United States Patent

Della Porta et al.

[15] **3,667,513**

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[54] **GENERATION OF ALKALI METAL VAPORS**

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[51] **Int. Cl.**.....**B65b 1/04,** B65b 3/04

[58] **Field of Search**.....141/8, 311, 65, 66, 82, 89, 141/85, 382–389; 313/174; 316/24

[56] **References Cited**

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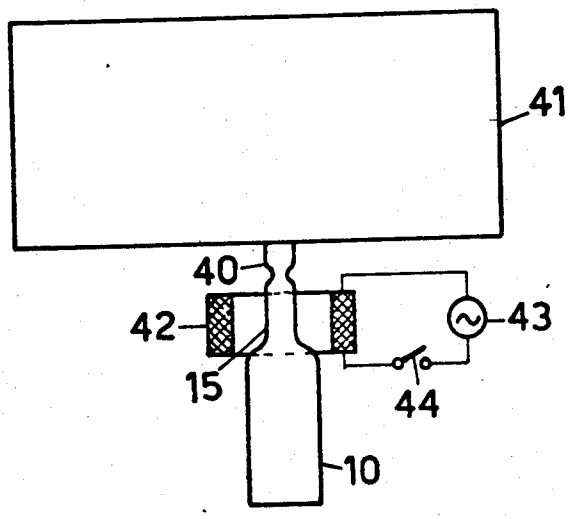
[57] **ABSTRACT**

An alkali metal generator comprising: an evacuated container; at least one heat-responsive source of an alkali metal vapor in the container; a closed conduit for connecting the evacuated container to a vessel to be charged with the alkali metal vapor; and means for opening said closed conduit. The container can also have a getter device.

13 Claims, 7 Drawing Figures



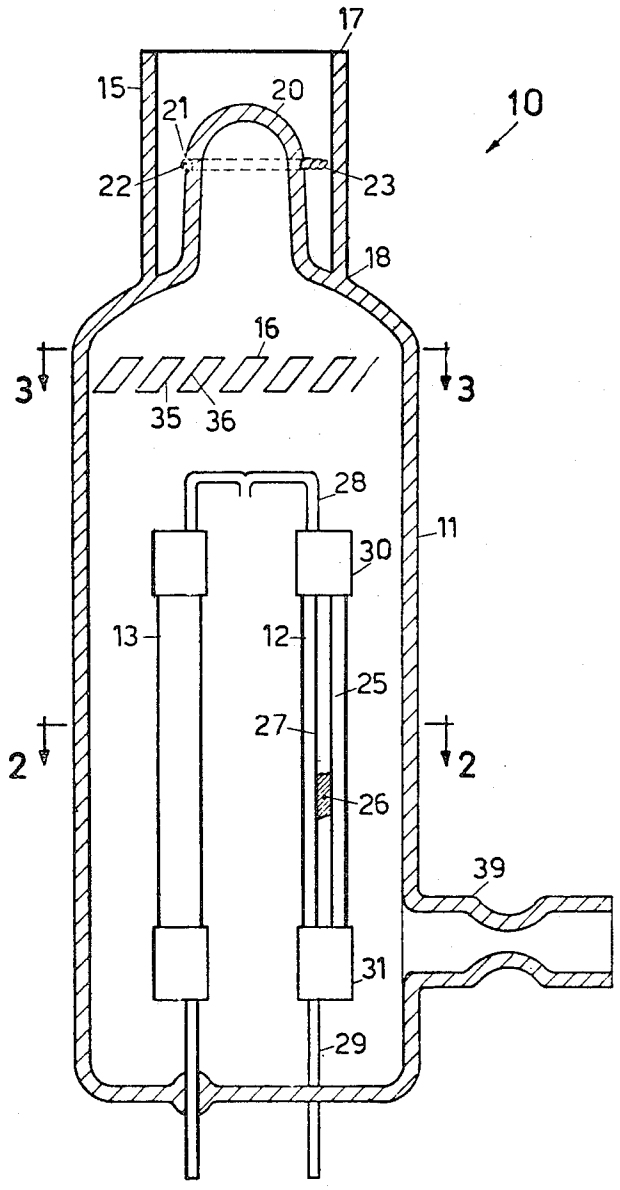


Fig. 1

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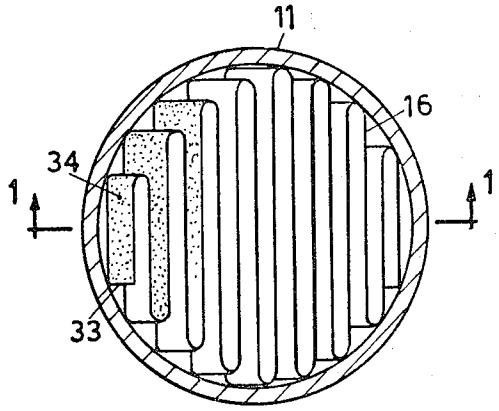

Fig. 3

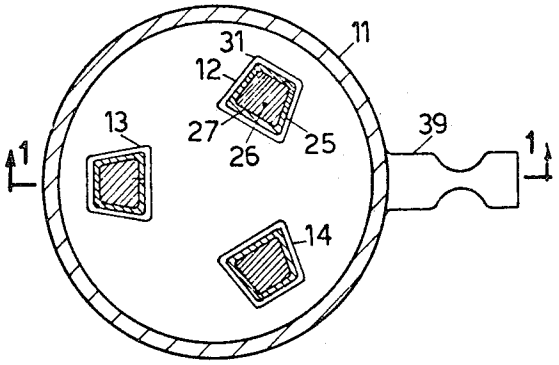

Fig. 2

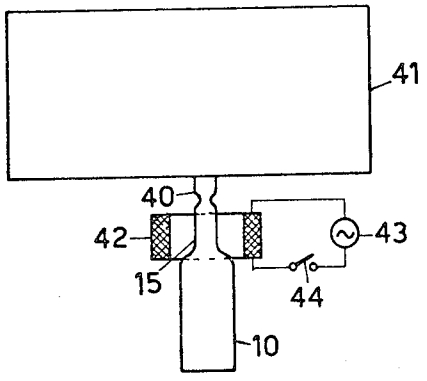

Fig. 4

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FIG. 5

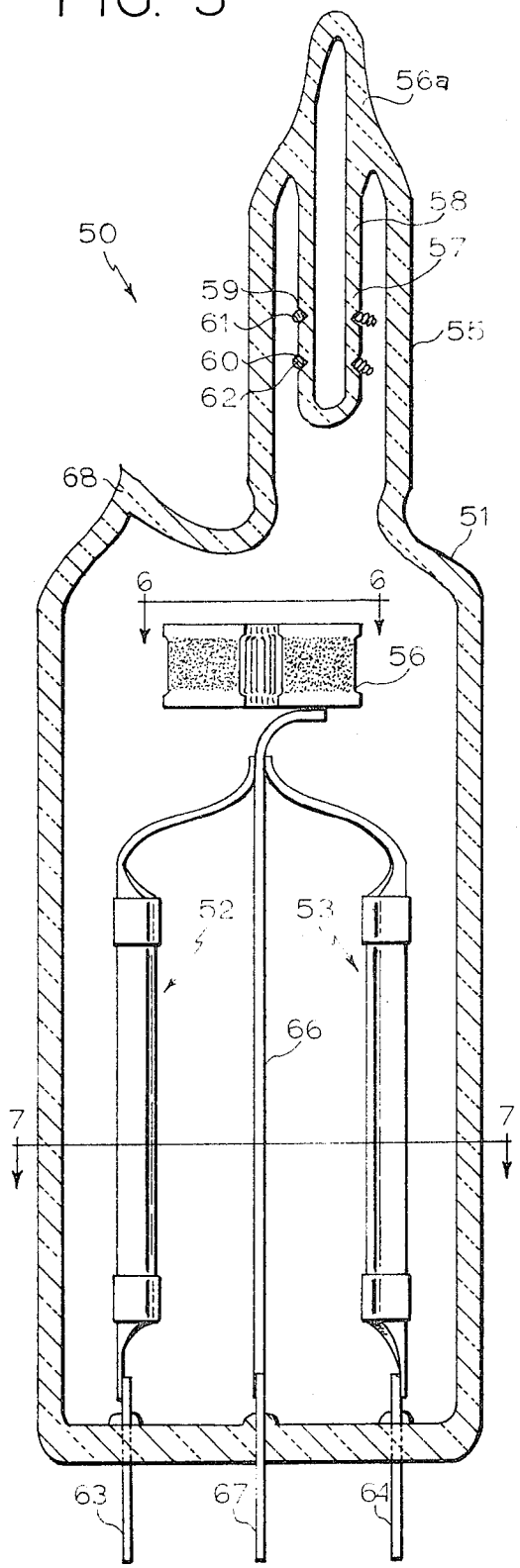


FIG. 6

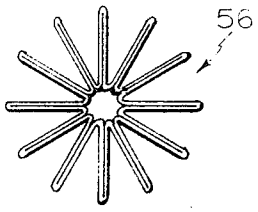
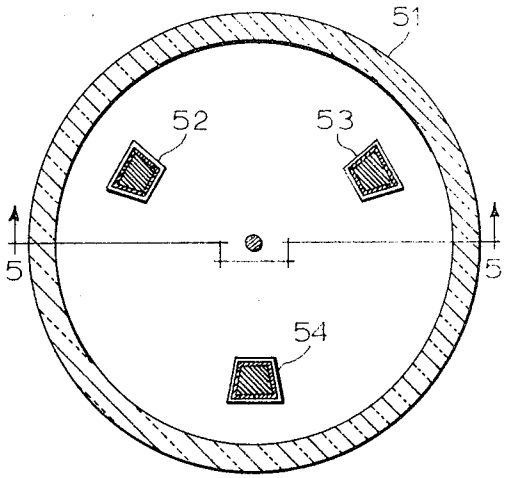


FIG. 7



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GENERATION OF ALKALI METAL VAPORS

Generators useful for introducing alkali metal vapors such as those of cesium, potassium, and/or sodium into vessels such as photo-multiplier tubes, image-intensifier tubes, and television pickup tubes for the purpose of producing photo-sensitive surfaces are well-known in the art. Unfortunately, these prior generators suffer from a number of disadvantages such as their tendency to release loose particles from the alkali metal vapor source which is generally a mixture of an alkali metal chromate and a reducing agent for the chromate. Furthermore, these prior generators must be degassed after they are attached to the vessel to be charged with alkali metal vapor. This degassing is accomplished by heating the generator to high temperatures such as 300°to 450°C for a period of time frequently six to ten hours while removing gases by means of a vacuum pump. Other prior generators release noxious gases such as oxygen during the period of evaporation of the alkali metal vapor. These noxious gases can react with the alkali metal vapor and/or the deposit of alkali metal on the photosensitive surfaces, damaging these surfaces.

It is therefore an object of the present invention to provide improved alkali metal generators substantially free of one or more of the disadvantages of prior generators.

Another object is to provide improved generators which do not require a separate step of degassing.

A further object is to provide improved generators which do not release loose particles.

A still further object is to provide improved generators which produce alkali metal vapors substantially free of noxious gases.

Additional objects and advantages of the present invention will be apparent to those skilled in the art by reference to the following detailed description thereof and the drawings wherein:

FIG. 1 is a sectional view of a generator of the present invention taken along line 1—1 of FIG. 2, and 1—1 of FIG. 3;

FIG. 2 is a plan sectional view taken along line 2—2 of FIG. 1;

FIG. 3 is a plan sectional view taken along line 3—3 of FIG. 1;

FIG. 4 is a schematic representation illustrating the method of use of the generators of the present invention;

FIG. 5 is a sectional view of a modified embodiment of a generator of the present invention taken along line 5—5 of FIG. 7;

FIG. 6 is a sectional view taken along line 6—6 of FIG. 5; and

FIG. 7 is a sectional view taken along line 7—7 of FIG. 5.

According to the present invention there is provided an alkali metal generator comprising: an evacuated container; a least one heat-responsive source of an alkali metal vapor in the container; a closed conduit for connecting the evacuated container to a vessel to be charged with the alkali metal vapor; and means for opening said closed conduit. In a preferred embodiment the container also has a non-evaporable getter device.

The container can be any suitable material which is readily attachable to the vessel to be charged but preferably has a conduit which is glass and in a preferred embodiment is entirely made of glass. The container is evacuated to a low pressure and generally below 10^{-6} and preferably below 10^{-8} torr.

In the broadest aspects of the present invention, any heat-responsive source of the desired alkali metal vapor can be employed in the container. Thus, alkali metals such as cesium, potassium, sodium, rubidium, and lithium can be produced by the generators of the present invention. Suitable alkali metal vapor sources are known in the art as described, for example, in Lester U.S. Pat. No. 2,117,735 (1938), and Eichenbaum et al. "Cesium Vapor Dispenser," The Review of Scientific Instruments, Vol. 35, No. 6, June 1964, pages 691–693. Other suitable alkali metal vapor sources are described in co-assigned, copending U.S. applications Ser. No. 856,529, now U.S. Pat. No. 3,598,384 and Ser. No. 856,567, now U.S. Pat. No. 3,636,302. The preferred alkali metal vapor source is a

mixture of alkali metal chromate and a reducing agent for the chromate. Although any reducing agent such as silicon can be employed, the preferred reducing agent is a zirconium-aluminum alloy and preferably one containing 84 percent zirconium, balance aluminum.

Also attached to the container is a conduit for connecting the container to the vessel to be charged with the alkali metal vapor. The conduit can be of any material but is preferably of glass, or at least has an open end of glass to permit its attachment to the vessel to be charged by conventional glass-blowing techniques. Alternatively, the open end of the conduit can be terminated by any suitable vacuum-tight flange.

Generally, the conduit can be provided with any suitable means for opening it, however the preferred means is a nipple having means responsive to an inductive field for breaking the nipple. This latter means is generally a groove in the outside wall of the nipple having an inductively heatable metal member in the groove. The member can have any form but is preferably a wire, the free ends of which are twisted in order that the wire contacts the walls of the groove. This contact ensures good heat transfer to cause thermal stresses in the nipple when the member is subjected to a high-frequency alternating inductive field.

In a preferred embodiment, any getter device employing any non-evaporable getter metal can be placed in the container to sorb gases which may be left after the mechanical pumping of the container, or which may be evolved during storage from the parts of the generator within the container. The getter device is preferably disposed in the container between the conduit and the alkali metal vapor source in order to remove noxious gases which can be released concurrently with release of the alkali metal vapor. The getter metal is preferably disposed in an optically opaque manner between the conduit and the alkali metal vapor source. By such optically opaque positioning, contact of the getter metal with the noxious gases is ensured. The getter device can employ any getter metal such as zirconium, tantalum, niobium, or titanium but preferably employs an alloy of 16 percent aluminum and 84 percent zirconium.

Referring now to the drawings, and in particular to FIG. 1, there is shown a non-limiting embodiment of the present invention in the form of a container 11 and alkali metal vapor sources 12, 13, and 14 (see FIG. 3). The generator 10 further comprises a conduit 15 and a getter device 16. The conduit 15 is open on the end 17 to permit attachment of the generator 10 to the vessel to be charged with the alkali metal vapor. The other end 18 of the conduit 15 is attached to the container 11. Closing the conduit 15 is a hollow elongated glass member in the form of a nipple 20. Circumferentially around the outside wall of the nipple 20 is a groove 21. Within the groove 21 and in contact with the walls thereof, is a tungsten wire 22 terminating in a twisted end 23.

The alkali metal vapor source 12 is exemplary of sources 13 and 14 and comprises an elongated tube 25 containing a mixture 26 comprising cesium chromate and an alloy of 84 percent zirconium and 16 percent aluminum in a weight ratio of one part of chromate to five parts of alloy. The sides of the tube 25 terminate in a slit 27. The ends of the tubes 25 are sealed by terminals 28 and 29 which are held in place by bands 30 and 31. The terminals 28 and 29 extend outside the container 11 in order to provide means for passing an electrical current through the tube 25. The sources 13 and 14 are of identical structure except that in the source 13 the cesium chromate is replaced by an equal weight of potassium chromate and in the source 14 the cesium chromate is replaced by an equal weight of sodium chromate.

Referring now to FIG. 3, there is shown the getter device 16 which comprises a substrate 33 having imbedded therein particles 34 of a non-evaporable getter metal. The substrate 33 is folded back and forth in a pleated manner, and the pleats then inclined to present an optically opaque getter metal surface such that noxious gas molecules following paths shown by arrows 35 and 36 (see FIG. 1) must strike the getter metal parti-

cles **34**. The container **11** is also provided with a conduit **39** to facilitate pumping down of the container **11**.

Referring now to FIG. **4** in conjunction with FIG. **1**, there is shown the manner of utilizing the generator **10** of the present invention. The conduit **15** is attached to a similar conduit **40** carried by the vessel **41** to be charged with alkali metal vapor. The vessel **41** is then evacuated and degassed by any suitable means. A torodial coil **42**, the windings of which are in series with a power source **43**, and a switch **44** is then positioned coaxially with the wire **22**, whereupon the switch **44** is closed. The toroidal coil induces induction heating in the wire **22**, causing transfer of heat to the walls of the groove **21**. This heat creates thermal stresses which cause a smooth break of the nipple **20** at the groove **21**. An electrical potential is then impressed across the terminals **28** and **29** to cause heating of the tube **25** and consequent release of the alkali metal vapor from the mixture **26**. In actual practice, potential is impressed across the terminals of the sources **12**, **13**, and **14** and in the desired sequence in order to release the desired alkali metal vapor.

The generator **10** can be fabricated in any suitable manner which will be readily apparent to those skilled in the art. In general, the getter device **16** and the sources **12**, **13**, and **14** are positioned in the container **11** through any suitable opening not shown, whereupon the container **11** is attached to a mechanical vacuum pump not shown via the conduit **39**. The pump reduces the pressure within the container **11** to approximately 10^{-6} torr, whereupon the conduit **39** is sealed.

Referring now to FIGS. **5**, **6** and **7** there is shown a modified embodiment of the generators of the present invention in the form of a generator **50**. The generator **50** comprises a container **51**, alkali metal vapor sources **52**, **53** and **54**, a conduit **55**, and a getter device **56**.

The conduit **55** is closed on the end **56***a*. In order to attach the conduit **55** to the vessel to be charged the end **56***a* is scored, broken off and attached by conventional glass blowing techniques. The conduit **55** further comprises a nipple **57** constructed of glass of a high thermal co-efficient of expansion. This glass is generally different than the glass of the downwardly extending portion **58** which is in turn attached to the remainder of the conduit **55**. To ensure breaking of the nipple **57**, it is provided with two circumferential grooves **59** and **60** having respectively wires **61** and **62**. By the use of two grooves the reliability of the breakage of the nipple **57** is greatly ensured. For example if one groove fails 5 percent of the time two grooves will fail only 0.25 percent of the time.

The getter device **56** is in the form of a star and in this embodiment is not optically opaque. The advantage of having a non-optically opaque getter device **56** is that the metal vapors issuing from the metal vapor sources **52**, **53** and **54** have a reduced tendency to deposit on the getter device **56**. Deposition of alkali metal on the getter device **56** is undesirable because in operation of the generator **50** subsequent release of another alkali metal can cause evaporation of the first alkali metal from the getter device **56** contaminating the second alkali metal. Mixtures of alkali metals are undesirable for the production of high quality photo cathodes.

In the generator **50** the sources **52**, **53** and **54** are connected on their lower end respectively to terminals **63**, **64** and **65** (not shown). The upper ends of the sources **52**, **53** and **54** are connected to a common conductor **66** which in turn is connected to a terminal **67**. By virtue of this arrangement and the high ohmic resistance of the sources **52**, **53** and **54** the desired alkali metal vapor can be released by impressing a potential across the terminal **67** and one of the terminals **63**, **64**, or **65**.

The generator **50** during construction is evacuated through a conduit on the top which is then sealed leaving the closing member **66** extending upwardly. This arrangement is superior to that shown with respect to the generator **10** since the closing member **66** does not increase the diameter of the generator **50** thereby increasing the inside diameter of the coil used to heat the wires **61** and **62**.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described above and as defined in the appended claims.

What is claimed is:

1. An alkali metal generator comprising:
A. an evacuated container;
B. at least one heat-responsive source of an alkali metal vapor in the container;
C. a closed conduit for connecting the evacuated container to a vessel to be charged with the alkali metal vapor; and
D. means for opening said closed conduit.

2. An alkali metal generator comprising:
A. an evacuated container;
B. at least one heat-responsive source of an alkali metal vapor in the container;
C. a closed conduit for connecting the evacuated container to a vessel to be charged with the alkali metal vapor;
D. means for opening said closed conduit; and
E. a non-evaporable getter device in the container.

3. An alkali metal generator comprising:
A. an evacuated container;
B. at least one heat-responsive source of an alkali metal vapor in the container;
C. a conduit for connecting the evacuated container to a vessel to be charged with the alkali metal vapor; and
D. a nipple closing said conduit and having means responsive to an inductive field for breaking the nipple.

4. An alkali metal generator comprising:
A. an evacuated container;
B. at least one heat-responsive source of an alkali metal vapor in the container;
C. a conduit for connecting the evacuated container to vessel to be charged with the alkali metal vapor;
D. a nipple closing said conduit and having means responsive to an inductive field for breaking the nipple; and
E. a non-evaporable getter device in the container between the conduit and the alkali metal vapor source.

5. An alkali metal generator comprising:
A. an evacuated container;
B. at least one heat-responsive source of an alkali metal vapor in the container;
C. a conduit for connecting the evacuated container to a vessel to be charged with the alkali metal of vapor;
D. a nipple closing said conduit and having a groove in the outside wall of the nipple and an inductively heatable metal member in said groove; and
E. a non-evaporable getter device in the container wherein the getter metal of the getter device is disposed in an optically opaque manner between the conduit and the alkali metal vapor source.

6. The alkali metal generator of claim **1** wherein there are three alkali metal vapor sources one of cesium, one of potassium, and one of sodium.

7. The alkali metal generator of claim **1** wherein the evacuated container is evacuated to an absolute pressure of 10^{-7} torr.

8. The alkali metal generator of claim **1** wherein the evacuated container is evacuated to an absolute pressure of 10^{-9} torr.

9. The alkali metal generator of claim **1** wherein the source of alkali metal vapor is a mixture of an alkali metal chromate and a reducing agent for the chromate.

10. The alkali metal generator of claim **9** wherein the reducing agent is a zirconium-aluminum alloy.

11. Alkali metal generator of claim **2** wherein the getter device employs an alloy of zirconium and aluminum as its non-evaporable getter metal.

12. The alkali metal generator of claim **11** wherein the alloy contains 84 percent zirconium-balance aluminum.

13. An alkali metal generator for releasing cesium, potassium, and sodium, said generator comprising:
A. a glass container evacuated to at least 10^{-7} torr;

B. a cesium releasing device within the container, said device comprising:
1. an elongated tube of high electrical resistance having a slit therein;
2. a mixture of cesium chromate and a reducing agent for the chromate within the tube;
3. two terminals one attached to each end of the tube;
4. means for impressing an electrical potential across the terminals to pass a current through the tube;

C. a potassium releasing device within the container, said device comprising:
1. an elongated tube of high electrical resistance having a slit therein;
2. a mixtured potassium chromate and a reducing agent for the chromate within the tube;
3. two terminals one attached to each end of the tube;
4. means for impressing an electrical potential across the terminals to pass a current through the tube;

D. a sodium releasing device within the container, said device comprising;
1. an elongated tube of high electrical resistance having a slit therein;
2. a mixtured sodium chromate and a reducing agent for the chromate within the tube;
3. two terminals one attached to each end of the tube;
4. means for impressing an electrical potential across the terminals to pass a current through the tube;

E. a glass conduit open on one end and attached to the container walls on the other end;

F. a hollow elongated glass member open to the interior of the container on one end and closed on the other end, said member extending into said conduit and closing said conduit;
1. a groove in the outside wall of said glass member;
2. an inductively heatable metal member in said groove in contact with the walls of the groove;

G. a getter device in the form of a pleated substrate having imbedded in its surface a particulate non-evaporable getter metal, said pleated strip being in said container between the alkali metal releasing devices and the conduit;

whereby the open end of the conduit can be attached to a vessel to be charged with alkali metal vapors followed by induction heating of said metal member causing breaking of the elongated glass member, whereby subsequent passage of current through each of the tubes causes release of alkali metal vapor which is scrubbed of noxious gases by the non-evaporable getter metal and then passes through the conduit and into the vessel to be charged.

* * * * *