

Alkali Metal Generation and Gas Evolution from Alkali Metal Dispensers*

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Technical Report TR 18

Abstract

In the manufacture of photosensitive devices, one of the most critical steps is the formation of the photosensitive surface. The degree of vacuum at this point is extremely important and it must not be spoiled during alkaline vapor generation. Hence, particular care should be exercised in the choice of alkali source and in its use as well as in the choice and means of pumping.

An extremely efficient getter alloy of the nonevaporable type, composed of 16% Al and 84% Zr, is utilized as the basis for improvement in both of these directions. The reduction of the alkaline chromates with this alloy enables the gases evolved from the generator during reduction to be gettered in situ, thus reducing gas evolution to a minimum.

By gas analysis, using a mass spectrometer, the gases released during alkali generation have been measured and identified. By means of a new triode technique the kinetics of alkali metal evaporation have also been studied.

It is possible to use small getter appendage pumps, in the construction of which the same Al-Zr alloy is used, to maintain high vacuum in phototubes. The pumping speed is not decreased by the presence of alkali metals.

1. Introduction

During the synthesis of photocathodes, alkali metal vapors are deposited onto a reactive cathode surface, for example Sb or Ag_2O .

Normally such a deposition is a relatively slow, controlled process carried out in a dynamic vacuum of 10^{-7} to 10^{-8} torr.

Deposition can be carried out by evaporating the pure alkali metal from a container connected to the vacuum system but it is much more convenient, especially for mass production, to use an alkali metal dispenser.

The dispenser usually consists of an alkali metal salt mixed with a reducing agent in a metal boat. By initiating the reduction reaction at high temperatures, the alkali metal may be generated in situ. Chromates are the salts most generally used and are reduced by metals and metalloids such as Si, Al, Zr, W and Fe.

The quality of a photocathode, its spectral response and sensitivity depend on many factors, not all of which are well understood. Among these factors, may be mentioned the nature of the substrate, the amount and rate of alkali metal deposition, the chemical reactions at the cathode surface and the cathode temperature.

Also, and most important, is that a photocathode may be permanently damaged following reactions, during and after synthesis, with gases such as H_2O , chlorine, CO, CO_2 , etc.¹

Because of these factors the design of the dispenser is extremely important. The rate of alkali generation must be known for an efficient control of deposition and the rate of gas evolution from the heated dispenser must be kept to a minimum, particularly during synthesis.

*Reference: *IEEE Conference on Tube Techniques, New York, September 1968.*

Thus it has been decided to define the quality of alkali dispensers in terms of these two variables and to develop standard tests for research and quality control purposes.

In the following pages these tests are described together with typical results obtained during the initial stages of this project.

2. Gas Evolution

2a. Experimental

The experimental technique used for the analysis of gases evolved from heated dispensers is illustrated by fig. 1 which shows the dispenser mounted in an all-glass high vacuum system.

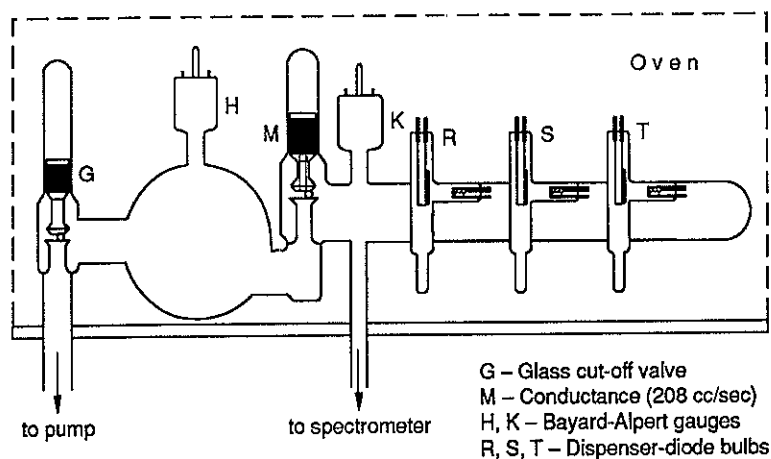


Fig. 1. Analytical system.

The rate of gas evolution was measured by the method of pumping the gases away through a limiting capillary conductance M and measuring the pressure drop ΔP torr across the conductance using the two Bayard-Alpert gauges H and K. (As these gauges were calibrated using nitrogen gas, all pressures are given in nitrogen equivalents.) Since the exit pressure of 10^{-6} to 10^{-7} torr was sufficiently low for Knudsen flow to be assumed, the flow Q cc torr in time t secs, across the conductance C cc/sec, may be described by the equation:

$$\frac{dQ}{dt} = C \Delta P$$

The gases were analyzed at the same time by leading off a small amount (about 5% of the total) to an Edwards 60° mass spectrometer calibrated for pure gases.

The various components of the gas mixture were identified and their proportions calculated using sets of simultaneous equations based on the cracking patterns of the various species.

The dispenser was mounted in a glass bulb connected to the apparatus by a narrow U-tube (see fig. 2). The commencement of evaporation was measured with considerable sensitivity by a diode mounted adjacent to the slit of the dispenser. The principle of this method is that the electron emission of an incandescent tungsten surface is greatly increased after contamination with an alkali metal. Thus the arrival of the first alkali metal vapors at the filament F caused a sharp increase of current across the diode.

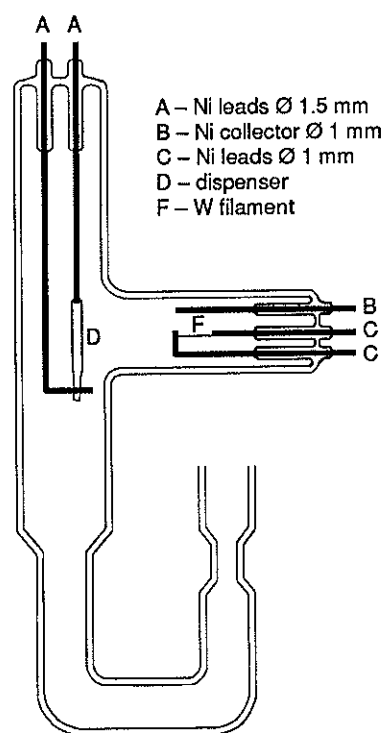


Fig. 2. Cross section of the dispenser diode assembly.

After activation of the dispenser, the gases measured were those not absorbed by the alkali metal film. Since the thickness and area of such films can profoundly affect their absorptive properties and hence gas measurement, it is necessary to use a standard bulb and

activation schedule to ensure standard rates of deposition. The following schedule was followed:

Time (mins)	Current through dispenser (Amps)
0	1.5
2	2.0
3.5	2.5
6	2.6
each successive minute increase of 0.1 amp	

The temperatures of the dispensers were found using calibration graphs based on the results of tests in which the temperature of the center of the dispenser was measured by a contact chromel-alumel thermocouple for each current used.

Because of the ability of the alkali metals to migrate through glass and contaminate the whole of the vacuum system, precautions were taken to ensure that a minimum amount of alkali vapor left the dispenser-diode bulb. The connecting U-tube was water-cooled and acted as a trap and after use the bulb was immediately removed from the vacuum system and discarded.

To minimize atmospheric contamination of the hygroscopic chromates, the dispensers were exposed as little as possible to the air and after mounting were degassed together with the vacuum system at 375°C overnight. All tests were carried out with the glass surfaces at ambient temperature.

The results of gas analysis must be divided into two parts.

1. *Pre-evaporation gases.* These probably become only of importance in the actual production of phototubes if the load on the pumps is too great for a good vacuum to be attained at the beginning of alkali generation.

2. *Post-evaporation gases.* These gases, evolved after the start of evaporation, may react with the deposited alkali metal and must be reduced to a minimum. Because of these reactions, the rates of gas evolution measured using the SAES test are less than the true values but provide valuable indicative results for dispensers generating the same alkali metal.

2b. Development of the New SAES Dispenser

(a) Preliminary studies

During early work at SAES it was found that the gas evolution from dispensers employing conventional agents was substantial and in some cases too great for a successful photocathode to be made. The degassing of an early Si-Cs prototype dispenser and that of a tungsten-cesium dispenser of another manufacturer are illustrated by figs. 3 and 4. Both these dispensers are characterized by high rates of gas evolution during alkali generation. CO is predominant in the case of the Si-Cs dispenser and this gas is most dangerous as it reacts very quickly with the cesium film. In the case of the W-Cs type, nitrogen is also present and the rate of gas evolution is extremely high.

Tests conducted on individual components showed that CO was liberated from the nichrome boat at high temperatures (>780°C) and, together with hydrogen, was evolved from the reactive mixture before and after the commencement of evaporation.

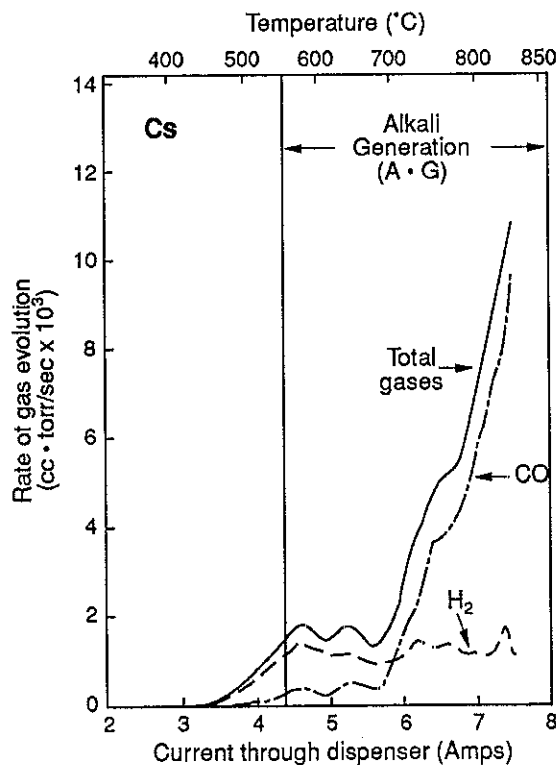


Fig. 3. Gas evolution from a Cs-Si dispenser SAES prototype.

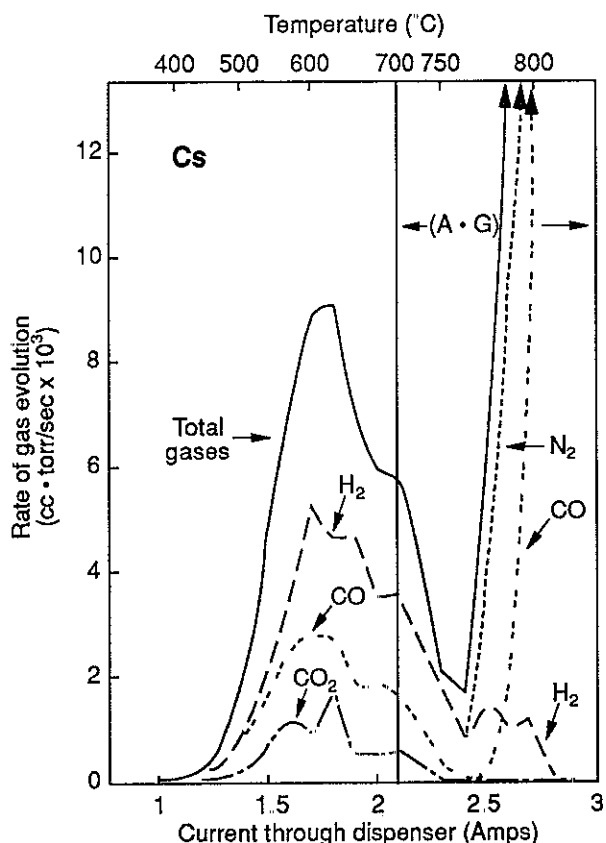


Fig. 4. Gas evolution from a Cs-W dispenser of another manufacturer.

(b) Use of a getter

It was decided, following these tests, to introduce an entirely new concept in dispenser design and to use a reducing agent that was also a getter capable of absorbing gases and in particular carbon monoxide. Such a reducing agent is the Zr-16% Al alloy, *St 101*, developed at SAES.²

This alloy has the advantage that for all the common gases except hydrogen the absorption rate increases with temperature and at the temperatures used for alkali metal evaporation (680 – 850 $^{\circ}\text{C}$), the surface continually reactivates by exposing fresh surface free of reaction products. The efficiency of the getter alloy is illustrated by fig. 5, which describes the degassing of a *St 101*-Cs dispenser and it is seen that the CO evolution is drastically reduced.

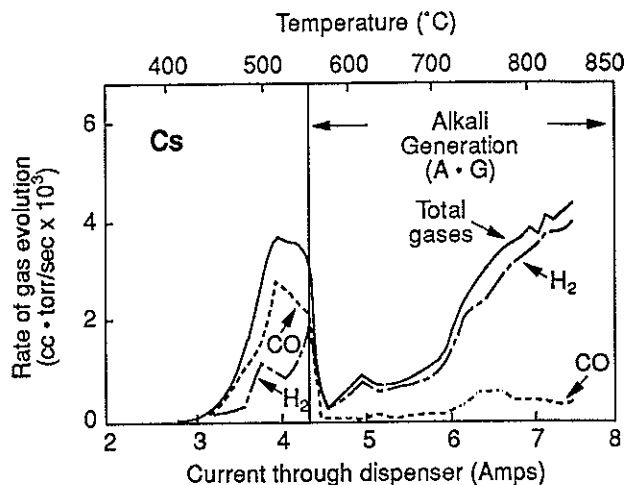


Fig. 5. Gas evolution from a SAES *St 101*-Cs dispenser.

A drop in gas flow out of the dispenser bulb at the beginning of alkali metal generation indicates reaction of the freshly formed film with the gas. From fig. 5 it is seen that the Cs film reacts with both hydrogen and carbon monoxide. The superiority of the *St 101* dispenser over the earlier types is again shown in fig. 6.

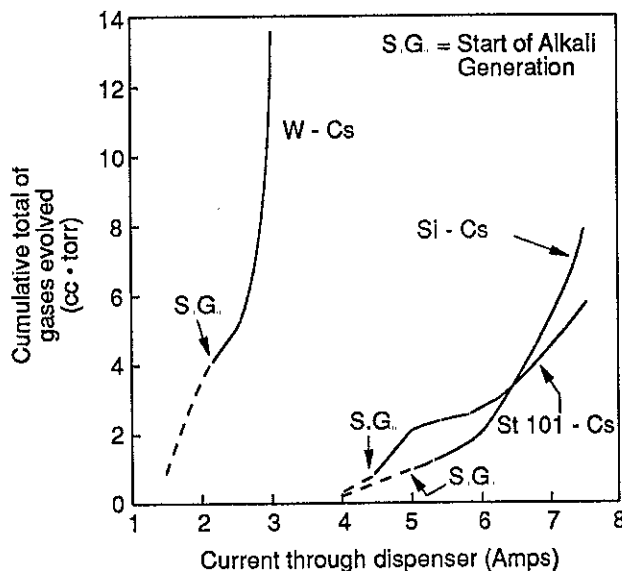


Fig. 6. Gas evolution from the dispensers expressed as cumulative totals.

(c) Sodium and potassium dispensers

The results so far obtained show that problems connected with reactions between alkali metals and gases may be rather different and perhaps less important for

the sodium and potassium dispensers. It is seen from figs. 7 and 8 that the only gases of importance during the heating of sodium and potassium dispensers are again carbon monoxide and hydrogen.

It is difficult to compare results after the commencement of evaporation for the three alkali metals as the absorption rate of CO and hydrogen by evaporated films of the alkali metals is not, as yet, well understood.

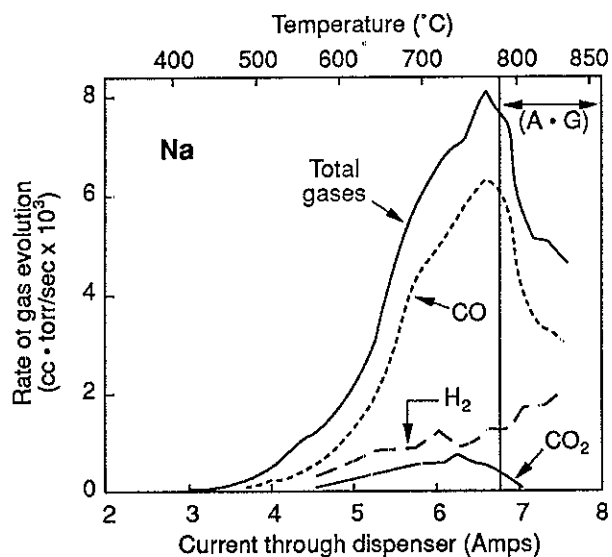


Fig. 7. Gas evolution from a SAES St 101-Sodium dispenser.

For instance, it appears from fig. 7 that the sodium film reacts with CO but not with hydrogen, while from fig. 8, it is seen that the evolution rate of both these gases is little affected by the presence of a potassium film.

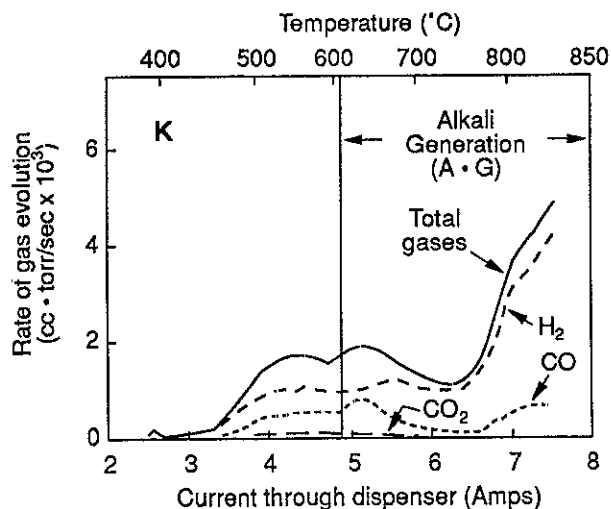


Fig. 8. Gas evolution from a SAES St 101-Potassium dispenser.

Again in these dispensers the CO evolution rate is held at a low level the St 101 alloy at high temperatures.

Thus it is seen that the gas reactions with the newly formed photocathode are likely to be complex especially when two or more alkali metals are evaporated onto the same substrate. The present work will be continued to study these reactions and to reduce the gas evolution from the SAES dispensers even further.

3. Measurement of the Alkali Metal Evaporation Rate

During photocathode synthesis it is most important that the deposition rate of alkali metal on the cathode surface be accurately controlled. This can only be done by control of the dispenser and therefore it is most desirable that the alkali metal evaporation rate be known as a function of both time and temperature.

To construct evaporation rate — time — temperature control graphs for the SAES dispensers it has been necessary to develop a method to measure the alkali metal atomic flux. This method and the initial results are described below.

It was first noted by Taylor and Langmuir³ that alkali metal atoms may be readily ionized by contact with an incandescent tungsten surface

By ionizing the alkali metal vapor generated from a dispenser and collecting the ions, it is possible to calculate the evaporation rate Q g/sec after measurement of the ion current I^+ amps by using the relation:

$$I^+ = Qe^+N/M$$

M is the mass of the alkali ion (a. m. u.)

N is Avogadro's number (6×10^{23})

e^+ is the charge on a single ion (1.6×10^{-19} coulombs)

It is assumed that all the evaporated metal is ionized and that each ion carries a single charge.

3a. Experimental

The experimental apparatus used is illustrated in fig. 9 and is based on the triode principle. The dispenser lies along the axis of a tungsten filament which in turn is surrounded by a cylindrical ion collector of Kovar.

The collector is water-cooled to minimize reevaporation of captured alkali metal.

The filament is heated to 1400°C. The dispenser is also heated by an independent power supply.

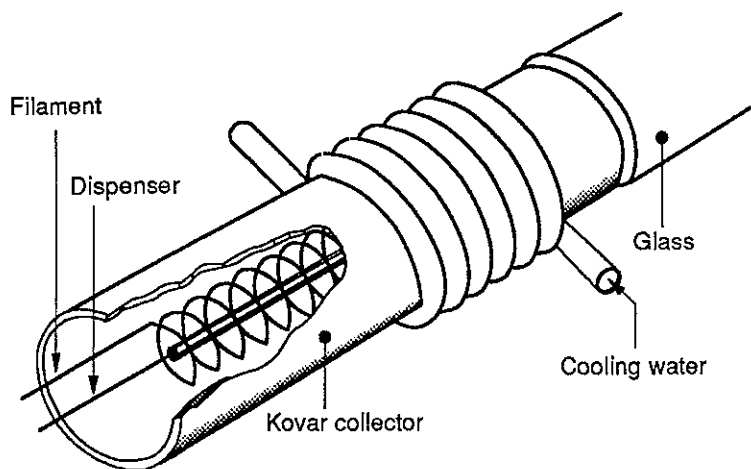


Fig. 9. Cross section of a triode experimental device for measuring rates of sublimation from alkali dispensers.

The filament also acts as a grid and is maintained at 30 V relative to the dispenser. This ensures that all the electrons emitted by the filament-grid are attracted to the dispenser, thus ensuring that background currents arising from this source are stable. The ions formed after collision with the filament are accelerated toward the collector which is maintained at -400 V with respect to the filament-grid. The use of higher voltages than this is not recommended, as this causes troublesome background currents due to ionization of residual gases and residual alkali metal vapors.

Before a test, the triode assembly was evacuated, and after bakeout at 375°C overnight, the pressure within the system was of the order of 1×10^{-8} torr. During the test the system was continually pumped. After the necessary adjustments of voltages, the filament was degassed and its surface cleaned by heating to 1200°C for one hour.

The dispenser was then heated to the required temperature and maintained at that temperature for about 140 minutes during which time the ion current was continually measured. In this first series of tests, the SAES

cesium dispenser was investigated and alkali metal generation was performed at 750°C, 800°C and 850°C.

3b. Results of Alkali Generation Tests

The results are presented in fig. 10 and show the variation of ion current with time for the temperature range 750 – 850°C. It is seen that at a constant temperature, the alkali evaporation rate diminishes according to an approximately exponential law.

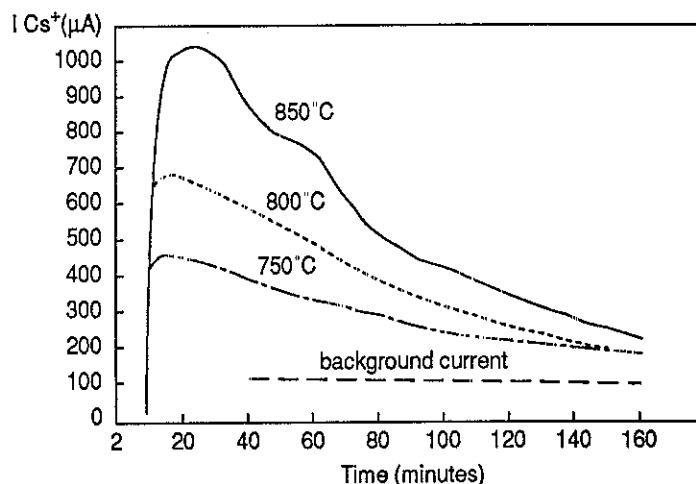


Fig. 10. Emission curves at various temperatures of a Cs-St 101 dispenser.

This is to be expected from mass action considerations which show that the consumption of chromate mass C grams at time t is given by the relationship:

$$-\frac{dC}{dt} = \text{constant} \times C$$

assuming the mass of St 101 (five times more by weight than the chromate) to be virtually unchanged.

The cesium evaporation reaction is also markedly temperature dependent and is associated with an activation energy of about 20 kcal/mole. As a consequence, if long evaporation times are used, it may be necessary to increase the temperature of the dispenser to maintain a steady rate of alkali generation. The reaction does not go to completion in the time of 140 minutes but tends asymptotically to a limiting value. It has been calculated at this time of 140 minutes, that 24% of the cesium was evaporated at 750°C, 37% at 800°C, and 56% at 850°C.

4. New Development in SAES Dispensers

In addition to the problems already described, the phototube manufacturer is faced with the more practical difficulty of obtaining reproducible performance from his dispensers. Such reproducibility depends on the invariability of the dispenser dimensions and the weight and compression of the reactive powder charge. Also the exposure to contaminants must be a minimum.

Reproducibility can only be obtained by the use of mass production techniques, and for this reason these have been used in SAES from the very beginning of dispenser production. Both the construction of the nichrome boat and the powder charging are carried out automatically.

The latest SAES dispenser is illustrated in fig. 11. This is provided with butting pieces which close the ends of the boat. The butting pieces are held in place by wrapping bands and the assembly so formed is held in place by welds.

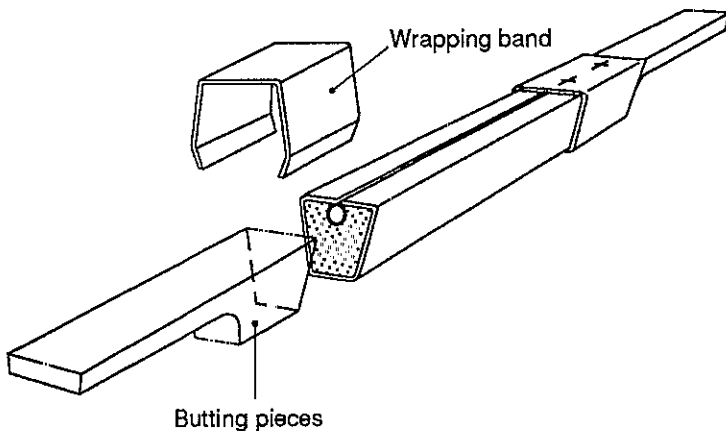


Fig. 11. The latest development of SAES alkali dispensers.

In this manner an excellent electrical contact, essential for reliable performance, is obtained and any danger of powder loss from the ends of the dispenser is completely eliminated.

Particles which fall from the dispenser during handling of the phototube can result in impaired performance during life and this unnecessary hazard has been, in the past, a source of some concern.

In order to remove any danger of loss of powder out of the slit, a strand of nichrome wire is positioned as shown in fig. 12. This also serves to increase powder compression.

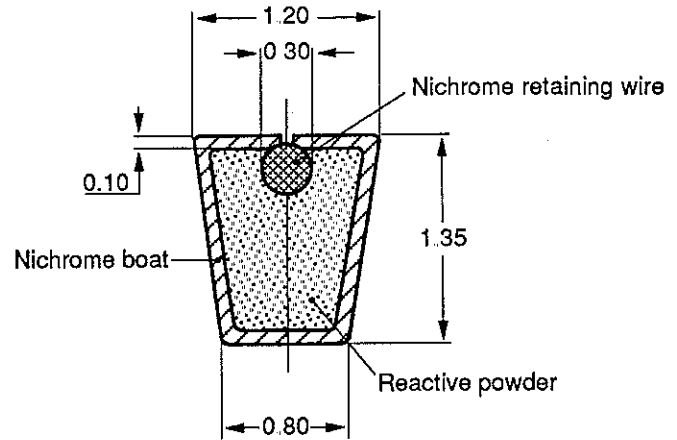


Fig. 12. Cross section of the central part of the dispenser (dimensions in mm).

5. The Use of a Getter Pump in Phototubes

The importance of the vacuum within the phototube during alkali metal deposition has already been stressed. However the sensitivity of the photocathode can be severely impaired during the first hours of life by residual gases released during seal-off and subsequent ionic bombardment.

It is most desirable, particularly in the case of sophisticated phototubes to have a vacuum pump actually within the glass bulb to maintain a high vacuum during the life of the tube. Obviously such a pump must be extremely small, have a considerable pumping speed at room temperature, particularly for carbon monoxide and hydrogen, and need no maintenance whatsoever.

All these requirements are fulfilled admirably by a getter pump fitted as an appendage to the phototube (fig. 13). This type of pump and its method of use have already been described.⁴ Its principle is again the capacity of the Zr-Al alloy, St 101, to absorb reactive gases but in this case the alloy is coated onto a pleated metallic strip.

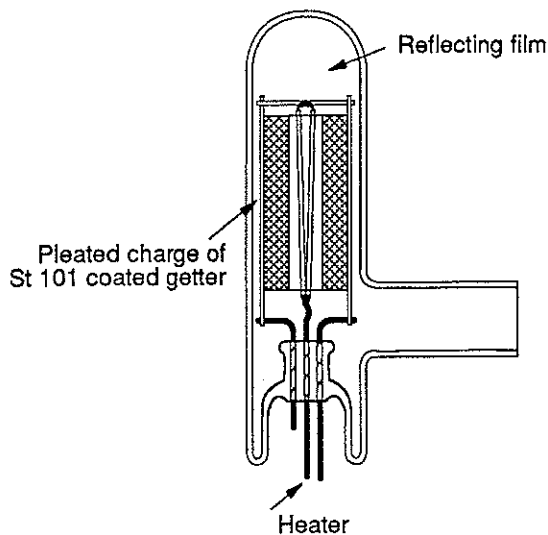


Fig. 13. SAES appendage getter pump.

That the functioning of this pump is unaffected by alkali deposition on its active surfaces is shown by fig. 14. At points A, B, C alkali metal was evaporated for 5 minutes at 850°C from the respective SAES dispenser. It is seen that the pumping speed of, in this case, a SAES 180 cm² getter pump for carbon monoxide was not reduced by the presence of alkali metal. On the contrary there is a slight improvement due to the gettering action of the alkali metals.

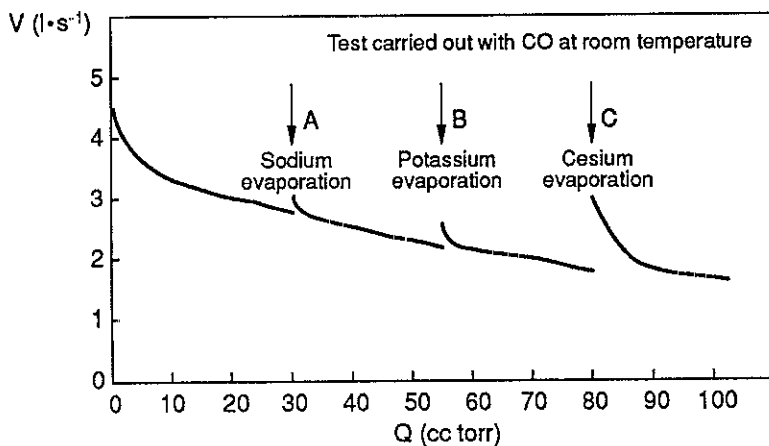


Fig. 14. Sorption curve of a SAES appendage pump for CO before and after contamination with alkali metals.

6. Conclusions

The initial results and achievements obtained during this major project are a considerable contribution to our knowledge of the behavior of gases in phototubes.

The results of mass spectrometry also provide valuable indications as to the merits of different types of dispensers, and in addition, the triode technique has proved to be a powerful tool in the elucidation of the kinetics of alkali metal evaporation.

Mechanical and geometrical improvements have greatly improved the reliability of alkali dispensers and have eliminated the loose particles problem.

The performance of a Zr-Al getter pump is not impaired by the presence of alkali metals.

Since the alkali metals are extremely reactive, future projects will be devoted to the investigation of displacement of gases from and attack of internal surfaces of phototubes by these metals.

References

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