SOUTHWESTERN RADIOLOGICAL HEALTH LABORATORY

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FLAME PHOTOMETRIC ANALYSIS

EVALUATION OF REVERSED OXYACETYLENE FLAME MODIFICATION

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SUMMARY

Flame photometric determinations for calcium and strontium are an established portion of the routine work of this laboratory. The use of flame photometry provides the most rapid and economical method of performing these determinations, but is subject to extensive interference problems. The inherent instability of the instrumental system requires considerable operating skill to obtain acceptable results.

An investigation was made of a reversed-gas flow system (to the atomizer-burner) to determine if improved operating characteristics could be achieved in this manner. The results show an increased flame temperature, without heating of the atomizer-burner during operation, and an impressive increase in flame stability resulting from elimination of the deposition of combustion products on the burner tip. The band spread can be reduced by the increase in sensitivity which reduces the interference problems.

By comparison with conventional burner operation, the reversed gas flow system results in markedly increased accuracy and precision. Establishment of routine procedures using this system is advised.

INTRODUCTION

Certain elements introduced into a high-temperature flame will emit a characteristic visible spectrum. In flame photometric analysis, these characteristic radiations are measured and compared to a standard to provide a quantitative estimate of specific elements.

In the normal operation of the Beckman model DU flame photometer, the sample is introduced into an oxyacetylene flame with oxygen used as the spraying gas (fig. 1). The flame is formed at the capillary tip, resulting in a heating of the burner and consequent carbon and salt encrustment of the capillary tip. These deposits are picked up in the flame, causing fluctuations in the flame temperature and position, resulting in an unstable system. The effect of this on normal operation is to cause flame photometry to be largely an empirical procedure compounded by inherent instability and short operating intervals with extensive interference problems. Nevertheless, flame photometry has proven to be a most reliable and time saving procedure for the determination of calcium, strontium, sodium, potassium and lithium on a routine basis.

A publication by Loken, Teal, and Eisenbery[1] proposed a procedure for calcium using a reversed oxyacetylene flame. The paper indicated that by modifying the standard Beckman DU flame photometer to use acetylene as the spraying gas, the problems inherent in normal operation are largely overcome; that is, a higher degree of stability and repeatability of the flame photometric system is achieved. It is the purpose of this investigation to determine if this modification would result in improvement of the flame photometric procedures that this laboratory has in use for calcium and strontium analysis.

EXPERIMENTAL

Apparatus

The following apparatus was used for this investigation:

Beckman model DU Spectrophotometer

Beckman #9200 Flame Attachment

Beckman #4030 Medium Bore Oxygen-acetylene Burner

This instrument was operated by the conventional manual procedure as per the manufacturer's recommendations with the exception that the gas lines inside the manometer housing were altered, as per fig. 2, to use acetylene as the spraying gas.

PROCEDURE

The gauges on the oxygen and acetylene tanks are set at 15 p.s.i. and 12 p.s.i. respectively. The acetylene is then set at one half to two thirds the recommended oxygen pressure for the burner: the oxygen pressure is set at one to three p.s.i. and the closed needle valve is opened about one half turn. The flame is lit. If it does not stay lit, then the oxygen is turned down, with special care not to get it too low (indicated by a very bright, white flame). The final adjustment of gas pressures is then made. The blue center cone at the flame base should be from 10 to 25 mm high. When water is sprayed through the burner, the center cone should decrease to 7 mm or less. Five mm appears to be an optimum height. The larger the center cone, the larger the amount of background light.

The mirror is then adjusted to give a maximum reading while a sample is being sprayed. This is done with 0.1 g/l calcium or strontium standard.[2] Ca, Sr, K and Na standards were made up in the following concentrations: 0.001 g/l, 0.005 g/l, 0.010 g/l, 0.015 g/l, 0.020 g/l, and 0.1 g/l. Standard curves were then run and interferences checked.

After final adjustment is made, the oxygen pressure is maintained at 1.2 p.s.i. and the acetylene pressure at 7.0 p.s.i.

The spectral lines at 422.7 mμ are used for Ca, 460.7 for Sr, 589.3 for Na, and 766.5 for K. In each case the background interference is scanned over an area of approximately 15 mμ with the wavelength of interest in the center of the scan. The sensitivity is adjusted to give a difference of approximately 10% transmission between standards.

RESULTS

The following changes in operating characteristics of the Beckman DU flame photometer were observed as a result of reversing the oxygen and acetylene feed to the atomizer-burner.

1. The oxygen pressure is reduced from one-half to two-thirds of that required by conventional operation. This results in a decreased flow rate of the sample solution and less of a cooling effect in the flame. An apparently higher temperature flame results which increases the instrument sensitivity and introduces a background interference from the CH and C_2 bands[4] in the visible and near-ultra violet spectral regions. This interference can be eliminated by proper adjustment of the focusing mirror[5] (fig. 3). When properly focused, the slit width can be reduced by a factor of ten as a result of the increase in sensitivity over the conventional system, and the major background interferences are largely eliminated.

2. The flame is formed at a distance of 4-5 mm above the burner tip. The burner remains cold, carbon and salt encrustment of the burner tip is eliminated and the instrument system shows a marked increase in operating stability. In effect this indicates that the reversed oxyacetylene flame modification will permit prolonged operating time, significantly reducing warm up time and maintenance requirements.

3. Table 1 and 2 demonstrate the reproducibility. The Beckman instrument manual[3] states that a mean deviation of ± 0.3 transmittance scale divisions is acceptable. The reversed flame therefore has an excellent reproducibility

with a mean deviation of $\pm$ 0.09 transmittance scale divisions. Not only is the reproducibility good on a short term basis, there is a low mean deviation of $\pm$ 0.28 mg on strontium standards run on 10 different days. This is compared with a mean deviation of $\pm$ 2.23 mg Sr with the conventional flame. Because of the slower aspiration rate, standards last much longer.

CONCLUSION

The comparative study of conventional and reversed oxyacetylene flame photometry indicates that the reversed system yields a greater sensitivity with reduced background interference, a higher order of precision, and longer periods of operation. The combined effect is to provide a greater confidence in the results and an increase in productive capacity for the flame photometer without adding to the cost of the equipment. Routine procedures for calcium and strontium are presently being modified to take advantage of this modification.

REFERENCES

(1) Loken, H. F., Teal, J. S., Eisenberg, E., Anal. Chem. 35, 875 (1963).

(2) & (3) Beckman Instruction Manual No. 334-A, 8-9 (1957).

(4) Handbook of Analytical Chemistry 6-221 (1963).

(5) Broida, H. P. and Heath, D. F. J. Chem. Phys. 26, 223 (1962).

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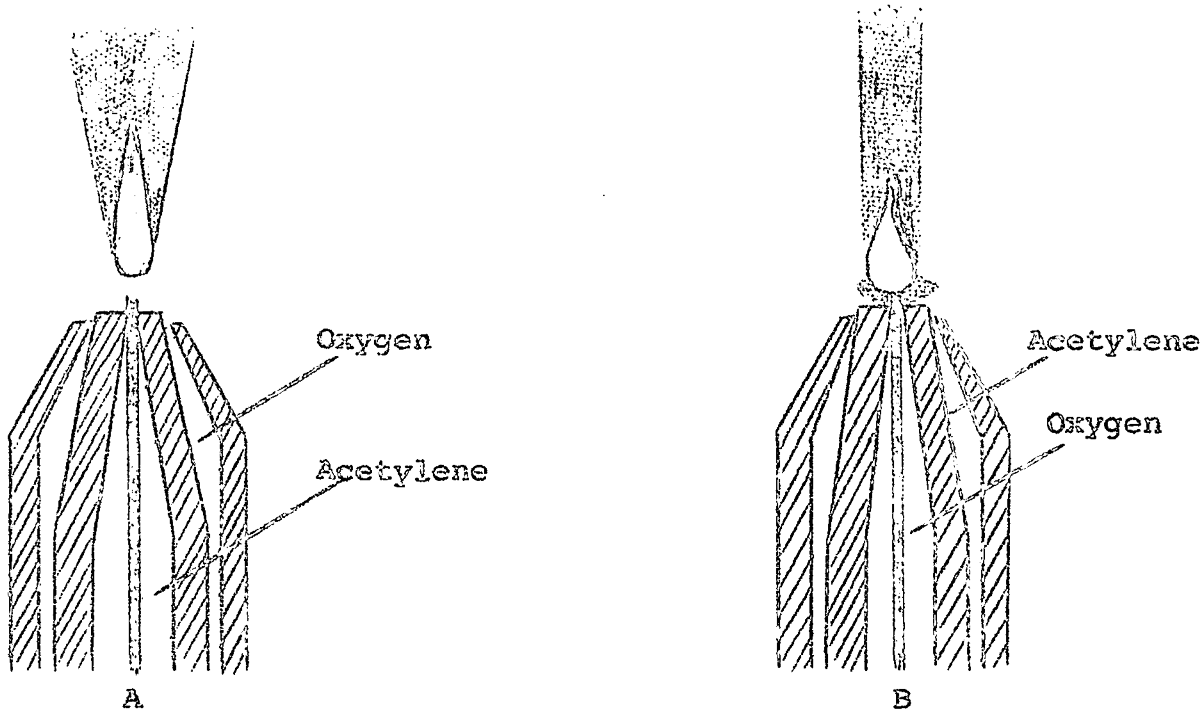


Figure 1. Schematic Drawing of oxyacetylene
Flames in Beckman oxyacetylene burner
A. With acetylene as spraying gas - Reversed
B. With oxygen as spraying gas - Conventional

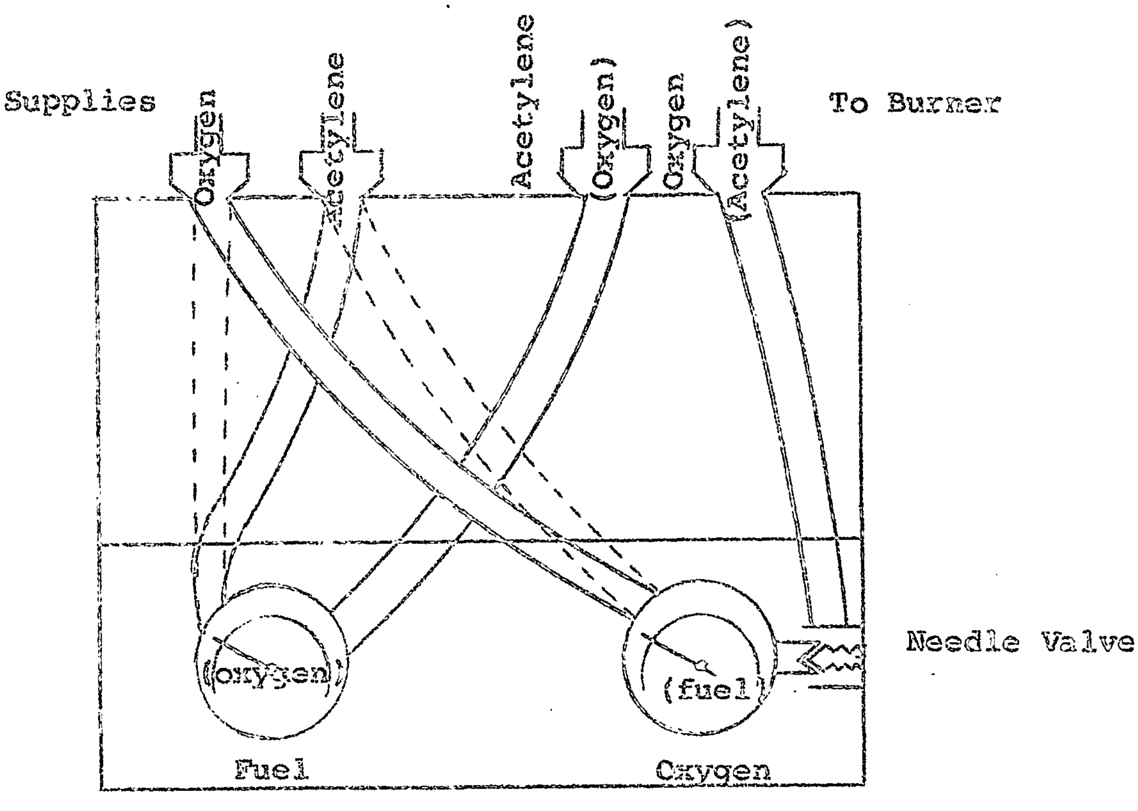
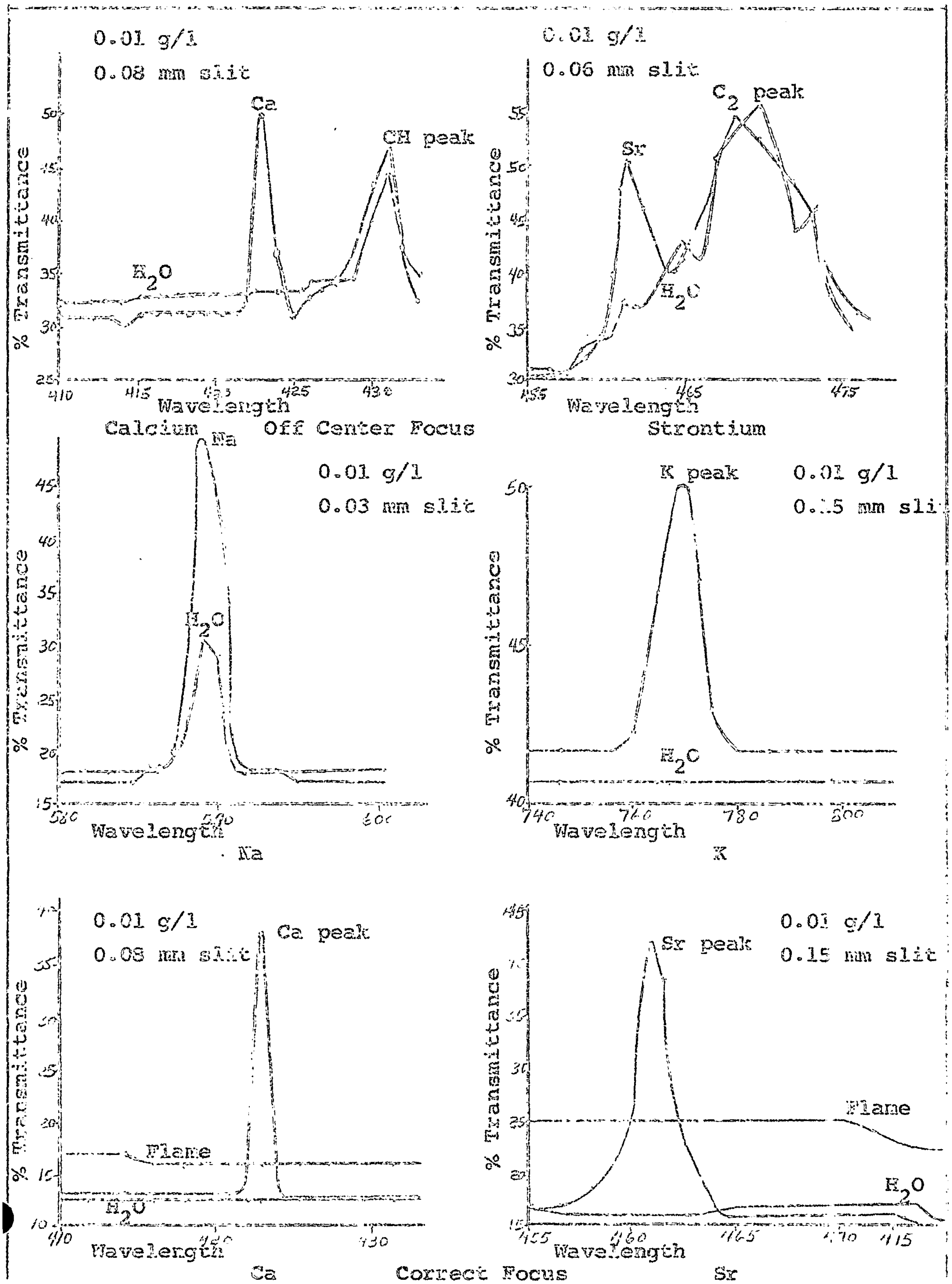
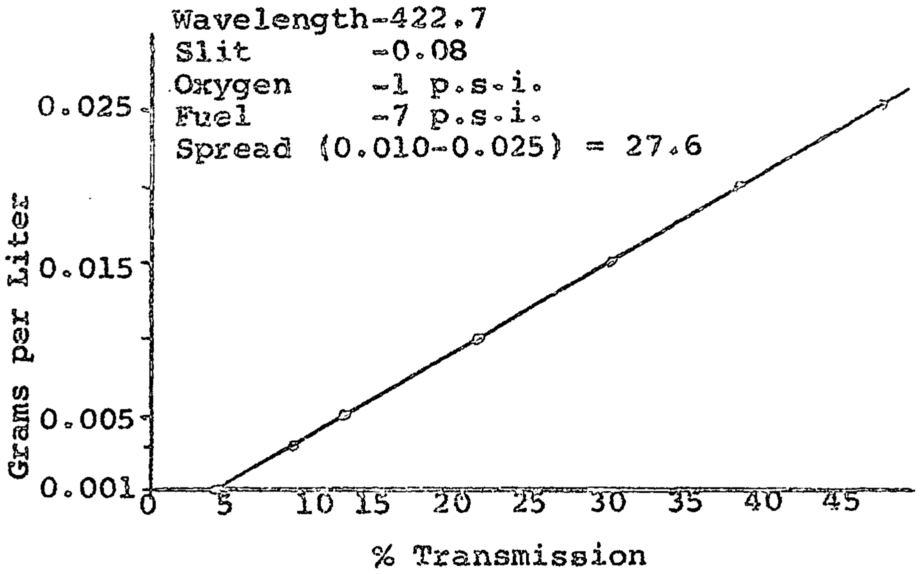


Figure 2. Arrangement of connections in Beckman manometer
housing for reversed system

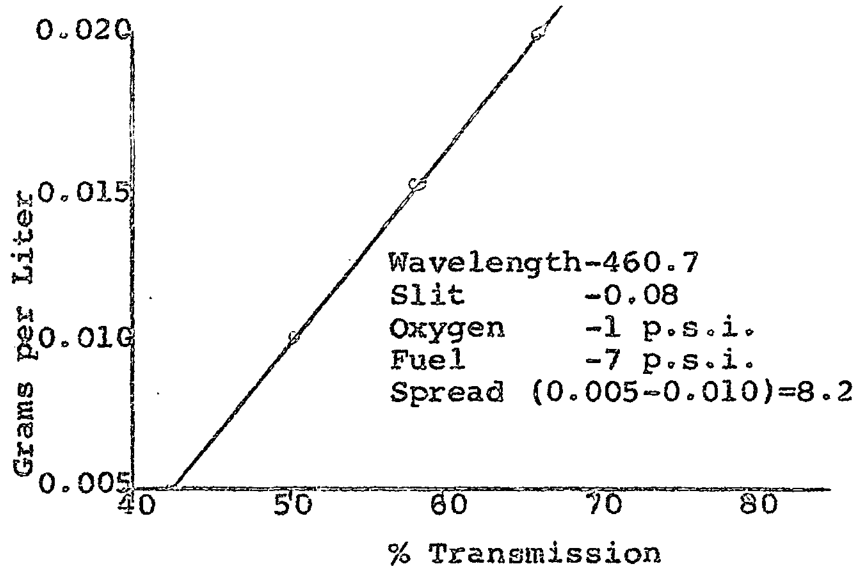
Figure 3



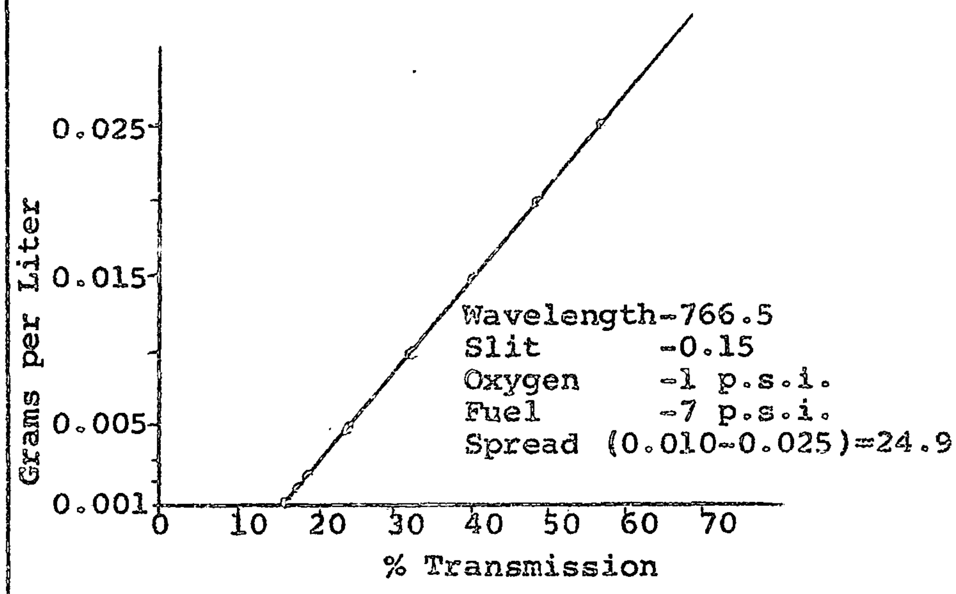
0.01 g/1
0.08 mm slit
Ca
CH peak
H_2O
% Transmittance
Wavelength
Calcium
Off Center Focus
0.01 g/1
0.06 mm slit
C_2 peak
Sr
H_2O
% Transmittance
Wavelength
Strontium
Na
0.01 g/1
0.03 mm slit
H_2O
% Transmittance
Wavelength
Na
K peak
0.01 g/1
% Transmittance
H_2O
Wavelength
K
0.01 g/1
0.08 mm slit
Ca peak
% Transmittance
Flame
H_2O
Wavelength
Ca
Correct Focus
Sr peak
0.01 g/1
0.15 mm slit
% Transmittance
Flame
H_2O
Wavelength
Sr



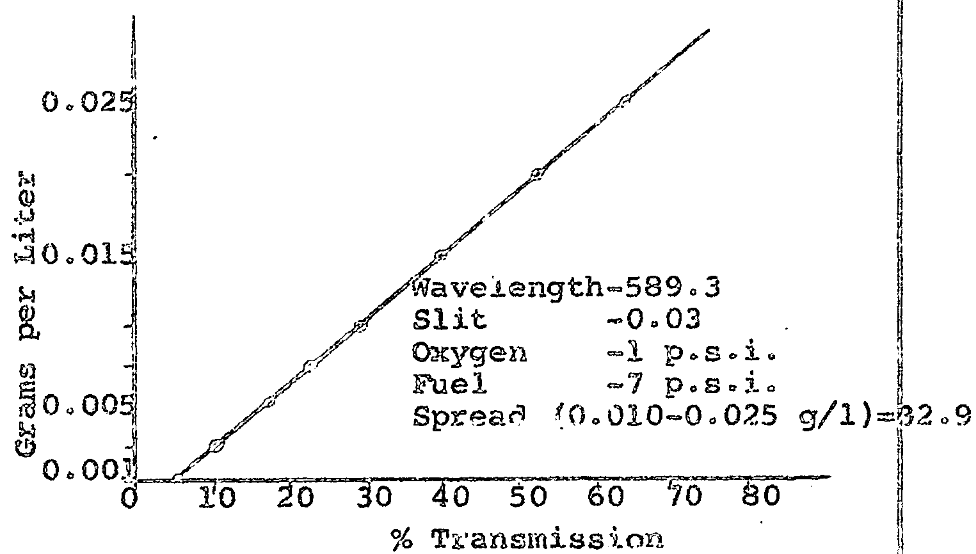
Calcium Calibration Curve (0.001-0.025 g/l)



Strontium Calibration Curve (0.005-0.020 g/l)



Potassium Calibration Curve (0.001-0.025 g/l)



Sodium Calibration Curve (0.001-0.025 g/l)

Figure 4

REPRODUCIBILITY OF THE FLAME

TABLE I. 1 Sample Run 10 Times in One Operation

Transmittance Scale Reading	Deviation from Average
67.1	0.0
67.1	0.0
67.0	0.1
67.1	0.0
66.9	0.2
66.9	0.2
66.9	0.2
67.3	0.2
67.1	0.0
67.1	0.0
Average 67.1	Sum 0.9

$$\text{Mean Deviation} = \frac{0.9}{10} = 0.09$$

0.09 Transmittance Scale Division

Conditions - Sr Carrier
460.7 mμ - Wavelength
0.06 mm - Slit Width
Maximum - Sensitivity
14.2% T - Spread Between 0.015 and 0.020
1.2 p.s.i. - Oxygen
7.0 p.s.i. - Acetylene

TABLE II. 1 Sample Run 10 Different Days

	mg Sr	Deviation from Average
6-14-63	79.5	0.3
6-17-63	79.0	0.8
6-18-63	80.0	0.2
6-19-63	80.0	0.2
6-19-63	79.5	0.3
6-20-63	80.0	0.2
6-24-63	80.0	0.2
6-25-63	80.0	0.2
6-25-63	80.0	0.2
6-25-63	80.0	0.2
Average	79.8	Sum 2.8

$$\text{Mean Deviation} = \frac{2.8}{10} = 0.28 \text{ mg Sr}$$

Note: It was necessary to find the mean deviation in mg Sr rather than % transmittance because of the different set of conditions each day.