Atomic Absorption Spectrometry of Alkali Metals
by Absorption Tube Technique

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Using a long absorption tube with a hydrogen-air flame from a ring burner, some effects of the external heating of the tube, the rate of exhaust of the burnt gas, and the hydrogen flow rate on the sensitivity, the detection limit, and the memory effect of alkali metals were studied. The considerable improvement in the sensitivity and the detection limit was attained. Especially the external heating caused the more remarkable improvement of the detection limit and the sensitivity for the heavier alkali metals examined, while the memory effect was little changed.

1. Introduction

The application of the atomic absorption spectrometry, using a hydrogen-air flame from a ring burner with a heated absorption tube, was reported for many elements except alkali metals. This special technique to improve the detection limit and sensitivity of many elements has not been applied for lithium and rubidium. For sodium and potassium techniques similar to the present one were used by Moldan and Ando et al. In their reports, however, the data about the detection limit and sensitivity or their temperature dependence with a heated tube were not adequately presented.

In the present paper, the effects of the external heating of the absorption tube with an electric furnace, the rate of the burnt gas, and the hydrogen flow rate on the sensitivity, the detection limit, and the memory effect for lithium, sodium, potassium, and rubidium were investigated quantitatively.

2. Experimental Method

The schematic diagram of the absorption tube (0.9 mm I.D.) is shown in Fig. 1. More detailed descriptions about the whole apparatus and the associated instruments used in the present study were described in the previous paper. Only a photomultiplier was replaced by R 446 UR (Hamamatsu TV Co., Ltd.), having fairly good spectral sensitivity in the longer wavelength region. Hitachi hollow cathode lamps, HLA-3, were used for lithium and rubidium, and Hamamatsu lamps, L-233, for sodium and potassium. Lamp currents were selected in the range of 4 to 18 mA for optimum measurements.

Stock solutions of alkali metals (1,000 ppm)
were prepared by dissolving their chlorides of analytical grade in double-distilled water. Standard solutions were prepared by diluting the stock solutions to suitable concentration steps with the distilled water. For the preparation and the storage of the stock and standard solutions of sodium and potassium, polyethylene or polypropylene wares were used.

At a constant flow rate of aspirating air, 2.3 l/min, a solution of the appropriate concentration of each alkali metal was nebulized into the flame. A sample aspirating rate was ca 2.40 ml/min. For maximum sensitivity and stability of signal, the rates of hydrogen flow and exhaust were chosen in the range of 4.0 to 13.5 l/min and 0.56 to 2.59 m³/min respectively. The absorption tube was externally heated by a cylindrical electric furnace from 400 to 1,200°C under the optimum flame conditions established above.

3. Results and Discussion

The sensitivity and the detection limit of alkali metals were dependent on the rates of hydrogen flow and exhaust, since the rates affected the temperature gradient and the oxidation-reduction environment along the absorption tube. The effects of the above two parameters on the sensitivity are shown in Fig. 2. In this figure the absorption intensity is used instead of the sensitivity and repre-

![Fig. 1. Schematic diagram of the absorption tube.](image)

![Fig. 2. Effect of the rates of hydrogen flow and exhaust on the absorption intensity of alkali metals.](image)
Table I. Optimum operating conditions and detection limit of alkali metals.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Lamp Current (mA)</th>
<th>Exhaust (m³/min)</th>
<th>Hydrogen (/min)</th>
<th>Detection Limit (ppb)</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>670.8</td>
<td>10</td>
<td>0.56</td>
<td>13.5</td>
<td>0.48</td>
<td>17.8</td>
</tr>
<tr>
<td>Na</td>
<td>589.0</td>
<td>5</td>
<td>0.56</td>
<td>6.6</td>
<td>0.72</td>
<td>2.8</td>
</tr>
<tr>
<td>K</td>
<td>766.5</td>
<td>10</td>
<td>0.56</td>
<td>6.6</td>
<td>0.73</td>
<td>21</td>
</tr>
<tr>
<td>Rb</td>
<td>780.8</td>
<td>10</td>
<td>0.56</td>
<td>6.6</td>
<td>2.5</td>
<td>—</td>
</tr>
</tbody>
</table>

The optimum operating conditions for alkali metals are summarized in Table I together with the detection limits obtained. The detection limit is represented by the metal concentration (ppb) in an aspirating solution giving the signal twice the noise (S/N=2). The values of factor in Table I are the ratios of the detection limits obtained from the present apparatus to those from a conventional Hitachi Atomic Absorption Spectrophotometer, Model 207, using an acetylene-air flame of 10 cm long. The same amplifier was used in both apparatuses. As shown in Table I, the present technique is excellent for the measurement of alkali metals as observed for many other elements.

The effect of the external heating of the absorption tube on the relative absorption intensity, based on the unheated value, is shown in Fig. 3. The values of the rates of hydrogen flow and exhaust are the same as in Table I except lithium, i.e., Li (2). The lower solid curve in Fig. 3 represents the variation of the absorption intensity of lithium at the low hydrogen flow rate, 9.0 l/min, and the upper one represents that obtained at the high rate, 13.5 l/min as listed in Table I. The extent of the influence of the external heating on the absorption intensity of alkali metals, as a whole, became higher with the order of atomic number.

At the furnace temperature of 1,200°C the detection limit, the sensitivity, and the memory effect for each element are summarized in Table II together with those of unheated. The sensitivity represented here shows the measurable upper limit of concentration (ppb) under the optimum operating conditions, since the calibration curve obtained by this technique is almost linear. The memory effect is expressed in the time (sec) required to restore the base line of a recorder, after the aspirating of the sample solution, to the initial one by subsequent nebulization of distilled water.
Table II. Heating effect of absorption tube on detection limit, sensitivity, and memory effect of alkali metals.

<table>
<thead>
<tr>
<th>Element</th>
<th>Unheated</th>
<th>Heated (1200°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Detection Limit</td>
<td>Sensitivity</td>
</tr>
<tr>
<td>Li</td>
<td>(ppb)</td>
<td>(ppb)</td>
</tr>
<tr>
<td>Na</td>
<td>0.72</td>
<td>56</td>
</tr>
<tr>
<td>K</td>
<td>0.73</td>
<td>100</td>
</tr>
<tr>
<td>Rb</td>
<td>2.5</td>
<td>320</td>
</tr>
</tbody>
</table>

It was observed that the heating improved the detection limit and the sensitivity for heavier alkali metals examined. The memory effects were scarcely dependent on the temperature of the absorption tube.

As evident from Fig. 3, the value of the absorption intensity of lithium at the low hydrogen flow rate approaches that obtained at the high rate with additional heating of the tube. Presumably the heating causes the increase of the gas pressure in the tube by the thermal expansion of the flame gas. In addition as rate of exhaust is fixed a priori at constant, the input rate of the air entrained decreases. The flame becomes fuel-rich relatively, though the hydrogen flow rate is still low. Thus the heating resulted in the increase of the absorption intensity of lithium. This could be readily found from the fact that the absorption intensity of lithium increased with the increase of the hydrogen flow rate as shown in Fig. 2.

Though the interaction between the alkali metals and the inner wall of the absorption tube at a high temperature was expected, the devitrification of the transparent quartz tube was hardly observed after the whole experiment. However, the memory effect, especially large for heavier alkali metals, was somewhat longer than that for other elements in the previous report. The invisible erosion of the tube was probably caused by hot alkali metal vapors in the flame.

In the practical determinations, the feasible concentration for alkali metals ranges from about 10-fold concentration of the detection limit to that of the measurable upper limit listed in Table II.

References