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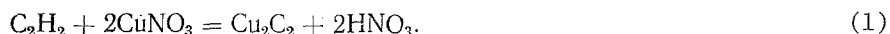
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The mechanism of the processes involved in the vaporization and dissociation of samples in electrothermal atomic absorption analysis (AAA) determines such important characteristics of the method as the sensitivity, the accuracy of the analysis, and the temperature regime for the atomization. In turn, this mechanism depends on the anionic species accompanying the metals being determined in the sample being assayed and on the nature of the interaction between the metal being determined and the sample matrix and the atomizer material.

The kinetics of the vaporization of metals in AAA in graphite atomizers has been investigated in [1-13] and, moreover, in [6-13] particular significance was attached to the question of the interaction between the metals being determined and graphite. In particular, the authors of [7-11] came to the conclusion that, during the atomic absorption determination of the elements Cu, Ag, Au, Ca, Sr, and Ba in the solid phase, these metals react with carbon to form MeC_2 and Me_2C_2 acetylide-type compounds. This conclusion requires direct proof and, furthermore, independent experimental confirmation of the above-mentioned hypothesis is of great importance both for AAA and for physical chemistry. In the first place, this would confirm the existence of an important additional step in the atomization process, determining the optimal temperature at which the analysis is carried out and, secondly, it would serve as a check on the reliability of the theoretical conclusions and the methodology of atomic absorption experiments, which predict the existence of such compounds.

Attempts have been made in [12, 13] to investigate the mechanism of the interaction between a number of metals (including copper, silver, and calcium) and graphite directly. In this work the authors made use of a color reaction of acetylene [14]



to reveal the corresponding acetylides. In the experiments reported in [12, 13], a graphite rod together with a nitrate salt of the metal under investigation was heated in a chamber filled with argon. After the rod had been allowed to cool, the chamber was opened and the rod together with the sample was placed in the indicator solution containing 60% water [14]. If the sample contained an acetylide, then acetylene must be evolved upon contact with water. If this occurs, the indicator solution would take on a reddish-violet coloration. In the experiments reported in [12, 13], no coloration of the solution was observed in the case of copper, silver, calcium, and europium. A color change only occurred in the case of gadolinium.

However, it should be noted that this result is strange, at least in the case of calcium, since the reaction



is generally known and used for the preparation of carbide [15]. Similar processes are also known in the case of strontium and barium [15], while MeC_2 crystalline compounds are known in the case of europium and gadolinium which only differ in the magnitude of the heat of formation (-65 and -105 kJ/mole, respectively) [16]. All this leads one to believe that some methodical error was possibly made by the authors of [12, 13] in carrying out their experiments. It is well known that the acetylides of silver and copper are only stable at high temperatures and unstable in the standard state [17]. They instantaneously decompose in air. Of the three other metals which were investigated, gadolinium possesses the most stable carbide [16]. In fact, the authors of [12, 13] also detected this carbide. It is therefore natural to suppose that the less-stable acetylides of calcium, europium, copper, and silver, which are formed on the surface of the graphite as a thin film would decompose upon cooling or upon contact with air. For the correct application of the technique which has been described for the detection of acetylides it is necessary to exclude the stage in which the

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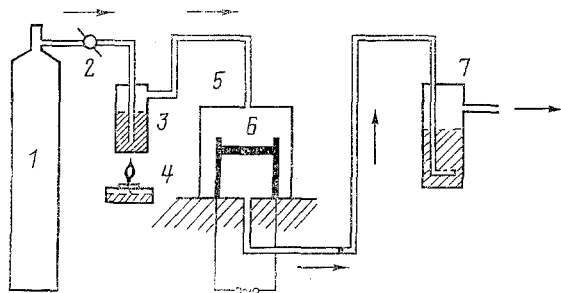


Fig. 1. Diagram of the experimental apparatus: 1) argon cylinder; 2) reducing valve; 3) mixer; 4) spirit burner; 5) chamber for AAA [18]; 6) atomizer; 7) bubbler with indicator solution.

sample is cooled and to prevent any possibility of it coming into contact with air. This served as the basis of the investigation carried out in this work. A diagram of the experimental apparatus is shown in Fig. 1. Argon from cylinder 1 was fed into the mixer 3 containing boiling water, from where the gas, saturated with water vapor, entered into the chamber 5 with the atomizer 6. Flowing water at a temperature of 340–350°K was circulated through the hood of the chamber, the base, and the contacts of the atomizer. The gas leaving the chamber entered into the bubbler containing 30 ml of the indicator solution, prepared according to the method described in [14]. A Schott No. 2 filter served as the diffuser in the bubbler. The argon flow rate through the chamber was 60 liters/h. The temperature of the atomizer was controlled by means of a "Promin" pyrometer or a Chromel–Alumel thermocouple. Rods made out of MPG-6 graphite, spectroscopic grade graphite (SG), and pyrolytic graphite with a length of 40 mm and a diameter of 5 mm were used as atomizers.

The cover was removed from chamber 5, an aliquot of a solution containing the nitrate of the metal under investigation was measured out onto the atomizer and this solution was dried out and heated at a temperature $T = 700\text{--}800^\circ\text{K}$. Subsequently, after argon saturated with water vapor had been blown through the chamber for 30 sec, the atomizer was heated up to the required temperature and fired for several minutes. On each occasion a control experiment was carried out in parallel, by firing a pure graphite rod with no metal under the same conditions. Argon saturated with water vapor was blown through the chamber throughout the duration of the experiment. If acetylides were to be formed by the metal reacting with the graphite, then, in the presence of water vapor, acetylene would be evolved in the chamber and the colorless indicator solution would take on a reddish-violet coloration [14]. The extent of the change in the color of the solution was measured both visually and with the help of an SF-16 spectrophotometer using 1-cm cells at a wavelength of 570 nm. The investigations were carried out with copper, silver, and calcium. For purposes of comparison, similar experiments were carried out with aluminum and chromium which do not form acetylides but which react with carbon to form carbides [15].

The experimental results are shown in Table 1. The formation of acetylene was observed upon the firing of calcium on a MPG-6 graphite rod at $T \geq 2100^\circ\text{K}$ in an atmosphere of argon with water vapor. Acetylene was not formed at $T = 1800^\circ\text{K}$. These results are in good agreement with the known data concerning reaction (2) which takes place at $T \geq 1870^\circ\text{K}$ [15].

In the case of copper, the formation of acetylene was observed upon the firing of the samples on an MPG-6 porous graphite rod or SU graphite rod at $T = 2000\text{--}2100^\circ\text{K}$, and, moreover, the amount of acetylene formed increases as the amount of metal added is increased. At $T = 1150^\circ\text{K}$, acetylene was not formed after a period of time required for almost complete vaporization of the sample. (The degree of vaporization was monitored visually through the window of chamber 5 from the gradual reduction and disappearance of the sample spot on the surface of the rod.) Also, no formation of acetylene was noted at 2100°K when the porous graphite was replaced by a smooth, isotropic pyrographite. Hence, it may be concluded on the basis of these experiments that copper acetylide is formed at $T \geq 2000^\circ\text{K}$ if the surface of contact between the copper and the graphite is sufficiently developed. Additional experiments were carried out with calcium and copper, by loading the powdered metal oxide (0.1 g) in a mixture with OSCh 7-3 graphite powder into a furnace made out of MPG-6 graphite (length 40 mm, internal diameter 4.5 mm, external diameter 7 mm). The furnace was fired in an atmosphere of dry

TABLE 1. Conditions and Results of the Experiments

Metal	Amount of metal added, g	Atomizer material	Firing temperature, K	Firing time, min	Color of solution	Optical density
Ca	$2 \cdot 10^{-4}$	MPG-6	2600	5	reddish-violet	0,065
—	0,00	MPG-6	2600	5	colorless	0,015
Ca	$2 \cdot 10^{-4}$	MPG-6	2100	5	reddish-violet	0,06
—	0,00	MPG-6	2100	5	colorless	0,01
Ca	$2 \cdot 10^{-4}$	MPG-6	1800	20	colorless	0,015
Cu	$6 \cdot 10^{-3}$	MPG-6	2100	4	reddish-violet	0,06
—	0,00	MPG-6	2100	8	colorless	0,015
Cu	$8 \cdot 10^{-3}$	SU	2050	1	reddish-violet	0,04
—	0,00	SU	2050	1	colorless	0,008
Cu	$4 \cdot 10^{-4}$	SU	2000	4	colorless	0,018
Cu	$2 \cdot 10^{-3}$	SU	2000	4	weakly reddish-violet	0,031
Cu	$8 \cdot 10^{-3}$	SU	2000	4	reddish-violet	0,05
Cu	$8 \cdot 10^{-3}$	SU	1150	6	colorless	0,01
Ag	$6 \cdot 10^{-2}$	SU	1700	1	weakly reddish-violet	—
—	0,00	SU	1700	1	cloudy, colorless	0,008
Ag	$6 \cdot 10^{-2}$	SU	1300	3	colorless	0,01
—	0,00	SU	1300	3	"	0,01
Al	$2 \cdot 10^{-3}$	MPG-6	2200	5	"	0,02
—	0,00	MPG-6	2200	5	"	0,015
Cr	$3 \cdot 10^{-2}$	SU	2000	1	"	—
—	0,00	SU	2000	1	cloudy, colorless	0,01

argon for 10 min at 2800°K in the case of calcium and at 2500°K in the case of copper and then cooled in an atmosphere of argon, after which it was rapidly loaded into the indicator solution. In the case of calcium, the solution took on an intense reddish-violet color which provided evidence of the presence of acetylene which was unable to decompose as the sample was covered with a layer of graphite powder. In the case of copper no coloration of the solution was observed. Since, it is known [15] that copper acetylide is decomposed upon cooling and upon contact with an oxidizing medium, this result appears to be quite normal.

In the case of silver no formation of acetylene was observed at $T \leq 1300^\circ\text{K}$. At $T = 1700^\circ\text{K}$ the indicator solution took on a weak reddish coloration but became cloudy at the same time which precluded us from determining the optical density. The clouding of the solution is due to the entrapment of extremely fine silver powder in it which was also precipitated out on the walls of the chamber when large amounts of silver were heated in the graphite furnace. Since the indicator solution remained colorless in the control experiments, the change in its color in experiments with silver at $T = 1700^\circ\text{K}$ is associated, apparently, with the formation of the acetylide Ag_2C_2 .

All these results are in good agreement with the data in [8, 9] where it was confirmed that Cu_2C_2 is formed in graphite cells at $T \geq 1400^\circ\text{K}$, Ag_2C_2 is formed at $T \geq 1450$, and CaC_2 is formed at $T \geq 2000^\circ\text{K}$.

In order to convince ourselves that the appearance of acetylene in our experiments was associated, in fact, with the formation of acetylides on the surface of the graphite, experiments were carried out with aluminum and chromium which form carbides of a different type. In both case no acetylene was observed to be formed.

Hence, the experiments carried out confirmed the hypothesis that the acetylides of copper, silver, and calcium are formed at high temperatures in graphite cells for AAA.

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