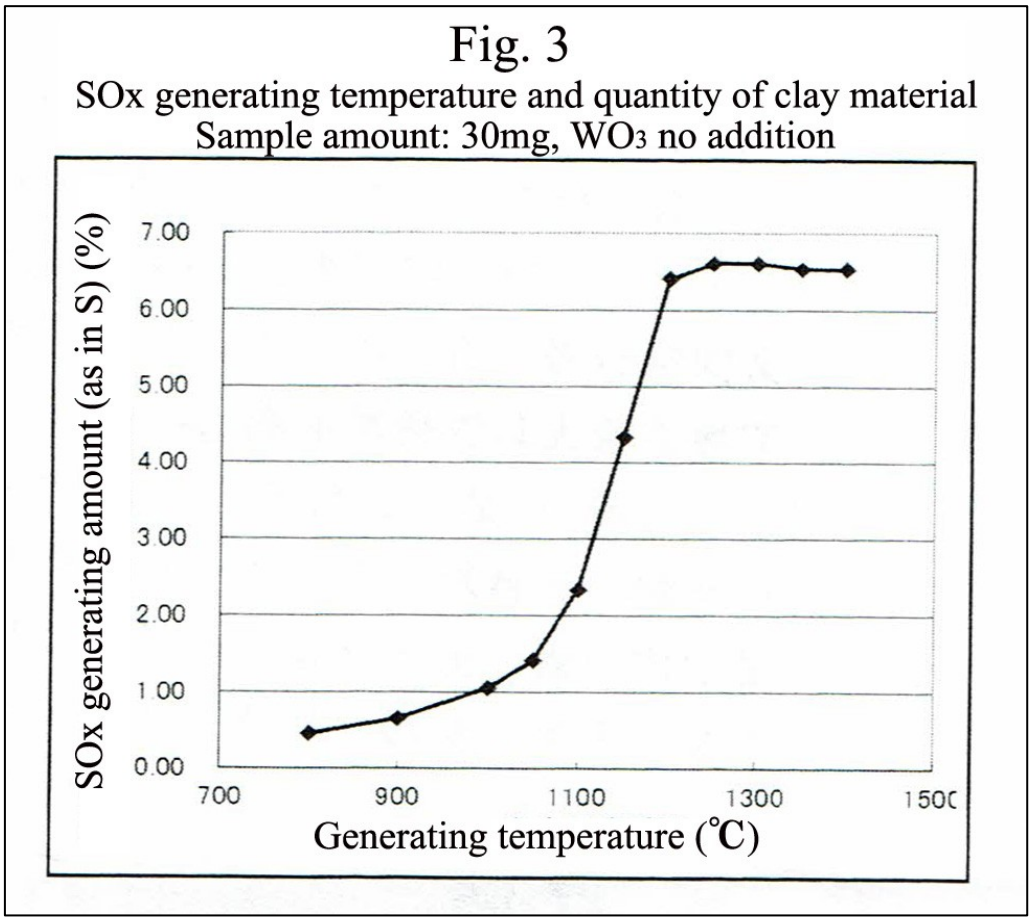
Table 2 Analysis result of BCR-681

Sample amount (mg)	Element	Displayed value (ppm)	Analyzed value	
			a) H_2O_2 added absorption solution	b) H_2O_2 --- NH_2NH_2 added abosrption
100	Cl	92.9 ± 2.8	92.3	93.3
	Br	98 ± 5	92.8	99.4
	S	78 ± 17	80.7	79.8

3) Measurement of actual sample

SOx generating temperature and generating quantity was measured for clay material for ceramic (Fig. 3). Since total S containing quantity indicates as 6.58% under the condition of WO_3 addition at 1,250℃, sulfur content is almost quantitatively discharged over 1,200℃. Also, as this sample contains a lot of iron portion, iron oxide is promoting decomposition interaction as the same in WO_3.

Fig. 3



4. Conclusion

From the investigation of thermal hydrolysis behavior, only high temperature combustion enables to obtain sufficient quantitative result such in $CaSO_4$, while only high temperature combustion is not effective to determine correct quantitative analysis such in $BaSO_4$. Also, additive decomposition accelerator (WO_3) is significantly effective, and we had recognized the collection yield could be drastically improved by combining addition of decomposition accelerator and high temperature combustion.

Bibliography

H. Nagashima, Y. Dewa, *Patent*, No. 5399795 (2013)