

# Atomic absorption evaporation flow rate measurements of alkali metal dispensers

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received 8 July 1985

*The preparation of photosensitive surfaces in phototubes is generally performed with alkali metal dispensers (AMDs). Since a very well controlled evaporation flow rate of the alkali vapours released from AMDs are of great importance, a method based on the atomic absorption technique, has been developed for its accurate measurement. This method can overcome some limitations of other methods such as those based on the work function change of cathodes in the presence of alkali vapours. The test AMD is mounted in a specifically designed glass cell which is evacuated and baked overnight at 350°C to have a residual pressure in the range of  $10^{-6}$  Pa. The cell is provided with a Ba getter to ensure a good vacuum, essential for the application of this technique, and with an Sb generator to capture the alkali metal vapour. After tip-off, the cell is mounted on the atomic absorption spectrophotometer in the burner position. An absorption signal is generated by the alkali atoms released by the AMD, when they intercept a monochromatic light beam resonant with the alkali metal. With an appropriate calibration the absorption signal can be converted into evaporation flow rate. This technique has been applied to the study of caesium generators and practical results are given. The sensitivity of the method is a flow of about  $1 \mu\text{g min}^{-1}$ .*

## 1. Introduction

Alkali metal dispensers are used to make thin photosensitive films, such as  $\text{Cs}_3\text{Sb}$ ,  $\text{K}_2\text{CsSb}$ ,  $\text{Na}_2\text{KSb-Cs}$  and  $\text{Ag-O-Cs}$ , employed in a wide variety of photoelectronic devices, e.g. photomultipliers, image intensifiers, camera tubes and so on. The principal characteristic and difference of the various photocathodes is that visible radiation produces a high emission of electrons. The efficiency of the conversion depends principally on the type of photocathode.

Normally an alkali metal dispenser consists of a mixture of powders, usually an alkali metal chromate and a reducing agent, such as Si, Zr or Al.

The powder mixture is packed in two preferential shapes: a ring or capsule form, usually called flash dispensers, and a metallic strip rolled around the powder to produce a wire. The two types of dispenser have complementary characteristics. The former is induction heated, and gives an uncontrollable flow rate of alkali metal. The latter, heated by passage of current, gives well controllable flow rates.

The wire dispensers are employed in manufacturing the more sophisticated photosurfaces, such as the S20 ( $\text{Na}_2\text{KSb-Cs}$ ), which requires closely controlled evaporation flow rates of the alkali metals. To prepare this common multi-alkali photosurface, having one of the highest quantum yields throughout the visible spectrum, it is necessary to evaporate small amounts of sodium and potassium alternatively until peak sensitivity is obtained. Then Cs and Sb are evaporated until peak sensitivity is again

achieved<sup>1</sup>. Even if there are many ways to evaporate the alkali metals following, for example, another sequence of evaporation arriving at the same result concerning peak sensitivity, the alkali evaporation flow must always be very slow and controlled to avoid excess of one alkali metal with respect to the others.

Nowadays the synthesis of photosurfaces is made with computerized systems and it is much more important than in the past to produce reproducible alkali dispensers. It is very important to know how the evaporation flow rate depends on the current and on the time. To give an answer to these questions a technique, which allows measurement of the evaporation flow rate of alkali dispensers, has been developed. This technique, based on atomic absorption spectrophotometry, permits continuous measurement of the rate of evaporation of the alkali metal.

## 2. Previous methods

Methods other than that proposed here have been used, principally the method based on the work function change of a hot tungsten filament<sup>2-4</sup>. The principle of this method is based on the ionization of the alkali metal by contact with a high temperature metal surface. When an alkali atom, evaporated from a dispenser, strikes a hot tungsten filament, it loses the valency electron with a probability expressed by the Saha-Langmuir equation:

$$p_i = (1 + 2\exp[(E - \phi)/kT])^{-1}$$

where:

- $p_i$  = ionization probability taking into account that the valency electron can occupy more than one energy level;
- $E$  = ionization energy of a free alkali metal in eV;
- $\phi$  = work function of the ionizing surface in eV;
- $k$  = Boltzmann's constant;
- $T$  = temperature in Kelvin.

If the temperature of the tungsten filament is sufficiently high, e.g. 1500°C, the ionization probability for potassium and caesium is practically 100% and for sodium 5%. Collecting the alkali ions with a collector maintained at a negative potential with respect to the ionizing filament, the alkali flow can be quantified with an appropriate calibration. The results obtained with this method, however, can be affected to some extent by the state of the surface, by the gases present in the glass bulb and by the electric space charge.

The atomic absorption (AA) method, to be described below, is not subject to these problems. The technique is, moreover, of simpler and easier application.

### 3. Theoretical basis of the AA measurement method<sup>5</sup>

Lambert's law of absorption is expressed as:

$$I = I_0 e^{-\mu l} \quad (1)$$

where:

- $I_0$  = intensity of the light incident on an absorptive medium;
- $I$  = intensity of the light after passage through a thickness  $l$  of the absorptive medium;
- $\mu$  = a constant related to the concentration and to the material of the absorptive medium.

Equation (1) can be written as:

$$\ln(I_0/I) = \mu l$$

$$\log(I_0/I) = K$$

where  $K = 0.43 \mu l$ .

The quantity  $\log(I_0/I)$  is referred to as the absorbance and can be measured by an atomic absorption spectrophotometer.

The constant  $K$  is proportional to the concentration of atoms or molecules resonant with the incident radiation and to the total path length through the absorbing medium. If the path length is kept constant the absorbance depends only on the concentration.

If an alkali metal source in a closed system is caused to release alkali metal vapour and the system also contains an alkali metal sink then, if the sink pumping speed is greater than the alkali metal evaporation rate a concentration gradient will be established between the source and the sink. At any given point between the source and the sink the alkali metal concentration, at equilibrium, will be proportional to the rate of evaporation of the alkali metal.

It is this concentration which is measured by the atomic absorption spectrophotometer in terms of absorbance which can be calibrated as flow rates.

### 4. Test dispensers

The test samples were caesium dispensers made by SAES Getters. A sketch of the dispenser type used is shown in Figure 1. A nichrome strip is formed around a compound mixture to obtain a

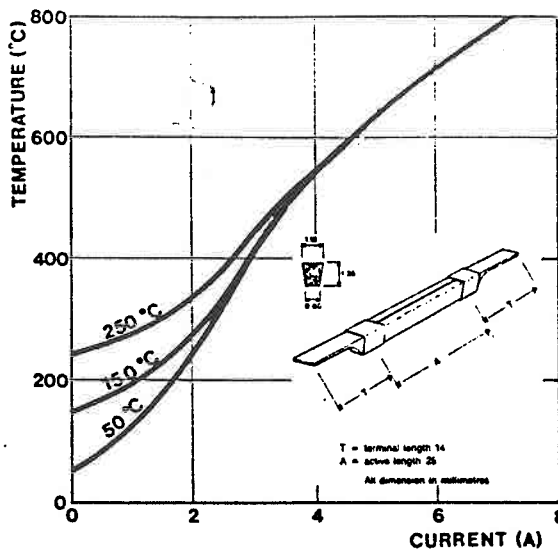


Figure 1. Temperature vs current curves for the alkali metal dispenser for various ambient environment temperatures.

wire of  $Cs_2CrO_4$  and Zr-Al alloy. The Zr-Al alloy acts both as a reducing agent to generate caesium from the chromate salt and as a gettering material to sorb the chemically active gases produced during the reduction reaction. The alkali vapours produced escape through the slit of the dispensers.

The dispensers can be heated to suitable temperatures by direct passage of current and the two terminals enable an easy spot-welding to the current feedthroughs. The shape of the terminals is such as to provide a homogeneous heating throughout the whole dispenser.

The generation of the caesium vapours starts at a temperature of about 600°C. The release of caesium depends on time and temperature. The latter is controlled by the amount of current passed through the dispenser and, to some extent, on the environment temperature. The practical range of currents is from 4.0 to 7.5A. Figure 1 shows the relation between current and temperature.

### 5. Apparatus

A schematic layout of the experimental apparatus is shown in Figure 2. It consists of a Varian model AA 1275 atomic absorption spectrophotometer with the burner replaced by a glass test cell, containing the dispenser, placed in an oven to prevent condensation of alkali metal near the dispenser. A temperature of 100–230°C is used depending on the alkali metal. The oven is also provided with Pyrex optical windows to allow passage of the AA beam through the cell. The glass test cell is shown diagrammatically in Figure 3, it contains the alkali dispenser with a thermocouple spot-welded on it, a barium getter and an antimony generator.

A barium getter is used to remove gases outgassed by the walls of the test cell and released by the reaction between the alkali chromate and the reducing agent. It maintains a good vacuum in the test cell and avoids oxidation of the alkali metal present as a low pressure vapour. Any oxidized alkali metal would not resonate with the monochromatic lights of the AA leading to false results.

The antimony generator is used to produce an antimony film sink for the alkali metal vapours. In order that the trapping speed

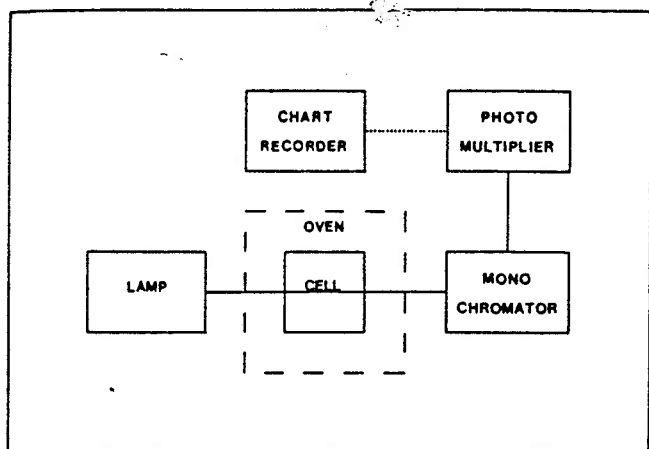


Figure 2. Block diagram of the experimental apparatus.

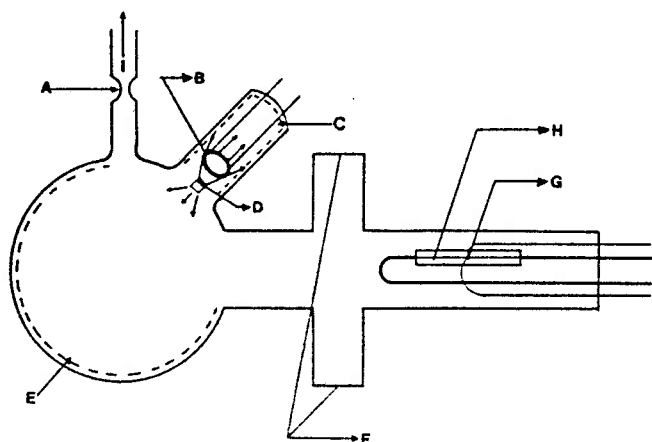


Figure 3. The glass test cell (not in scale). (A) Pinch off constriction. (B) Ba getter. (C) Ba film. (D) Sb generator. (E) Sb film. (F) Optical window. (G) Thermocouple. (H) Alkali metal dispenser. (I) To pumps.

is faster than alkali metal generation, the area on which the film is deposited is quite large, about  $450 \text{ cm}^2$ . The temperature of the film, being that of the oven, also ensures rapid reaction with the alkali metal.

## 6. Experimental

Before starting the absorption test, this test cell must be evacuated. Thus the cell is connected to an ultrahigh vacuum pumping system (rotary and diffusion pump with a liquid nitrogen trap) through a glass tubulation, and is baked overnight at  $350^\circ\text{C}$ . At the end of the degassing process, the residual pressure is in the range of  $10^{-6}$  Pa. Before isolating the glass bulb from the vacuum system, the antimony generator and the barium getter, mounted in opposite directions, are activated using the coil of a high frequency generator around the two dispensers which are heated simultaneously.

The monochromatic radiation, resonant with the alkali metal to be evaporated, passes through two optical windows made of Pyrex glass: the alkali metal vapour released by the dispenser, passes through the light beam before being captured by the antimony trap.

(a) **Calibration.** As the output signal is expressed in absorbance, a calibration has to be performed to convert the absorbance into evaporation flow rate. Current is passed through a dispenser to cause evaporation of alkali metal and the AA signal is then maintained constant by suitable (small) current adjustments. The output signal is maintained constant for long time (30 min or even more) so that the time required to reach the constant value of absorbance and to return to zero after switch off of the current, is negligible compared to the time of permanence at constant absorbance. By chemical analysis, the total amount of alkali metal evaporated during the heating is known.

Dividing the alkali yield by the time of permanence a certain absorbance corresponds to a precise evaporation flow expressed in  $\mu\text{g min}^{-1}$ .

This process is repeated at different absorbances so that a calibration curve giving the evaporation flow vs the absorbance can be constructed.

Figure 4 shows the caesium calibration curve in the most sensitive conditions, that is, working with a wavelength of

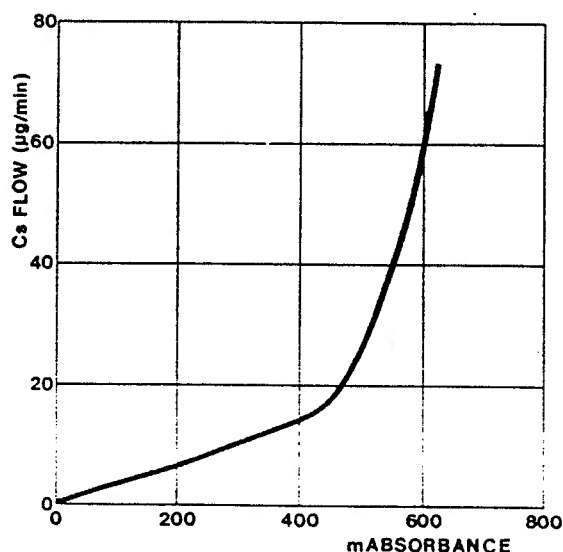


Figure 4. Caesium calibration curve at a wavelength of  $852.1 \text{ nm}$ .

$852.1 \text{ nm}$ . At low absorbance, that is lower than 0.4, caesium shows a linear dependence on the evaporation flow rate vs the absorbance while at absorbances higher than 0.4, a step increase of the flow rate, due to a saturation of the response of the spectrophotometer is detectable. Measurement of evaporation flow rates ranging from  $1 \mu\text{g min}^{-1}$  to about  $80 \mu\text{g min}^{-1}$  can be achieved. If higher flow rates must be studied, another calibration should be performed at the less sensitive wavelength of  $455.5 \text{ nm}$ , in this case the sensitivity ranges from  $20 \mu\text{g min}^{-1}$  to  $400 \mu\text{g min}^{-1}$ .

(b) **Dispenser flow rate measurement.** The caesium flow rate evolution at the firing current (that current at which alkali metal generation starts) and the evaporation flow rate at different currents have been studied by means of the technique described.

No particular conditions must be satisfied concerning the heating schedule of the dispenser. For the tests performed the



following heating schedule has been applied:

- 0.5 A min<sup>-1</sup> until 4 A;
- 0.1 A min<sup>-1</sup> until the generation start current (firing current);
- 15 min at the firing current;
- decreasing the current by 0.3 A every 5 min until the evaporation flow rate is no longer detectable.

Figure 5 shows a typical increase of the flow rate at the firing current. After about 15 min, the evaporation flow reaches so high a value that it is beyond the straight portion of the calibration line even though the current was maintained constant.

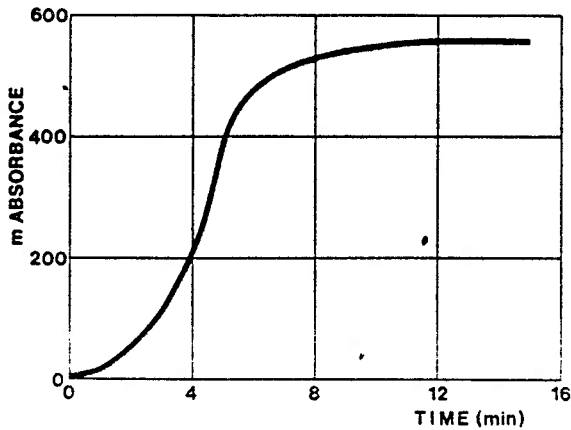


Figure 5. Caesium flow rate evolution at the firing current (4.8 A).

Diminishing the current step by step, for example 0.3 A each step, both the temperature of the dispenser and the evaporation flow decrease until, after a few minutes, an equilibrium is again reached. In this way a fixed current, or temperature, can be related with a precise caesium evaporation flow rate, as shown by Figure 6. Thus complete information on the evaporation flow rate

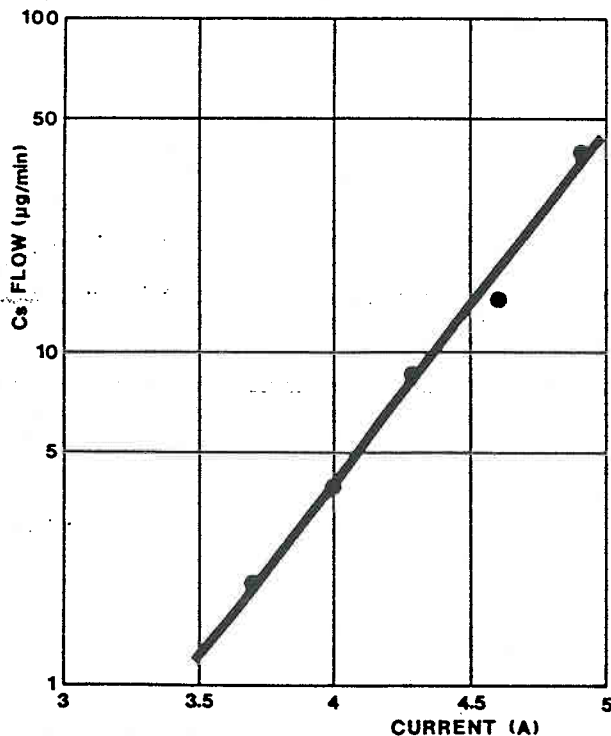


Figure 6. Caesium flow rate vs current.

of a caesium dispenser can be achieved with the technique based on atomic absorption spectrophotometry.

(c) Comparison with previous results. The data available in the literature are limited; with reference to Hellier<sup>3</sup>, Figure 7 shows a comparison between the results obtained with the method described in this paper (curves a) and those obtained in<sup>3</sup> (curves b). In both cases the current has been increased by 0.1 A min<sup>-1</sup> until the value of 5 A or 6 A were reached. As it can be seen the trends are similar in the 5 A case; more evident differences are observed in the 6 A case.

The reference 3 reports some problems which have been recalled in part 2 of the present paper.

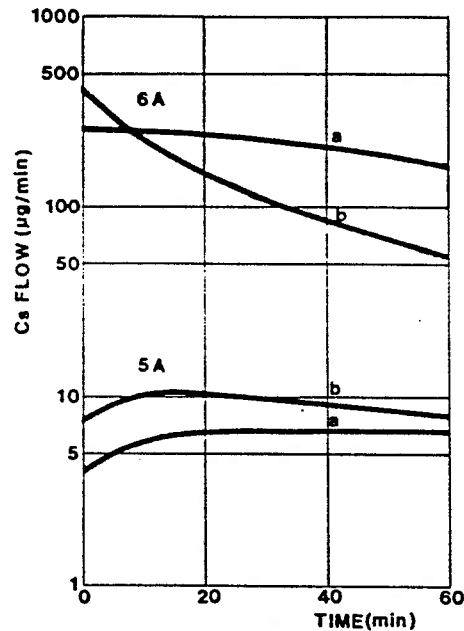


Figure 7. Comparison of results of present work (curves a) and previous<sup>3</sup> results (curves b).

### 7. Conclusions

A method to monitor the caesium evaporation flow rate from a dispenser has been described. With the same methodology, all the other alkali metals released by an alkali metal dispenser could be studied. This technique should be a valuable means to study the characteristics and reproducibility of alkali metal dispensers used in phototube technology.

### References

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