Pyrolytic Sulfurization Gas Chromatography. X. The Reduction of the Analysis Time by Means of High-frequency Heating

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Synopsis. With the objective of reducing the analysis time in the previous PSGC method, a high-frequency induction furnace was used instead of an electric furnace. By using the present furnace, the time necessary for the pyrolytic sulfurization was reduced from 40 min to 1 min with satisfactory results.

By using pyrolytic sulfurization gas chromatography (PSGC), which was originated by the present authors, the atomic ratio between C, H, O, and N in a usual organic compound,[1] a metal organic chelate compound,[2] a polymer,[3] and an organic halogen compound[4] has been successfully and simultaneously determined. Moreover, the atomic ratio between C, H, O, N, Cl, Br, and I in an organic halogen compound has been successfully determined[5] using only one sample by a combination of gas chromatography and ion chromatography. Since the analysis by the PSGC was, however, batch-by-batch and time-consuming, a high-frequency induction furnace instead of the electric furnace used in the previous work[1-7] has been employed in order to reduce the reaction time of the pyrolytic sulfurization. The new furnace designed by the present authors consists of a work coil and an ampule holder in which an outer quartz tube is packed with granulated tungsten. By the use of the present furnace, the reaction temperature between a sample and S in a quartz ampule can be raised from the 950 °C in the previous work[1] to about 1500 °C; also, the reaction time is reduced from 40 min to 1 min. Various organic compounds were analyzed under experimental conditions similar to those used in the previous PSGC method.

Experimental

Apparatus. To subject an organic compound to the pyrolytic sulfurization, a high-frequency induction furnace (type: HFT-10S, frequency: 13.5 MHz, maximum power: 1 KW) was introduced instead of the electric furnace used in the previous work.[1] The furnace consists of a work coil and an ampule holder in which an outer quartz tube is packed with *ca.* 10 g of granulated tungsten as the heating medium. The furnace is shown in detail in Fig. 1.

Reagents. The granulated tungsten used as the heating medium was commercially available (purity: 99.9%; particle size; 10—20 mesh). The organic compounds used as standard samples were of a reagent grade for elemental analysis except for cyanoguanidine, which was of a reagent grade for a melting-point standard.

Procedure. The ampule containing a sample and S was prepared in a manner similar to that used in the previous work,[1] except that the ampule was shortened from 5 cm to 3 cm because of the furnace conditions, and placed in the ampule holder in the furnace. After replacing the contents of the furnace with helium, the ampule was treated for 1 min by high-frequency heating and then left standing for 3 min in the furnace. The ampule thus obtained was inserted into a gas sampler, and the reaction products in the ampule were analyzed by means of gas chromatography under the same conditions as in the previous work.[6]

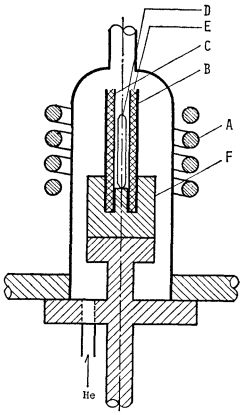

Fig. 1. High-frequency induction furnace.
A: Work coil, B: outer quartz tube (10.5 i.d., 12.5 o.d., 50 mm long), C: inner quartz tube (5.5 i.d., 6.5 o.d., 50 mm long), D: ampule containing a sample and S, E: granulated tungsten (10—20 mesh), F: ceramic support.

The atomic ratio between C, H, O, and N was calculated by the use of correction factors[6] which had been obtained from the analytical results of cyanoguanidine and sucrose by the above-mentioned procedure.

Results and Discussion

High-frequency Heating. Several kinds of granulated metals were examined as heating medium in high-frequency heating, and tungsten was found to be best. Since tungsten was easily oxidized to the oxide under the experimental conditions in the air, it was used in an atmosphere of helium, the tungsten being usable repeatedly. By using 10 g of granulated tungsten as the heating medium, an ampule containing a sample and S could be heated at about 1500 °C in a moment.

Reaction Time. The time necessary for the reaction between a sample and S in an ampule was investigated for 8-quinolinol as a standard sample; the relationship between the reaction time and the amounts of gases evolved from 1 mg of a sample is shown in Fig. 2. As can be seen from Fig. 2, the reaction between the sample and S in an ampule was completed within 40 s. The reaction products also indicated the same composition as in the previous PSGC method. In the present study, therefore, an ampule containing a sample and S was heated for 1 min by means of a high-frequency induction furnace.

Table 1. Analytical results of various organic compounds

Sample	C (wt%)			H (wt%)			O (wt%)			N (wt%)		
	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error
8-Quinolinol	74.47	74.18	−0.29	4.86	4.93	+0.07	11.02	10.99	−0.03	9.65	9.90	+0.25
Cholesterol	83.87	84.23	+0.36	11.99	11.98	−0.01	4.14	3.79	−0.35			
Thiourea[a)]	27.26	27.08	−0.18	9.15	9.11	−0.04				63.59	63.81	+0.22
2,2-Bis(ethylsulfonyl)propane[a)]	51.21	51.30	+0.09	9.82	10.06	+0.24	38.97	38.64	−0.33			
Naphthalene	93.71	93.56	−0.15	6.29	6.44	+0.15						
Anthraquinone	80.76	80.53	−0.23	3.87	4.05	+0.18	15.37	15.42	+0.05			
Tris(2,4-pentanedionato)iron(III)	60.59	60.72	+0.13	7.12	7.19	+0.07	32.29	32.09	−0.20			
Bis(2,4-pentanedionato)-magnesium(II)	51.27	51.32	+0.05	7.75	7.77	+0.02	40.98	40.91	−0.07			

a) The sulfur atom was neglected in considering the composition of a sample, since it could not be determined.

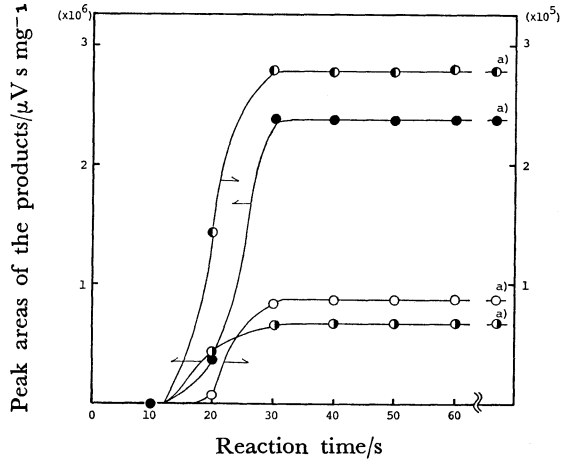

Fig. 2. Relationship between the reaction time and the amount of the reaction product.
○: N_2, ◑: H_2S, ◐: COS, ●: CS_2. a): By the previous PSGC method.

Standing Time after the Reaction. The effect on the result of the standing time of an ampule after high-frequency heating was investigated for 8-quinolinol as a standard sample. A standing time of less than 20 min had no effect on the analytical results of organic compounds analyzed by the present procedure. Therefore, the reaction products in an ampule were analyzed after leaving the ampule standing for 3 min in the furnace.

Analytical Results of Various Organic Compounds. Various organic compounds and metal organic chelate compounds were analyzed by the present procedure; the results are shown in Table 1. As can be seen from Table 1, both the precision and the accuracy were similar to those in the previous PSGC method.

From the results obtained by the present study, it can be concluded that the introduction of a high-frequency induction furnace reduces not only the reaction time between a sample and S in an ampule, but also the overall time necessary for an analysis. This will be very valuable for the further improvement of the PSGC method.

References

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