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Witte

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[54] **TUBULAR SAMPLE CELL HAVING RADIALLY EXTENDING FLANGES AT THE ENDS OF THE CELL FOR FLAMELESS ATOMIC ABSORPTION**

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[51] **Int. Cl.**......................... **G01n 21/16,** G01j 3/30

[58] **Field of Search**.......................... 356/85, 87, 244

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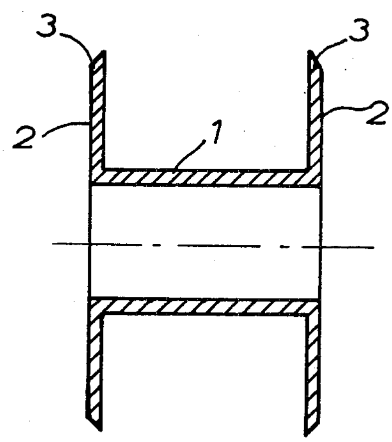
[57] **ABSTRACT**

This is a tubular cell for atomizing samples in flameless atomic absorption spectroscopy of the type in which electric current is passed through the tubular cell to generate the heat for vaporizing the sample therein. The improvement comprises the use of radially extending flanges at the ends of the tube which are in both physical and electrical contact with the tube, and the electric current is supplied to the outer rim of the flanges. This construction reduces the tendency of the ends of the tube to be cooler than the center of the tube, since the flanges themselves generate heat and also their relative thinness inhibits large heat losses from the ends of the tube to the relatively massive electrodes which supply the electric current. The flanges may be shaped in various ways and may include cut-out portions to further increase current density therein and to reduce further their heat conductivity.

24 Claims, 10 Drawing Figures



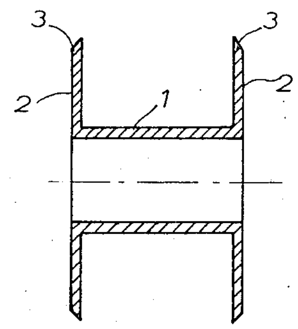


Fig.1

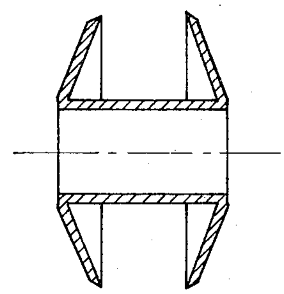


Fig.2

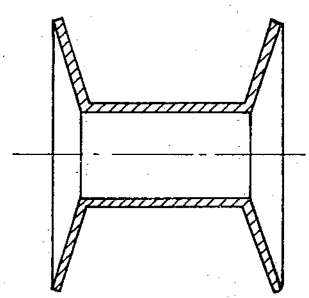


Fig.3

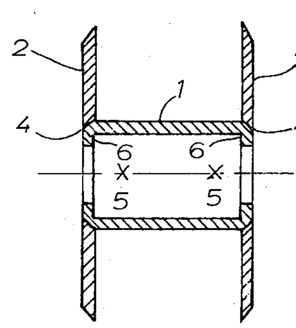


Fig.4

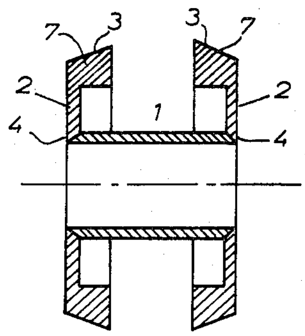


Fig. 5

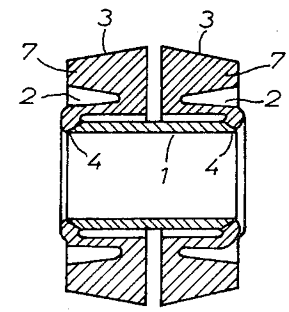


Fig. 6

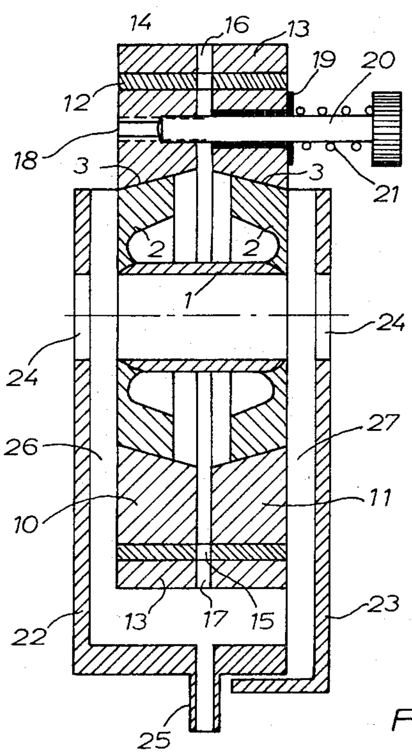


Fig. 7

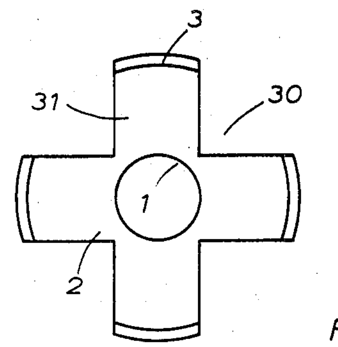


Fig. 8

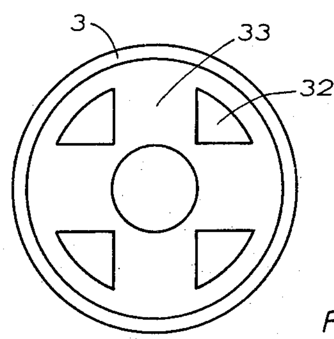


Fig.9

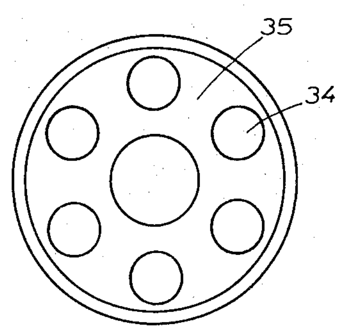


Fig.10

TUBULAR SAMPLE CELL HAVING RADIALLY EXTENDING FLANGES AT THE ENDS OF THE CELL FOR FLAMELESS ATOMIC ABSORPTION

This invention relates to a tubular cell for atomizing samples in flameless atomic absorption spectroscopy.

A graphite tube sample cell is prior art in which electric heating current is supplied to and carried from the graphite tube at the tube ends. Current supply is effected by means of solid contact bodies bored for the passage of rays therethrough. The contact bodies conduct heat very well, the consequence being a temperature profile or gradient in the graphite tube such that the temperature substantially decreases from the hottest location in the center towards the tube ends. At these cooler ends, for example, smoke-like products of decomposition produced by the thermal decomposition of the sample may deposit. In a subsequent sample atomization which takes place at a higher temperature than the previous decomposition, this deposit may again be discharged into the gas space (i.e. the hollow portion of the tubular sample cell) and falsify the measurement.

To correct the temperature profile, it has been suggested (German Pat. application No. P 21 48 777.4 filed Sept. 30, 1971) to make graphite tube have a wall thickness varying over the length. Though the hottest zone in the center can be enlarged by this technique, nevertheless, a substantial cooling effect of the contact bodies on the tube ends cannot be prevented.

In the same patent application it has also been suggested (see FIG. 8) to make the ends of the tube in the form of outwardly extending flanges and to have these flanges be, at least in their inner portion, so thin that (similarly to the tube wall itself) they act as a heat source. However, according to the said application these flanges are only provided to aid in the temperature profile (i.e. gradient) leveling effect caused by the variation of the wall thickness over the tube length. A general application of such flanges independently of a wall thickness variation over the tube length has hitherto not been known.

Moreover, it has been suggested (Austrian Pat. application Ser. No. A 2696/72 to heat a graphite tube in a perpendicular direction, i.e., to carry the heating current substantially in a peripheral (radial) direction through the tube walls. The electric current is supplied to the tube jacket through webs or spiders which are either vane-shaped and integral with the tube or are pressed against the tube jacket from the outside. In the former case the tubes are difficult to manufacture in production quantities. In the latter case it has been found that the tubes have the tendency to deform so as to approach ellipse-shape under the pressure of the contact webs and to break particularly at the contact points. On the other hand, the transversely heated tubes in both designs show a uniformity of temperature profile which has hitherto not been achieved even approximately in the lengthwise heated tubes (i.e., where the current flow is solely parallel to the longitudinal axis of the tube).

It is an object of this invention to provide a tube of uniform temperature for flameless atomic asorption which is sufficiently stable mechanically to withstand the contact pressure and is simple to manufacture in production.

According to the invention this object is achieved by providing that the electric current is supplied to the tube ends substantially in a radial direction from the outside via flange-shaped or flange-like parts, hereinafter called "flanges" for short, and that the flanges are so shaped, particularly with respect to their thickness and thickness distribution, that enough heat is produced in them and their heat conductivity sufficiently low that a cooling of the tube ends is prevented to a sufficient extent to avoid the above-noted problem.

Pressure on the tube is substantially exerted in a longitudinal direction, thus, in a direction in which the tube is very strong and stable mechanically.

In a first type of embodiment of this invention these flanges are integral with the tubes. In a second type of embodiment of this invention the flanges are mechanically separate from the tube and are pressed against the tube ends from the outside.

Basically, the flanges gripping around the tube can also be moved and pressed from the tube center towards the tube ends against the tube contact faces, for instance, if the tube carries slight outwardly facing flanges at the ends. However, each flange must then be divided into at least two parts as otherwise the flanges cannot be positioned over the tube (i.e., inside the flanges at the ends of the tube). Such a design, however, is space-saving.

In one embodiment of this invention the flanges have a constant wall thickness throughout their radial extent. In another embodiment of this invention the flanges are thickened for increase in their external contact surfaces (i.e., with the current source).

Both the outer and also the inner contact faces of the flanges and the corresponding surfaces contacting them may be conical or be in the form of spherical surfaces in the various respective embodiments of this invention. A shape deviating from both conical and spherical is, however also possible.

In some embodiments of this invention the flanges are formed plane and are perpendicular to the tube axis. In other embodiments of this invention the flanges are designed to project in an oblique plane, tilted slightly inwardly or outwardly, so as to have conical (or more accurately frusto-conical) surfaces.

In further embodiments of this invention the flanges are provided with recesses, apertures or bores for increase in the electric current density and decrease in their heat conductivity.

The tubes of the type used in the invention must be operated in a protective gas atmosphere. The various embodiments according to the invention can either be operated in a large encompassing protective gas volume or the tubes can be supplied with protective gas in the manner of the prior art graphite tubes through cross-bores, said protective gas leaving at the tube ends; or else the tube ends can be effectively closed by flow curtains.

The sample can be injected into the tube from the tube ends. Alternatively, a central radially extending bore may be provided for sample injection.

Furthermore, for accommodation of a large sample volume the tube may be designed barrel-shaped or have small flanges extending inwardly at the ends.

It is a further feature of at least some embodiments of this invention to make the flanges extend over the tube towards the tube center for reduction of the radiation losses, so that they effectively surround the tube in the manner of a protective tube.

Finally, it is a separate feature of this invention to make the tube and the flanges of graphite.

A few illustrative embodiments of this invention will more fully be described hereinafter with reference to the accompanying drawings in which:

FIGS. 1 to 3 are longitudinal sections through three embodiments with integral flanges;

FIGS. 4 to 6 are similar longitudinal sections through three embodiments with separate flanges;

FIG. 7 illustrates an embodiment with its protective gas circulating means; and

FIGS. 8 to 10 are axial elevations of three embodiments with recesses, apertures and bores, respectively, in the flanges.

FIG. 1 illustrates a first embodiment in a longitudinal section. The graphite tube 1 has two planar flanges two extending perpendicularly to the tube axis which have conical contact faces 3 at the outer rim.

From tube to rim, the flanges 2 have a constant wall thickness which is equal to the wall thickness of the tube 1. In spite of this, the cross-section for the radially extending electric current increases outwardly, as the cross-sectional areas of equal electrical potential are annular and concentric with the tube axis, and their circumference increases outwardly. At the tube junction, therefore, the electric current density in the flange (and therewith also the amount of heat produced in a unit volume of the wall) is just as great as in the tube, while the electric current density is smaller at the outer rim of the flanges. In the embodiment of FIG. 1 the outer diameter of the flanges is approximately double the size of the tube diameter. Therefore the electric current density in the flange decreases to half from the tube to its outer rim.

FIGS. 2 and 3 illustrate two modifications of the first type (integral flanges) with conically formed flanges. In FIG. 2 the flanges extend inwardly toward the tube center; in FIG. 3 they extend outwardly.

The embodiment in FIG. 4 is distinguished from the embodiment according to FIG. 1 in two aspects. First, tube 1′ and flanges 2′ are physically separate from each other. The flanges 2′ are pressed against the tube ends from the outside. The contact faces between tube and flanges are spherical surfaces at 4. The centers of curvature of these spherical surfaces are illustrated in FIG. 4 by crosses 5, the left center of curvature being associated with the left contact face 4 and the right center of curvature being associated with the right contact face 4. In this manner, good contact between tube and flanges still exists if the flanges are displaced with respect to each other in the direction perpendicular to the tube axis or if the flanges are not exactly aligned parallelly to each other. If the contact faces were, for instance, conical, then minute deviations in the support of the flanges would lead to imperfect contact engagement. This, however, does not mean that, for instance, in the case of exact alignment of the flanges conical contact faces cannot be used. The invention is not restricted to spherical contact faces, such contact faces rather only represent one illustrative embodiment.

A second change as compared with the embodiment according to FIG. 1 resides in the fact that the tube is provided with an interior shoulder or flange extending slightly inwardly at the ends. This interior flange 6 assists in holding the sample and therefore permits the

use of a greater sample volume. The same type of result can be achieved if the tube is formed barrel-shaped or has a similar (concave toward the inside) shape.

Of course, such a form of the tube can also be provided when the flanges are integral with the tube; thus, for instance, the embodiment according to FIG. 1 can be provided with small inwardly facing flanges (like 6 in FIG. 4) at the tube ends.

Another embodiment is shown in FIG. 5. Tube 1′ and flange 2″ are again separate components which contact each other at the contact faces 4. Similar to FIG. 4, the flanges have a constant thickness; however, they terminate in thickened contact rings 7 on the outside, in order to increase the area the outer contact faces 3′. A modification of this embodiment consists in that tube and flange are manufactured from one piece, while maintaining the shape shown in FIG. 5.

FIG. 6 illustrates a further embodiment. Tube 1′ and flange 2a represent separate components which contact each other at the contact faces 4. The flanges 2a are drawn towards the tube center and tubularly surround the graphite tube 1′. The flanges have thickened contact rings 7′ with the large contact face 3″ for the outer current supply. Of course, these contact faces 3″ need not necessarily be conical as in FIG. 6, but may, for instance, also be in the form of spherical surfaces. This arrangement is power saving, as the outer radiation losses of the tube 1′ are reduced by the flanges 2a.

In the immediate vicinity to the inner contact faces 4, the flanges 2a project slightly beyond the tube ends. Of course, this is not necessary for this embodiment. The flanges 2a may also readily be designed such that they do not project beyond the tube ends.

FIG. 7 illustrates an embodiment in which the manner is shown by which tube and flanges can be mounted and in which suitable pathways for the protective gas can be realized. The graphite tube 1′ is clamped between the annular graphite flanges 2b. In this embodiment, the flanges 2b do not have a constant wall thickness a fact, which is used merely to indicate the multiple design possibilities of the flanges, but in general is not necessary for this embodiment. The graphite flanges 2b have their outer conical contact faces 3b disposed in metal rings 10 and 11. Over both rings an electrically insulating sleeve 12 is placed which is surrounded by a metal ring 13. The insulating sleeve 12 and the metal ring 13 are cemented to each other. Also, the insulting sleeve 12 and the inner metal ring 10 are cemented to each other. However, the metal ring 11 can slide in the insulating sleeve 12. The insulating sleeve 12 contains one bore 14 and 15 both at the top and at the bottom. Aligned with these bores 14 and 15 the outer metal ring 13 contains two bores 16 and 17.

The metal ring 10 has three threaded bores 18 distributed at regular distances in the peripheral direction over the ring. FIG. 7 only shows the upper bore. The two lower bores are disposed above and below, respectively, the plane of the paper. The metal ring 11 has correspondingly distributed bores, however, without threads and somewhat larger in diameter, into which electrically insulating bushings 19 are inserted. Three screws 20, engaging with the threads in the threaded bores 18 of the metal ring 10, are guided through these bushings 19. Three pressure-loaded spiral springs 21 press the metal rings 10 and 11 against each other.

Thereby, also the flanges **2b** are pressed against the ends of the tube **1'**.

The whole device is arranged in a box-like housing which is open at the top, comprised of two parts **22** and **23.** Both parts each have an aperture **24** for the passage of rays. The "cover" part **23** grips over the part **22** like a cover. The part **22** has a gas inlet socket **25.** The part **22** is tightly connected and gas-tight with the metal rings **10** and **13.** The part is tightly connected and gas-tight with the metal ring **11.** The part **22** is mounted in the spectrometer in a manner not shown.

When loosening the screws **20,** the fixedly interconnected pars **11** and **23** can be removed from the also fixedly interconnected parts **10, 13** and **22,** for instance, to insert a new graphite tube **1'**.

The protective gas enters into the housing **22,23** through the socket **25.** A small proportion of the protective gas enters through the bores **17** and **15** between the two flanges **2b**, circulating around the graphite tube **1** from the outside and passing through the bores **14** and **16** at the top to leave into the open air. The major proportion of the protective gas, however, flows through the two flat channels **26** and **27** and effectively closes off the inner volume of the graphite tube **1'** at the ends in the manner of flow curtains against the outside air, before the gas leaves the channels **26** and **27** at the top.

The electric current is supplied to the metal rings **10** and **11** (or more accurately is supplied to one of metal rings and ultimately from the other) in a manner not illustrated.

FIG. **8** shows one type of embodiment in an axial view. The flange **2c** includes four recesses **30** so that four radially aligned webs **31** of constant width are provided.

Both flanges have the same shape. om FIG. **8,** the second flange in the projection coinciding with (behind) the visible flange. The current distribution in the tube **1** itself becomes somewhat more uniform, if the second flange is rotated through 45° with respect to the first flange.

By the recesses **30** the area of the outer contact face **3c** is also reduced. This can be avoided by providing webs between apertures, such as in the form of the apertures **32** in the embodiment of FIG. **9.** Thereby, spoke-like webs **33** are provided. The outer contact face, **3d**, however extends over the whole circumference of the flange. The apertures **32** provide a uniform current density distribution within the spokes **33,** but are not easy to manufacture in production quantities. In this respect, the embodiment in FIG. **10** is more favorable. Herein, the apertures **32** are replaced by bores (round holes) **34.** Though the spokes **35** do not have a constant width, however, they provide a desired increase in the electric current density and decrease in heat conduction.

In the embodiments, the bores and apertures are arranged circumferentially on a circular line concentric with the tube axis. Of course, the bores and apertures may also be arranged on several circular lines or in any desired distribution. One alternative embodiment is providing the entire flange with relatively small holes like a sieve at uniform distribution. In a similar embodiment the density of the hole distribution, the diameter of the holes and/or the mutual distance of the holes may be varied in the radical direction along the flanges in order to obtain a favorable distribution of the electric current density over the flange.

Of course, recesses, apertures, and bores can be used in combination as desired on any one of the flanges.

I claim:

1. A tubular cell for vaporizing the sample for flameless atomic absorption by means of electric current heating, comprising:

a hollow tube;

generally disc-shaped flanges at and in physical contact with the ends of said tube so that said flanges extend from said ends in a substantially radial direction;

contact means at the outer rim of said flanges for receiving electric current;

said flanges having dimensions, particularly with respect to their thickness and thickness distribution, such that the amount of heat produced in them by such electric current is large compared to the heat lost by conduction so that cooling of the tube ends is substantially prevented.

2. A tubular cell as claimed in claim **1,** in which:

said flanges are integral with said tube, so that said flanges and tube are a single integral unit.

3. A tubular cell as claimed in claim **1,** in which:

said flanges and said tube are mechanically separate components which contact each other at the tube ends at mutually mating contct faces (**4**).

4. A tubular cell as claimed in claim **3,** in which:

said contact faces (**4**) are conical in form.

5. A tube cell as claimed in claim **3** in which:

said contact faces (**4**) are spherical surfaces.

6. A tubular cell as claimed in claim **1,** in which:

said contact means (**3**) at the outer rim of said flanges are conical.

7. A tubular cell as claimed in claim **1,** in which:

said contact means (**3**) at the outer rim of said flanges are spherical surfaces.

8. A tubular cell as claimed in claim **1,** in which:

said flanges have a constant thickness at least except for the outer rim thereof.

9. A tubular cell as claimed in claim **1,** in which:

said contact means comprise thickened portions of the outer rim portion of said flanges, so as to increase the contact area of said contact means (**3**).

10. A tubular cell as claimed in claim **1,** in which:

said flanges are planar in form and are arranged prependicularly to the tube axis.

11. A tubular cell as claimed in claim **1,** in which:

said flanges are inclined relative to the axis of the tube, so as to present a conical surface at said tube ends.

12. A tubular cell as claimed in claim **1,** in which:

said flanges extend from the tube ends initially towards the tube center so as to surround at least partially said sample tube (**1**).

13. A tubular cell as claimed in claim **1,** in which:

said sample tube (**1**) has at its ends short inwardly extending secondary flanges to increase the quantity of sample which may be held within said tube.

14. A tubular cell as claimed in claim **1,** in which:

said tube (**1**) and said flanges (**2**) are both made of graphite.

15. A tubular cell as claimed in claim **1,** in which:

said tube (**1**) has a cross-bore for sample introduction.

16. A tubular cell as claimed in claim 1, in which: a housing substantially surrounds said tube (1) and said flanges (2), so that the tubular cell is operated in a protective gas volume.

17. A tubular cell as claimed in claim 16, further comprising:

means for introducing into said housing a forced protective gas flow which is passed through said tube.

18. A tubular cell as claimed in claim 1, in which: means are provided for closing off said tube ends by protective gas flow curtains.

19. A tubular cell as claimed in claim 1, in which: said flanges are cut away at their rims so as to provide recesses (30).

20. A tubular cell as claimed in claim 1, in which: said flanges are perforated at a small plurality of positions so as to provide apertures (32).

21. A tubular cell as claimed in claim 1, in which: said flanges are perforated by a plurality of circular shape apertures so as to provide bores (34).

22. A tubular cell as claimed in claim 1, in which: said flanges are relieved in some symmetrical manner so as to provide some type of apertures;

and said two flanges are rotated with respect to each other so as to misalign said apertures.

23. A tubular cell as claimed in claim 1, in which: said flanges contain a plurality of small holes in sieve-like manner.

24. A tubular cell as claimed in claim 23, in which:

at least one of the size and respective distance between said holes varies in a radial direction along each flange in order to obtain a favorable electric current density distribution across said flanges.

* * * * *