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Effect of gas-chromatography column regeneration during the CHN/S analysis of copper-chromium disulfide

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Abstract

The effect of gas-chromatography column (GCC) regeneration during the CHN/S analysis of copper-chromium disulfide $CuCrS_2$ (CCDS) samples on the Euro EA 3000 analyzer was identified. The effect results in a perfect straight baseline on the chromatograms of both $CuCrS_2$ and standard samples. The obtained straight baseline causes high-quality peaks separation. In addition, the reported regeneration procedure reduces significantly the GCC regeneration duration that usually takes up to several days.

Keywords

CHN/S analysis
chromatography column regeneration
copper-chromium disulfide

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Key findings

- Regeneration of gas-chromatography column during CHN/S analysis of $CuCrS_2$ samples on the Euro EA 3000 analyzer was detected.
- The effect results in a perfect straight baseline on the chromatograms.
- The described effect is important for CHN/S analysis of samples with low sulfur content.

1. Introduction

Nowadays the analysis for C, H, N, S contents is required for the study not only of organic compounds but also of various metal-organic complexes and sulfur-containing compounds [1–10]. Due to a wide range of promising physicochemical properties, these compounds are used as advanced energy [2, 6], thermoelectric [11, 12] and magnetic [13, 16] materials. From among the above mentioned compounds, the $CuCrS_2$-matrix and solid solutions were chosen for the CHN/S analysis of the sulfur content due to the fact that electrical properties of these materials depend strongly on the sulfur content [12, 15, 16]. Moreover, this method was used to control the content of C, H, and N admixtures in these materials because the synthetic procedure of $CuCrS_2$ involves the thermal sulfidation of the initial Cr_2O_3 and CuO oxides by the thermolysis products of NH_4SCN [11, 14–17].

As it is known, gas-chromatography column (GCC) regeneration is required during the operation of CHN/S analyzers. To this aim, the GCC is usually purged with high-purity helium at high temperatures for a day or two. This article describes the effect of GCC regeneration observed after the CHN/S analysis of copper-chromium disulfide $CuCrS_2$ samples. The effect results in a perfect straight baseline on the chromatograms of both $CuCrS_2$ and standard samples. The mechanism of this effect was studied by the differential scanning calorimetry (DSC) method.

2. Experimental

2.1. Instrumentation

A Euro EA 3000 CHN/S analyser (EuroVector, Italy) with a GCC “Separation Column Sulphur 0.8m PTFE 26007800 E3002 BN203557” (Elemental Microanalysis, UK) was used for the CHN/S analysis. The procedure was carried out using the optimized technique [18]. The DSC analysis was performed using an STA 449 F1 Jupiter thermoanalyzer (NETZSCH, Germany). The experiment was run in an open Al_2O_3 crucible in synthetic air flow at a heating rate of 10 K/min. The sample weight was ~ 10 mg.

2.2. Reagents and materials

Tungsten oxide (VI) (Elementar, Germany) was used in the reactor oxidation zone and “Copper wires reduced 6x0.65 mm” (Elemental Microanalysis, UK) were used in the reduction zone. Sulfanilamide (SAM) and atropine sulfate (ATRS) (Elemental Microanalysis, UK) were used as the standards. High purity helium N5.0 was used as a carrier gas.

The studied effect was noticed during the analysis of $CuCrS_2$ samples. The samples had the following element content: copper (35 wt.%), chromium (29 wt.%), and sulfur (36 wt.%). Sulfur content was determined by analyzing fourteen 0.6–0.7 mg samples. The content of C, H, and N admixtures was determined by analyzing fourteen 3.5–4.0 mg samples. The analysis time for each sample was 960 seconds. Thus, the total analysis time was ~8 h.

3. Results and Discussion

The CHN/S analysis was carried out in a high-temperature quartz reactor shown schematically in Figure 1. To be analyzed, the CCDS sample was placed in a tin capsule introduced into the pyrolysis zone at 1020 °C (point 1 in Figure 1) and burnt with oxygen dose in helium atmosphere. Then the gaseous products (SO_2, SO_3, CO, CO_2, H_2O, NO, NO_2) were passed through the oxidation zone filled with WO_3 catalyst grains (point 3 in Figure 1) for complete conversion of CO to CO_2. After that, sulfur and nitrogen oxides were reduced to SO_2 and N_2, respectively, in the reduction zone filled with copper wires (point 4 in Figure 1). Finally, the mixture of SO_2, N_2, CO_2, and H_2O gases passed into the GCC for separation. The resulting chromatographic signal was recorded using a thermal conductivity detector.

It was observed during the experiment that the baselines of a number of $CuCrS_2$ samples became perfectly straight after the CHN/S analysis. This effect was studied by comparison of the chromatograms of SAM and ATRS standards, which were recorded after the standard procedure of GCC regeneration and after the $CuCrS_2$ analysis. As it can be seen in Figure 2, the baselines of SAM and ATRS standards became perfectly straight after the analysis of all $CuCrS_2$ samples.

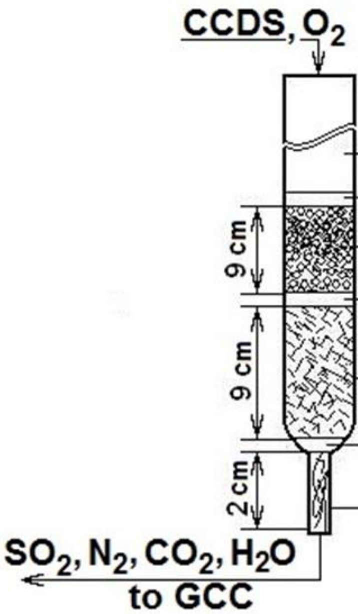

Figure 1 Scheme of reactor for sample decomposition: pyrolysis zone (1); separation zone (quartz wool) (2); oxidation zone (3); reduction zone (4); halogen capture zone with silver wire (5).

Usually baseline flattening is a result of long-lasting column regeneration in helium. Note that a straight baseline is necessary for qualitative separation of N_2, CO_2, H_2O, and SO_2 peaks. Baseline flattening may be important for the analysis of the samples with a low content of elements in various metal-organic complexes and sulfur-containing compounds. In this case the straight baseline diminishes the absolute error of determination. As it can be seen in Figure 2, H_2O and SO_2 peaks are shifted slightly towards the increased retention time on the SAM and ATRS chromatograms after the $CuCrS_2$ analysis. This effect can be explained by the fact that free adsorption centers appear in the column filler, thereby increasing the retention of incoming pyrolysis products.

The mechanism responsible for the effect of $CuCrS_2$ regeneration was investigated by the DSC method (curve 1 in Figure 3) As seen, the sample undergoes no significant weight changes until 400 °C (curve 2 in Figure 3). Between 400 and 600 °C the weight of the sample increases due to the oxidation of elements (Cu, Cr, S) in its composition. The DSC curve shows a sustained smooth exothermic effect up to 600 °C, apparently, due to sulfur oxidation. At ~600 °C the DSC curve has an intense double-split peak associated with an exothermic effect, possibly, due to copper and chromium oxidation. Then at the temperature of ~600 °C a little weight loss peak is observed. This could be due to partial evaporation of sulfur oxides under a strong temperature increase. Then the weight of the sample continues to increase until 670 °C and drops significantly after 700 °C due to evaporation of sulfur oxides. Between 750 and 800 °C the DSC curve (curve 1 in Figure 3) shows two endothermic effects that are probably caused by high-temperature phase transitions of the formed copper and chromium oxides.

Thus, it was established by the DSC data that oxidizing $CuCrS_2$ causes an intense heat release. As a result, SO_2 is overheated (compared to normal conditions of the CHN/S analysis) when reaching the GCC. Since SO_2 is a reducing agent, this process can be accompanied by the reduction and removal of adsorbed pyrolysis products that were left from other samples in the course of numerous preceding CHN/S analysis procedures.

The baseline shape influence on the measured C, H, N, S contents was estimated by analyzing the SAM and ATRS standards after GCC regeneration using the above procedure. Table 1 summarizes the determined C, H, N and S contents in the SAM and ATRS samples. The confidence interval was calculated from the data of five parallel measurements.

As can be seen from Table 1, the determined composition of SAM and ATRS standards is very close to the theoretical values. Note that the C, H, N, S contents were measured immediately after the $CuCrS_2$ analysis without preliminary GCC regeneration using a standard procedure.

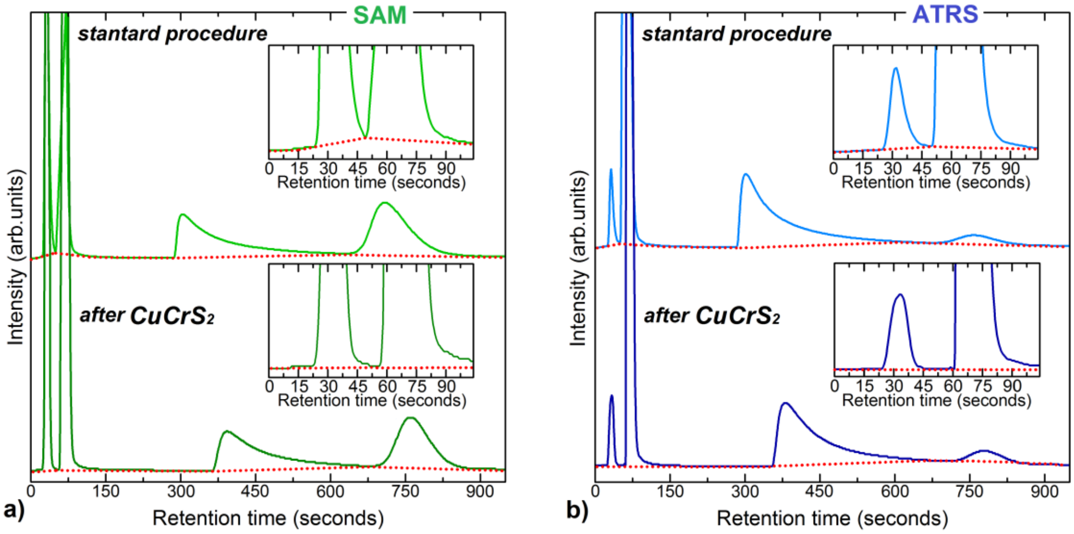

Figure 2 Chromatograms: SAM (green solid line) after standard procedure of GCC regeneration and after $CuCrS_2$ analysis (a); ATRS (blue solid line) after standard procedure of GCC regeneration and after $CuCrS_2$ analysis (b). Baselines are shown as dotted red line. In the top right-hand corners, there are the insets showing the nitrogen and carbon dioxide peaks separation at a larger scale.

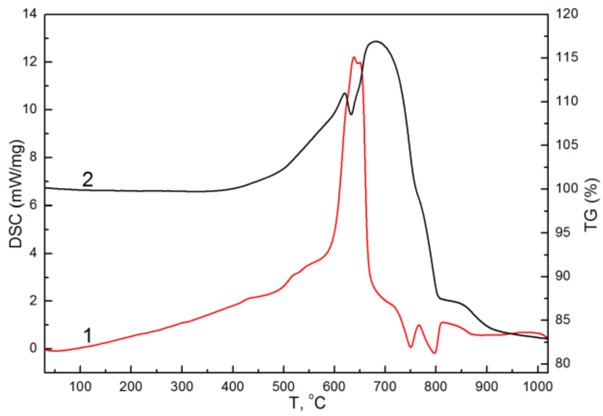

Figure 3 DSC (curve 1) and TG (curve 2) for the $CuCrS_2$ sample.

Table 1 CHN/S analysis data for SAM and ATRS samples.

Element	N	C	H	S
		SA standard		
Theoretical value, wt.%	16.267	41.848	4.683	18.621
Found, wt.%	16.27±0.04	41.87±0.11	4.7±0.06	18.62±0.08
		ATRS standard		
Theoretical value, wt.%	4.032	58.772	7.253	4.615
Found, wt.%	4.03±0.06	58.77±0.09	7.25±0.05	4.62±0.12

4. Conclusions

The GCC regeneration effect when determining C, H, N, S contents in the composition of $CuCrS_2$ was described. The effect results in a perfectly straight chromatogram baseline for standard samples. Such baseline shape provides good separation of chromatographic peaks and a highly accurate determination of C, H, N, S contents in the subsequent measurements. The observed effect allows one to diminish the GCC regeneration time from one or two days to 8 hours.

Supplementary materials

No supplementary materials are available.

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Conflict of interest

The authors declare no conflict of interest.

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