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BRIEF COMMUNICATIONS

## **Bismuth(V)** Oxide and Silver Bismuthate as Oxidizing Agents for Gas-Chromatographic Elemental Microanalysis

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Abstract—Bismuth(V) oxide, silver bismuthate, and a mixture of bismuth(V) oxide with fine silver powder were studied as oxidizing additives in gas-chromatographic elemental microanalysis of readily combustible organic substances and coal.

Gas-chromatographic elemental analysis (GCEA) is one of fast and automated methods for analyzing organic compounds. The accuracy and reproducibility of this method are comparable with, and sometimes, exceed those of conventional elemental analysis.

One of serious problems of GCEA is efficient and almost instantaneous oxidative thermolysis of an organic sample to form products suitable for chromatographic analysis. To provide compete oxidation of a sample, appropriate oxidizing agents or their mixtures with combustion catalysts are added to the sample, and oxidation is performed in a carrier gas (usually helium) containing oxygen. A wide range of oxidizing agents and combustion catalysts providing reliable and complete oxidation of a sample are used in modern GCEA. However, frequently samples of organoboron, organosilicon, and organogermanium compounds, salts of polybasic carboxylic acids, salts of sulfonic acids, various solid caustobioliths, and their derivatives (lignite, coal, peat, sapropels, humic acids, and their extracts) are incompletely burnt in the presence of these oxidizing agents. This is due to high content of mineral fraction (up to 95%) in these materials. Therefore, a search for new effective oxidizing agents and combustion catalysts for difficultly oxidizable organoelemental compounds and solid caustobioliths is an urgent problem.

Diverse inorganic compounds and their mixtures were studied as oxidizing additives to samples to be burnt up [1-4]. Some of them such as PbO<sub>2</sub> and MnO<sub>2</sub> are oxygen donors. Other compounds, e.g., NiO, Cr<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, and CeO<sub>2</sub> are surface combustion catalysts. Compounds of the third groups  $(V_2O_5,$ 

 $Ag_2O$ ,  $AgMnO_4$ ,  $AgVO_3$ ,  $Ag_2Cr_2O_7$ , and  $Ag_2O_2$ ) are both oxygen donors and oxidation catalysts. Among compounds of the third group, silver-containing substances  $AgMnO_4$  and  $Ag_2O_2$  are the most effective. Metallic silver formed in their thermolysis is a very active catalyst for surface oxidation of the organic component of organoelemental compounds as well as high-ash and high-carbon caustobioliths. These oxidizing agents are suitable for highly effective and complete combustion of difficultly combustible samples in GCEA. The procedure of GCEA of solid caustobioliths, with coals as example, using a Carlo Erba-1100 elemental analyzer was developed and optimized in [4]. AgMnO<sub>4</sub>, PbO<sub>2</sub>, Ar<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, and Ag<sub>2</sub>O<sub>2</sub> were studied as oxidizing catalysts for sample combustion. The most effective were  $AgMnO_4$ ,  $PbO_2$ , and  $Ag_2O_2$ . In addition, the procedures for weighing and pretreatment of the samples were substantially modified, and mathematical treatment of the chromatrograpms was improved. As a result, the accuracy and reproducibility of the analysis sharply increased.

Bismuth(V) compounds,  $Bi_2O_5$ , and  $AgBiO_3$ , have not been used as oxidizing agents for GCEA. We suggest that bismuth(V) oxide should be an active oxygen donor; AgBiO<sub>3</sub> should be both an oxygen donor and a catalyst of surface oxidation owing to the presence of silver in its composition. The influence of catalytic additives of fine metallic silver powder on the oxidizing power of inorganic compounds that are used in modern GCEA as oxygen donors but are not oxidation catalysts was not fully understood. In this work we studied synthesis of bismuth(V) oxide and silver bismuthate and tested these compounds as oxidizing agents for GCEA. We

Oxidizing agent	p-Nitrophenol, %			Coal, %		
	С	Н	N	С	Н	N
AgMnO <sub>4</sub>	51.83	3.58	10.05	68.37	5.18	0.20
Bi <sub>2</sub> O <sub>5</sub>	51.79	3.55	10.05	54.01	5.06	0.23
$Bi_2O_5 + Ag$	51.81	3.57	10.06	68.24	5.21	0.21
AgBiO <sub>3</sub>	51.82	3.63	10.08	57.08	5.17	0.21
Calculated data	51.80	3.60	10.07	68.38*	5.19	0.20

Average results of elemental analysis of p-nitrophenol and coal of Yakutiya basin in the presence of the oxidizing agents

\* Determineded by conventional elemental analysis

also studied the influence of catalytic additives of fine metallic silver powder on the oxidizing properties of these compounds in combustion of microamounts of difficultly combustible samples.

## EXPERIMENTAL

 $\gamma$ -Bi<sub>2</sub>O<sub>5</sub> was prepared by treatment of NaBiO<sub>3</sub>· 2H<sub>2</sub>O with a large excess of 68% HNO<sub>3</sub> at -15°C for 1 h [5-7]:

$$\begin{aligned} 2\text{NaBiO}_3 \cdot 2\text{H}_2\text{O} + 2\text{HNO}_3 + (n-5)\text{H}_2\text{O} &\rightarrow \text{Bi}_2\text{O}_5 \cdot n\text{H}_2\text{O} \\ + 2\text{NaNO}_3. \end{aligned}$$

After reaction completion, excess HNO<sub>3</sub> was neutralized to pH 7 with an NaHCO<sub>3</sub> solution cooled to 0°C. The Bi<sub>2</sub>O<sub>5</sub> · nH<sub>2</sub>O precipitate was filtered off, washed many times with water, and predried at 20°C for 48 h over freshly calcined CaCl<sub>2</sub>. Anhydrous bismuth(V) oxide was prepared by drying Bi<sub>2</sub>O<sub>5</sub> · nH<sub>2</sub>O at 105°C for 10 h in a drying oven:

$$\operatorname{Bi}_2\operatorname{O}_5 \cdot n\operatorname{H}_2\operatorname{O} \rightarrow \operatorname{Bi}_2\operatorname{O}_5 + n\operatorname{H}_2\operatorname{O}.$$

AgBiO<sub>3</sub> was prepared by reaction of 28-fold excess of AgNO<sub>3</sub> with NaBiO<sub>3</sub>  $\cdot$  2H<sub>2</sub>O in an aqueous solution at 20°C for 1 h [5]:

$$\text{NaBiO}_3 \cdot 2\text{H}_2\text{O} + \text{AgNO}_3 \rightarrow \text{AgBiO}_3 \downarrow + \text{NaNO}_3 + 2\text{H}_2\text{O}_3$$

The AgBiO<sub>3</sub> precipitate was filtered off, washed many times with distilled water, and predried at 20°C for 48 h over freshly calcined CaCl<sub>2</sub>. Anhydrous AgBiO<sub>3</sub> was obtained by heating at 60°C for 24 h in a drying oven.

To study the influence of catalytic amounts of silver on the oxidation power of  $Bi_2O_5$ , bismuth oxide was mixed with fine silver powder prepared by reduction of  $[Ag(NH_3)_2]Cl$  with  $N_2H_4 \cdot HCl$  in excess

 $NH_4OH$ . The resulting mixture was thoroughly ground in an agate mortar and stored without air access. The weight fraction of Ag(0) in the mixture was 22.56 wt %.

Bi<sub>2</sub>O<sub>5</sub>, AgBiO<sub>3</sub>, and Bi<sub>2</sub>O<sub>5</sub> + Ag(0) were studied as oxidizing additives to samples for GCEA. We also studied AgMnO<sub>4</sub> as reference effective oxidizing agent. The organic compound to be analyzed was *p*-nitrophenol. Coal of Yakutiya basin was used as the sample of difficultly combustible high-carbon caustobiolith. The average rounded weight (mg) of Bi<sub>2</sub>O<sub>5</sub>, AgBiO<sub>3</sub>, Bi<sub>2</sub>O<sub>5</sub> + Ag(0), and AgMnO<sub>4</sub> added to the sample was 9.6, 11.4, 28.5, and 43.7, respectively, with their volume being approximately the same. The chromatographic analysis and mathematical treatment of the results were performed by the procedure in [4]. The results of the elemental analysis are summarized in the table.

Since  $Bi_2O_5$  and  $AgBiO_3$  are loose powders, their bulk density is minimal among the examined oxidizing agents.  $AgMnO_4$  has the highest bulk density. The bulk density of  $Bi_2O_5$  increases by a factor of approximately 3 after addition of Ag(0), i.e., addition of Ag(0) increases the  $Bi_2O_5$  amount in the sample, on the average, by a factor of 2.3. Hence, the amount of "active" oxygen liberated in thermolysis of  $Bi_2O_5$ increases by the same factor, which should make oxidation of the sample more complete. Thus, the increase in the bulk density of  $Bi_2O_5$  after grinding with fine Ag(0) powder should increase the completeness of sample combustion owing to an increase in the amount of the oxidizing agent added to the sample, even if there were no catalytic effect of Ag(0).

As seen from the table, the results of elemental analysis of p-nitrophenol, performed with all the tested oxidizing agents, agree with each other and with the calculated values. Hence, all these oxidizing agents can be used in GCEA of readily combustible organic compounds like p-nitrophenol (or their mix-

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 77 No. 7 2004

tures). On the contrary, the carbon contents in coal determined in the presence of these compounds strongly differ. Only nitrogen and hydrogen contents are consistent. The carbon content determined with  $Bi_2O_5$ (54.01% C) is lower by 14.36% than that determined with  $AgMnO_4$  (68.37% C). The carbon content determined in the presence of  $AgBiO_3$  (57.08% C) is underestimated by 11.29%. The results obtained with a  $Bi_2O_5 + Ag$  (68.24% C) mixture are close to those obtained with  $AgMnO_4$ . Hence, addition of fine Ag(0)powder sharply increases the oxidizing power of  $Bi_2O_5$  under GCEA conditions. This mixture can be used to analyze difficultly combustible materials like caustobioliths. Probably, Ag(0) can also enhance the oxidizing power of  $AgBiO_3$  and other compounds.

## CONCLUSIONS

(1) Bismuth(V) oxide, its mixture with fine silver powder, and sliver bismuthate can be used as effective oxidizing agents for combustion of readily combustible organic compounds in chromatographic elemental microanalysis.

(2) The nitrogen and hydrogen contents determined in coal samples by gas-chromatographic elemental microanalysis in the presence of the tested Bi(V) compounds and their mixtures are consistent. The carbon content in coal, determined with bismuth(V) oxide and silver bismuthate, is lower than that determined in the presence of  $AgMnO_4$ . The carbon content determined with  $Bi_2O_5 + Ag(0)$  mixture is close to that determined with  $AgMnO_4$ . This mixture can be used as oxidizing additive in gas-chromatographic analysis of solid caustobioliths.

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