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Physics

Study of the Absorption Signal in the Flame of the Burner with Ring-Shaped Slot for Atomic-Absorption Spectrometry

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ABSTRACT. In this article, the original structure of a burner with ring-shaped slot for atomic-absorption spectrometer (AAS) is considered. This burner forms the lateral cylindrical flame with the length limited by the screen and the air stream. The beam from the light source to the monochromator passes through the ring-shaped slot and coincides with the symmetry axis of the cylinder, formed by the flame. We offer the method of calculation of the absorption signal (the number of studied atoms in the absorption zone) at raying of the flame parallel to the velocity of air flame, when the process is stationary and the transverse shift of the absorbing atoms in the flame takes place only due to diffusion. The absorption signal dependence on such parameters as ring-shaped slot radius, flame length, the flame air velocity and the distance between the light beam and the center of the ring-shaped slot was studied. It is shown that absorption signal increases with increase of the flame length, decrease of the ring-shaped slot radius and the flame air velocity. From the obtained results, we may conclude that the design offered by us allows effective concentration of absorbing atoms in the absorption zone. The absorption signal (sensitivity) sharply increases compared with common slot burners in the same conditions. The device has reserves for further increase of the absorption signal.

The burner also allows increase of the absorption signal, when it is used as a "pulsed vaporizer-flame" type atomizer. At this, it is possible to detect hardly atomized elements as there is no need of application of nickel or quartz tube, which is successfully replaced by cylindrical flame. *© 2009 Bull. Georg. Natl. Acad. Sci.*

Key words: *atomic-absorption spectrometer, cylindrical flame, ring-shaped slot.*

Growth in the number of flame atomic absorption units had been steady till 1991. Then some tendency to decline was noticeable. Even though, at high rates of growth of complementary techniques such as ICP-AES and ICP-MS, more than 3000 units of AA were sold annually by 1996 [1].

Over recent years, flame-based methods have shown a decreasing proportion of the total number of papers reporting developments in AA methods. In the Atomic Absorption Updates for 1998, the proportion of papers reporting flame methods was 33% compared with 35% in 1997 [2] and 42% in 1996 [3]. Some researchers even considered the possibility of removal of commercial AAS instruments from the marketplace, but they are still in use in almost every laboratory and there is no indication that they will be replaced by any other technique in the near future [4]. There are many studies on mechanisms of atomization, interferences (influence) etc. Also there are numerous methodological and instrumental innovations that keep the rate of publications above 1000 annually with no sign of decline [4-10]. The proposed work is one of such attempts to improve the analytical characteristics of flame atomizers. One may say that flame AAS still plays a significant role in many laboratories in metal analysis at amounts less than 1ppm. FAAS and ETV-AAS are widely used in geoanalytical laboratories [11] because of their simplicity, low cost, quick performance, weak dependence on the matrix, which makes it very expedient.

In order to improve sensitivity (the detection limit), “pulse vaporizer-flame” type atomizers were developed on the basis of flame atomizers. These are, for instance, “Delves” system, or tantalum boat [12-16], which are successfully used mainly for atomization of easily evaporating elements. The atomizer proposed in this article has prospects for further enhancement of detection limit of pulse atomizers and allows analyzing of hardly vaporized and hardly atomized elements as well. It can be effectively utilized in atom trapping techniques [2, 3, 11, 17] and thermospray systems [18].

Usually, linear slot burners are used and longer absorption zones are created in order to increase the absorption signal in Atomic-Absorption Spectrometers (AAS) [13, 14, 19]. It is shown both theoretically and experimentally that sensitivity does not increase when the light propagation path is enlarged by extension of the linear slot of the burner at constant gas flow and input speed of the element to be determined [20].

In the known flame atomyzers, free atoms within the airs of the flame travel transversely to the light beam and they stay in the absorption area for a very short period of time. Amplification of an absorption signal can be attained by enlargement of the time during which the atoms stay within the light path. From this point of view, construction of a burner with a ring-shaped slot, where the element atoms studied travel parallel to the light beam is a subject of interest [21, 22]. In this case, transverse migration of free atoms takes place due to diffusion and they enter the central area of the cylindrical flame, where the light passes and they stay there for a longer period of time. The absorption rate depends on the amount of atoms within the light path, which is determined by their distribution in the flame and depends on parameters such as slot radius, flame length, gas flow in the flame etc. Investigation of the distribution of the atoms as subject to those parameters is an interesting task; it allows us to determine the most advantageous design of the burner with ring-shaped slot, this being the main goal of this work.

In order to calculate the distribution of atoms in the cylindrical flame of a ring-shaped slot, we have considered the following simplifications:

1. Evaporation of dry particles in aerosol takes place in a narrow area of the flame. Let us for convenience consider that the flame is directed upward. Further, we can say that the source of atoms is presented by the line ring-shaped thread located above the ring-shaped slot at the point where evaporation of an element reaches its maximum. The radius of the source thread is the same as that of the slot - *R*. The atoms enter the flame at constant rate through the whole length of the thread end - *l*. The total amount of atoms that enter the flame for a unit of time is *N*. The process is a stationary one.

2. The flame area of our interest is presented by a cylinder with axis *z*, which coincides with the vertical axis of the flame. Let the dimensions of the cylinder be $0<r<\infty$, $-\infty<z<\infty$. The particles inside the cylinder with constant velocity v migrate along the axis *z* directed at right angle to the thread plane passing through the centre *o* of the ring (Fig.1). Transition of atoms transversely to *z* occurs only as a result of diffusion. Variations of a number of atoms caused by various processes (oxidation, carbonization, etc.) and convective flows are neglected. The diffusion constant *D* of the atoms in gaseous environment is constant and equals $D=5$ cm^2/sec in the area involved [23].

Formula for atom distribution in similar conditions is presented in [23, 24]. The only difference is that atoms enter the flame from the point source placed in the center of the cylinder plane (bottom) *O* with coordinates $z=0$, $r=0$. Distribution of the atoms is expressed by the following equation:

$$n(z,r)=\frac{n_1}{4\pi D}\frac{1}{\sqrt{z^2+r^2}}e^{-\frac{v}{2D}\left(\sqrt{z^2+r^2}-z\right)}, \qquad (1)$$

where $n(z, r)$ is concentration of atoms at any point of the cylinder with coordinates *z* and *r*; n_1 is the amount of atoms that enter the flame within unit of time.

The number of atoms in the absorption area for the space of z^1 when line beam passes parallel with flame velocity in the case of point source may be expressed as the integral of function (1):

$$N\left(z^1,r\right)=\frac{n_1}{4\pi D}\int_0^{z^1}\frac{e^{-\frac{V}{2D}\left(\sqrt{z^2+r^2}-z\right)}}{\sqrt{z^2+r^2}}dz\,. \qquad (2)$$

Absorption signal (i.e. optical density) *A* is proportional to the amount of the atoms $N(z^1, r)$ on the light way calculated by expression (2) – $A \sim N(z^1, r)$. This value will be taken as a basis for our further calculations and it describes (reflects) the integral of absorption.

To calculate the integral of absorption in the case of an atomic field created by a line ring-shaped thread, when light beam is directed transversely to its plane (Fig.1), the thread is fractured into small sections with *dl* length. The number of atoms from each *dl* section is equal to

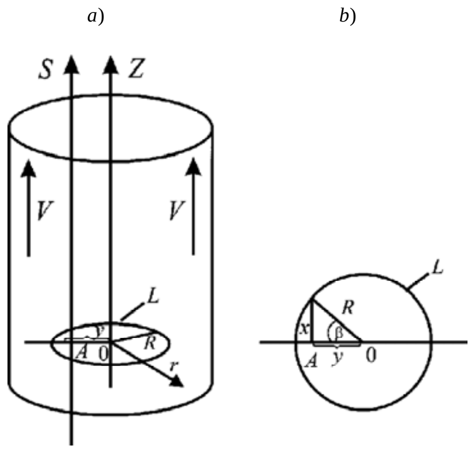

Fig. 1.

$$n_1 = \frac{N_1}{l} dl, \qquad (3)$$

where N_1 is the number of atoms appearing in a flame from the circle source per unit of time.

Each *dl* sector of the line ring-shaped thread can be considered as a point source of atoms with the rate of inflow of absorbing atoms equal to $n_1 = N_1/ldl$ and field of atoms created by the whole source may be calculated using formulae (1) and (3).

Figure 1b shows a line ring-shaped thread (flat $z=0$) when one looks at it in the direction of *z* axis. The total integral absorption is calculated for point *A* (light beam *S* passes through this point). β is an angle between the radius from the center to the source of atoms *dl* and the one to point *A*. Taking into account expressions (2) and (3), the integral of absorption caused by the point source *dl* at the point *A* is expressed as follows:

$$N(z^1, x) = \frac{N_1 dl}{4\pi Dl} \int_0^z \frac{e^{-\frac{\mathrm{v}}{2D}\left(\sqrt{z^2+x^2}-z\right)}}{\sqrt{z^2+x^2}} dz. \qquad (4)$$

The integral absorption at any point may be considered as the sum of integral absorptions created by all *dl* elements of the circular thread:

$$F(z^1, y) = \int_0^l N(z^1, x)\, dl, \qquad (5)$$

where $F(z^1,y)$ is integral (total) absorption at the point *A* located at distance *y* from the center *O* of the thread ring. As it can be seen from Fig.1b.:

$$x = \sqrt{R^2 + y^2 - 2ry\cos\beta}, \qquad (6)$$

$$dl = Rdb, \qquad (7)$$

$$l = 2\pi R. \qquad (8)$$

If we insert expressions (6), (7) and (8) in the formula (5) and integrate it by β instead of *l*, considering that when *l* changes from 0 to $2\pi R$, then β changes from 0 to 2π, the result will be:

$$F(z^1, y, R) = \frac{N_1}{8\pi^2 D} \int_0^{2\pi} \int_0^{z^1} \frac{e^{-\frac{\mathrm{v}}{2D}\left(\sqrt{z^2+R^2+y^2-2Ry\cos\beta}-z\right)}}{\sqrt{z^2+R^2+y^2-2Ry\cos\beta}} dz d\beta. \qquad (9)$$

This formula determines the number of atoms on the way of light beam, when it passes through the cylindrical flame of z^1 length parallel with the flame airs velocity and the distance from the axes *z* is *y*.

Let us calculate the integral absorption for the case when the light beam passes through the centre *O* of the ring: $y=0$

$$F\left(z^1, 0, R\right) = \frac{N_1}{4\pi D} \int_0^{z^1} \frac{e^{-\frac{\mathrm{v}}{2D}\left(\sqrt{z^2+R^2}-z\right)}}{\sqrt{z^2+R^2}} dz = N\left(z^1, R\right). \qquad (10)$$

The Results and Discussion.

Calculations of different parameters were carried out on a personal computer. As one can see from expression (1), the function $n(z,r)$ tends to infinity as $r \to 0$ and $z \to 0$. Thus, $z^1 = 0.2$ cm was taken as the lowest value.

The calculated dependence of function $N(z^1,r)/n_1$ on *r* is shown in Fig.2. It shows that the function increases with decrease of *r* at constant z^1 and $\alpha = \mathrm{v}/2D$. The dependence becomes sharper at larger α, signifying an increase of the relative number of atoms near the cen-

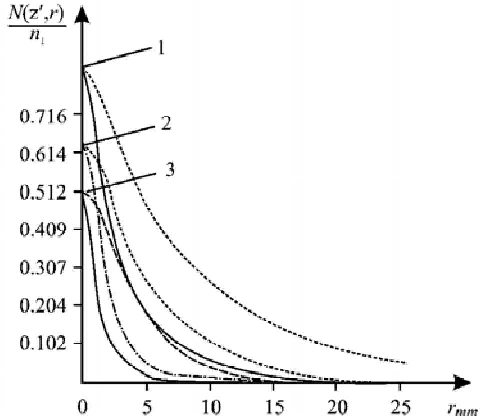

Fig. 2.

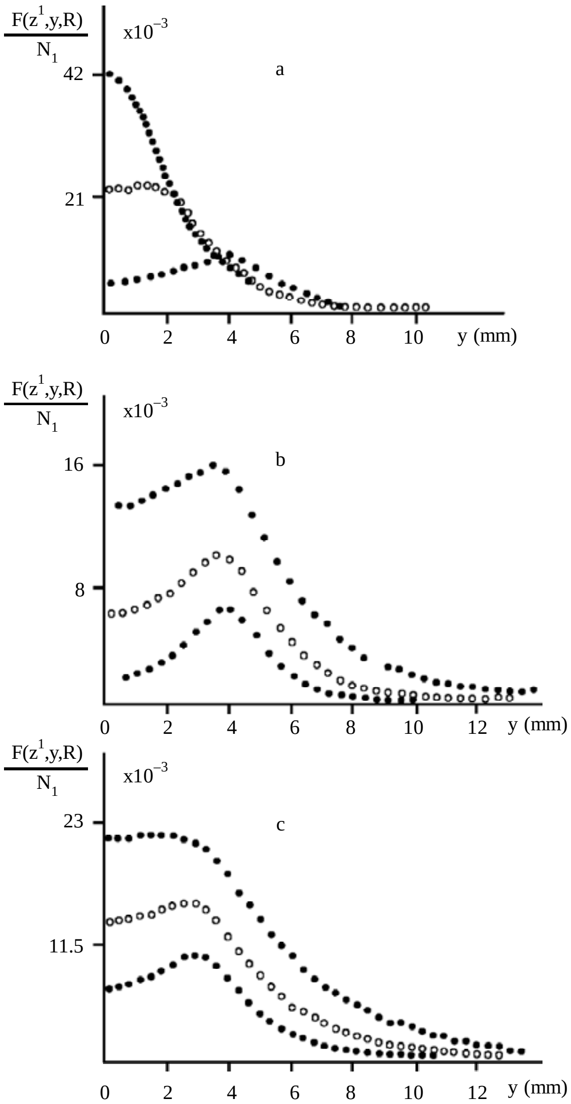

Fig. 3.

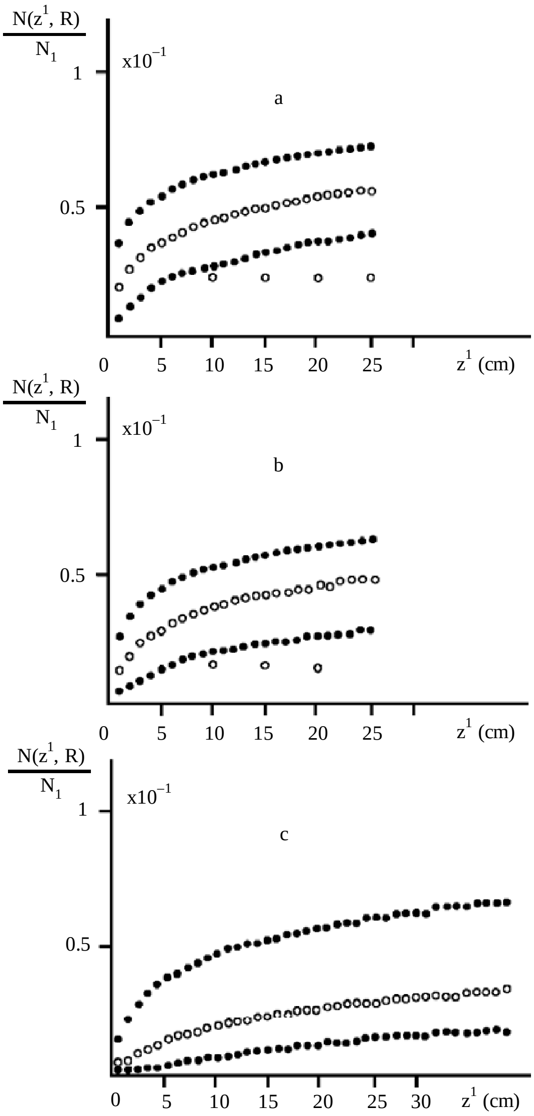

Fig. 4.

tral axis of the cylinder, where $r = 0$. At $r = 0$, the integral is not dependent on α and depends only on z^1 – the length of integration. The function goes up, when z^1 increases at any r and α. At the same time, the graph becomes wider, because at large z^1 atoms have more time to diffuse in transverse directions. Function $N(z^1,r)/n_1$ increases at decrease of α (when flame gas flow – v goes down).

The results of calculations of function $F(z^1, y, R)/N_1$ from (9) of y at different parameters z^1, α and R are presented in Fig.3.

The obtained results show that at small R radiuses of the slot $F(z^1, y, R)$ function has its maximum at the center of the slot ($y=0$) and decreases at an increase of y. At large radiuses, the function reaches its maximum at $y=R$ (above the ring-shaped slot) and declines at the centre of the ring. Maximum of the function is distinctive at high velocities v and small z.

Comparing formulae (10) and (2), one may see their similarity. It may be concluded that the number of atoms across the light beam passing along the axis z of the cylindrical flame is equal to those that lie parallel to axis z at distance r from the point source and r is equal to the radius of the slot - R, if atoms enter at the same rate in both cases ($n_1 = N_1$). Consequently, we may use the same conclusions as the ones for a flame of point source of atoms:

1. Absorption signal in the centre of cylindrical flame increases with decrease of the radius of the slot R in at constant z and α.

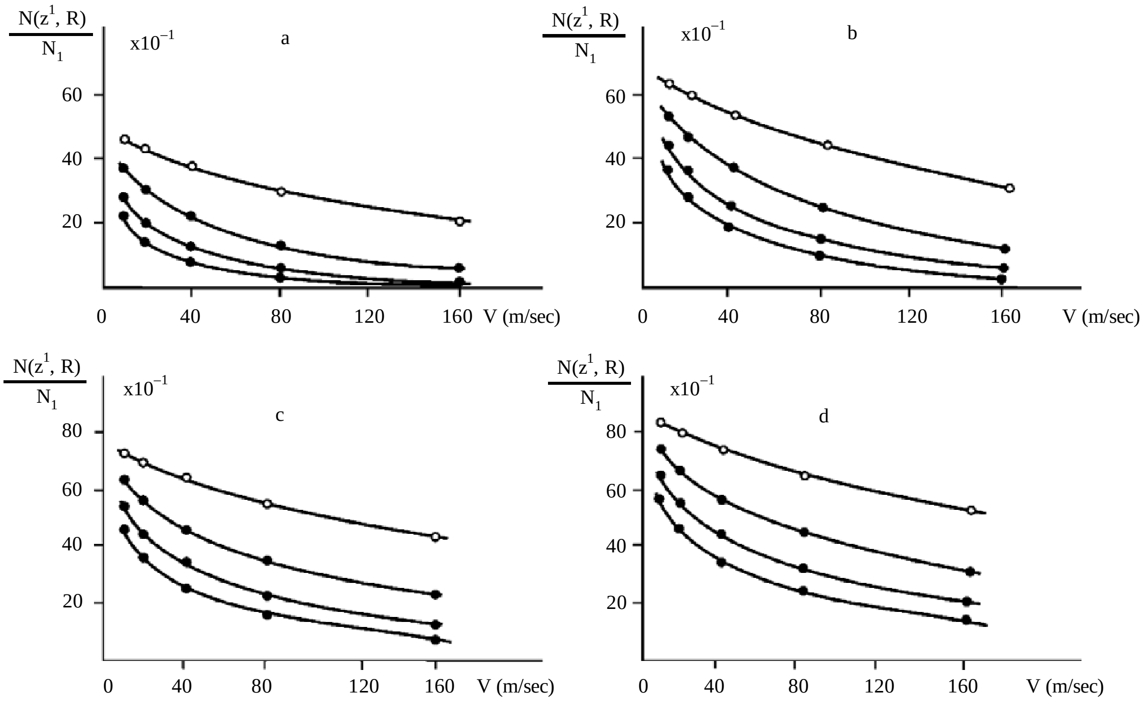

Fig. 5.

2. Relative amount of atoms in the center of cylindrical flame decreases at increase of α.

3. The function $d(z^1,R)/N_1$ increases at any R and á at increase of integration length z^1.

Further values of function $N(z^1,R)/N_1$ were calculated in dependence on integration length z^1 for fixed R and α parameters. The obtained dependences are presented in Fig. 4. There are also analogous dependences for an ordinary linear slot burner (dependence of $(nl)/N$ on z^1), when the light beam is parallel to the slot and placed above it is presented in the same figure. They are calculated by formula $(nl)” = 0.28N/\sqrt{D}vy$, which was obtained in paper [20], where $(nl)”$ is an effective length of the flame layer; N - rate of atom flow in the flame from a linear slot of l length; y - distance of the light beam from the area where evaporation in the flame is maximal; D - diffusion constant; v - flame gas flow velocity.

The value of y is considered equal to R - radius of the comparable ring-shaped slot burner. The other parameters are identical.

As one can see from the results, the absorption signal at a ring-shaped slot burner depends on the length of absorption zone z^1 in contrast to regular linear slot burner, but at increase of the length z^1, this dependence becomes slighter. Therefore, excessive increase of the length is irrational. Increase of sensitivity as compared to an ordinary burner depends on α, R and z and may reach half an order when α =80, R=0.3cm, and z^1=40 cm. Sensitivity gets worse at decrease of v and z^1 and increase at $R=y$. Sensitivities become equal when z^1=40cm and α=80 (v=8m/sec). Values of the function $F(z^1,R)/N_1$ in dependence on a flame gas flow v at fixed R and z were calculated. The dependence graphs are presented in Fig.5. They show monotone decrease at increase of v. This decrease is more drastic at smaller slot. At reduced flame length those patterns remain the same at common decrease of the absorption signal.

ფიზიკა

აბსორბციის სიგნალის შესწავლა ატომურ-აბსორბციული სპექტრომეტრის წრიულღრეჩოიანი სანთურას ალში

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(წარმოდგენილია აკადემიკოს გ.ხარაძის მიერ)

განხილულია წრიულღრეჩოიანი სანთურას (ალიანი ატომიზატორის) ორიგინალური სქემა ატომურ-აბსორბციული სპექტრომეტრისათვის. სანთურა ქმნის ცილინდრული ფორმის ჰორიზონტალურ ალს, რომლის სიგრძე შემოსაზღვრულია ეკრანითა და ჰაერის ნაკადით. სხივი სინათლის წყაროდან მონოქრომატორში გაივლის წრიული ფორმის ღრეჩოს გზით და ემთხვევა ცილინდრის სიმეტრიის ღერძს.

შემოთავაზებულია ატომური აბსორბციის სიგნალის გამოთვლის მეთოდი, ანუ შთამნთქმელი ატომების რაოდენობის გამოთვლის მეთოდი სინათლის სხივის გზაზე (შთანთქმის ზონაში). სინათლის ვიწრო სხივი პარალელურია ალის გაზების სიჩქარის, პროცესები სტაციონარულია და ატომების გადაადგილება სხივის პერპენდიკულარულად ხდება მხოლოდ დიფუზიის გამო. ნაჩვენებია, რომ აბსორბციის სიგნალი იზრდება ალის სიგრძის გაზრდისას, წრიული ღრეჩოს რადიუსის შემცირებისას, ალის გაზების სიჩქარის შემცირებისას. შთანთქმის სიგნალი მცირდება, როდესაც იზრდება სინათლის სხივის დაშორება წრიული ღრეჩოს ცენტრიდან. აბსორბციის სიგნალი (მგრძნობიარობა) მკვეთრად (5-ჯერ) იზრდება ჩვეულებრივ ღრეჩოიან სანთურებთან შედარებით, როდესაც გაზომვის პირობები ერთნაირია. მოწყობილობას გააჩნია აბსორბციის სიგნალის შემდგომი გაზრდის რეზერვი.

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