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**FLAME PHOTOMETRIC DETERMINATION
OF STRONTIUM IN WATER**

By

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OBJECTIVE OF PRESENT PROJECT

The objective of the present project has been to develop a procedure for the flame photometric determination of Sr in natural water samples, utilizing the Beckman Model DU spectrophotometer with flame photometer attachment, the oxygen-hydrogen flame, and a photomultiplier tube attachment. Of special concern was the determination of Sr at relatively low concentrations, i.e. 0 to 50 ppm.

INTRODUCTION

Preliminary search of reported methods of Sr analysis revealed several investigations which have been made for the determination of Sr with the flame photometer, both at relatively low concentrations (0 to 50 ppm Sr) and at higher concentrations. Generally the procedures described involved measurement of Sr emission at either 460.7 mu or at 681 mu. There is disagreement among those reporting methods for Sr as to the preference of the one wavelength over the other. The 681 line (or band) seems to be preferred because of its greater reproducibility and relative freedom from interference. The 460.7 mu line, however, lies in the region of greater sensitivity of the photomultiplier tube, and hence for this reason is preferred by some. This is an advantage, of course, when determining Sr at very low concentrations.

This investigation is concerned with determining the optimum conditions for the determination of Sr at low concentration levels in water samples. Early experimental work indicated a greater sensitivity for the 460.7 mu (hereafter designated as 461 mu) Sr line. Therefore, most of the subsequent work was based on a study of the effects of various other materials and conditions on the emission of Sr at this wavelength.

EQUIPMENT

The instrument used for this investigation was the Beckman Model DU spectrophotometer with a Beckman flame photometer attachment. The flame photometer consists of a small atomizer-burner which sprays the sample directly into an oxygen-acetylene flame. The manufacturer's recommendations state that optimum efficiency is obtained when the

a/ A summary report of a research project carried out on a part-time basis, St. Olaf College, Northfield, Minn., September 1956 to May 1957.

atomizer-burner is operated at an oxygen pressure of 10 lb./sq. in. By observation of the flame while varying the oxygen pressure, it was concluded that this pressure does give the most satisfactory flame as far as size, shape, and stability are concerned. Further testing showed that the optimum pressure for acetylene lies between 5.0 and 6.0 lb./sq. in. At acetylene pressures less than 5.0 lb./sq. in. the emission intensity drops off rapidly due to the decrease in flame temperature. At pressures above 6.0 lb./sq. in. the stability of the flame was greatly decreased and rapid, more or less erratic fluctuations in emission intensity were observed. Optimum operating conditions were thus established at 10 lb./sq. in. oxygen pressure, and at either 5.0, 5.5, or 6.0 lb./sq. in. acetylene pressure.

The photomultiplier attachment is the standard unit supplied by Beckman Instruments, Inc., and consists of an auxiliary battery box, containing the necessary "C" batteries, and a special phototube housing with a special 1P28 multiplier tube. The resistor box, mounted on the phototube housing, is equipped with a 22 megohm load resistor for operation with the photomultiplier tube. A red-sensitive phototube and two additional load resistors (2,000 megohm and 10,000 megohms) mounted in the phototube housing and resistor box permit the instrument to be operated as a spectrophotometer or flame photometer over a wide range of wavelengths and sensitivities.

Sensitivity of the photomultiplier tube was adjusted by varying the potential applied to the tube. This was done by eliminating one or more of the "C" batteries supplying the high voltage to the tube, thus decreasing the sensitivity of the tube. In most cases the photomultiplier tube was operated at full sensitivity. Excellent stability and freedom from fluctuations and drift was attained.

Experiment 1... Calibration of Solutions of NaCl, KCl, SrCl₂ and CaCl₂.

To test the operation of the instrument and particularly the photomultiplier attachment which was installed specifically for this investigation, calibration curves were run on solutions containing a single salt: NaCl, KCl, SrCl₂ or CaCl₂.

A stock solution of NaCl and of KCl was prepared by drying reagent grade salt for several hours at 110°, weighing carefully the calculated amount of reagent, transferring the weighed amount quantitatively to a volumetric flask, and diluting to exact volume with distilled water. Usually 500 ml of stock solution was prepared, requiring about 1.27 g of NaCl and about 1.00 g of KCl to prepare a solution of about 1000 ppm of the cation. The exact concentration of the metal ion was calculated in each case. Aliquots of the stock solution were diluted to 100 ml in volumetric flasks in order to prepare standard solutions varying in concentration from 0 to 100 ppm or more as desired.

Stock solutions of Sr and Ca (chlorides) were prepared by carefully weighing thoroughly dried, reagent quality SrCO₃ and CaCO₃

and transferring the weighed salt to a volumetric flask. Dilute (10%) HCl was then added in small portions until the sample was completely dissolved. The solution was then diluted to exact volume.

All stock solutions and any diluted standard solutions were transferred immediately after preparation to polyethylene bottles for storage.

Figures 1, 2, 3, and 4 show typical calibration curves obtained for NaCl, KCl, SrCl₂ and CaCl₂ solutions respectively. The operating data is shown in table 1.

Table 1... Operating conditions for calibration data

| Solution | NaCl | KCl | CaCl ₂ | SrCl ₂ |
|------------------------|------|--------|-------------------|-------------------|
| Oxygen, lb./sq. in. | 10 | 10 | 10 | 10 |
| Acetylene, lb./sq. in. | 6.0 | 5.0 | 5.0 | 5.0 |
| Wavelength, mu | 589 | 770 | 422 | 461 |
| Phototube | FM | Red | FM | FM |
| Load resistor, megohms | 22 | 10,000 | 22 | 22 |

Experiment 2... The effect of added Na on Sr emission (461 mu). A series of standard solutions were prepared, each containing 13.4 ppm of Sr. To each was added varying amounts of Na (NaCl standard solution) up to 105 ppm of Na.

Whereas Na alone showed no emission at 461 mu (Sr), the addition of NaCl to strontium solutions increases the intensity of the Sr emission. See table 2 and figure 5. Background intensity measured at 459 mu is included for comparison. These data indicate that the presence of even 10 ppm of Na (as NaCl) will cause an error in measurement of Sr at 461 mu.

The effect of the presence of Na on Sr emission at 680 mu was also measured. The effect was not as great at this longer wavelength as at 461 mu, but because of the much decreased sensitivity of the photomultiplier unit at these wavelengths, no further tests were made. The data in table 3 illustrate the effects observed.

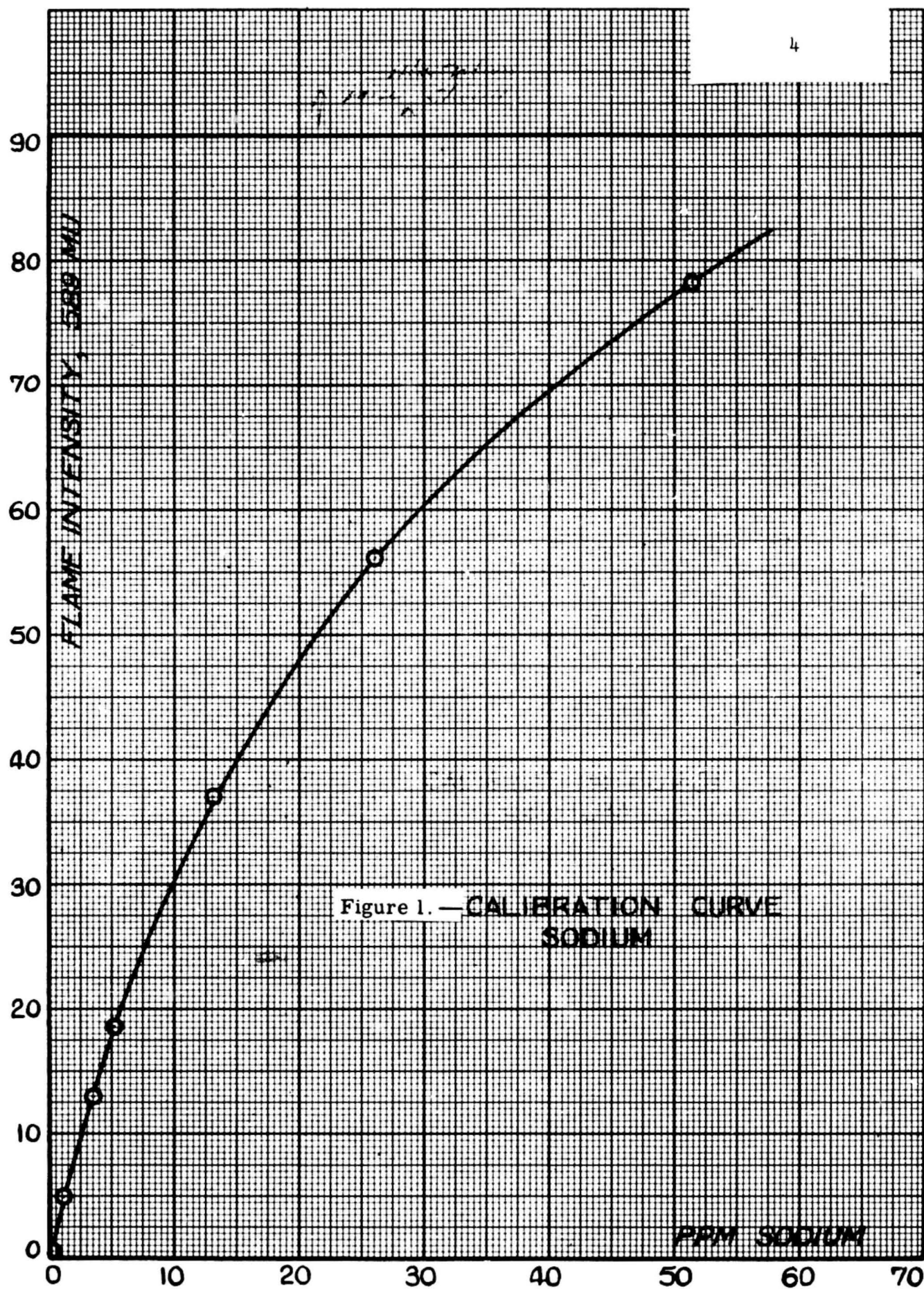
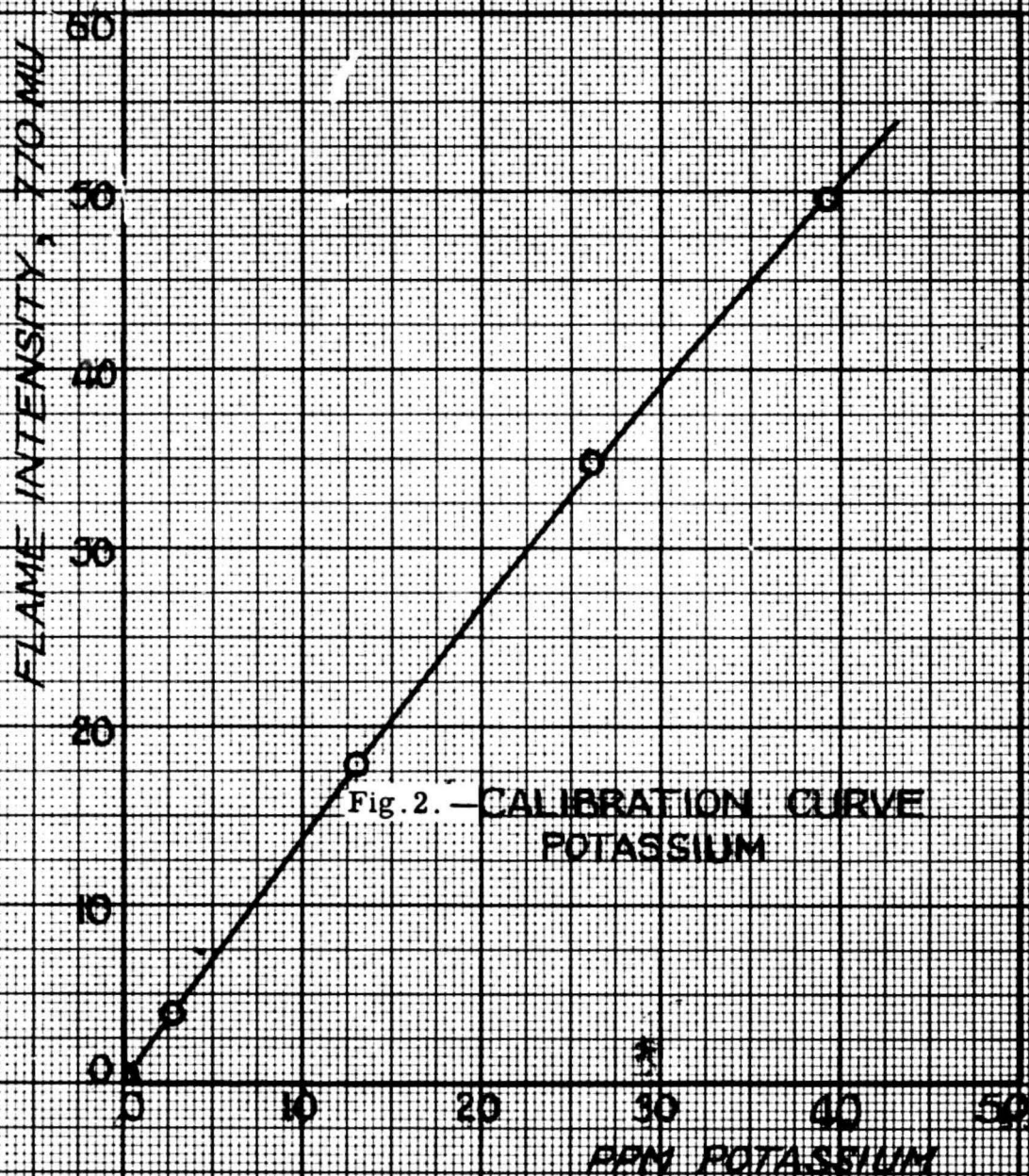
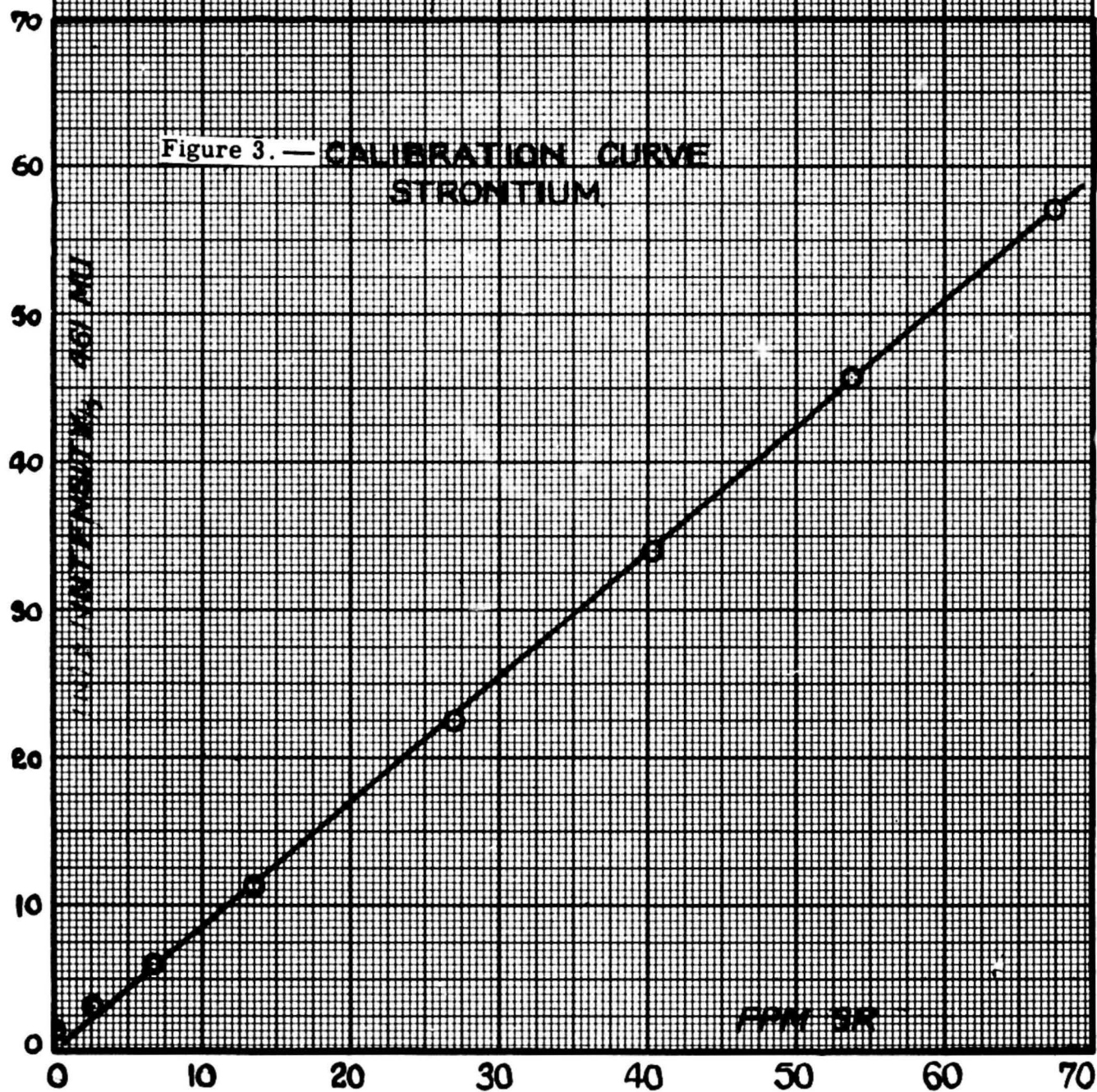


Figure 1. — CALIBRATION CURVE
SODIUM





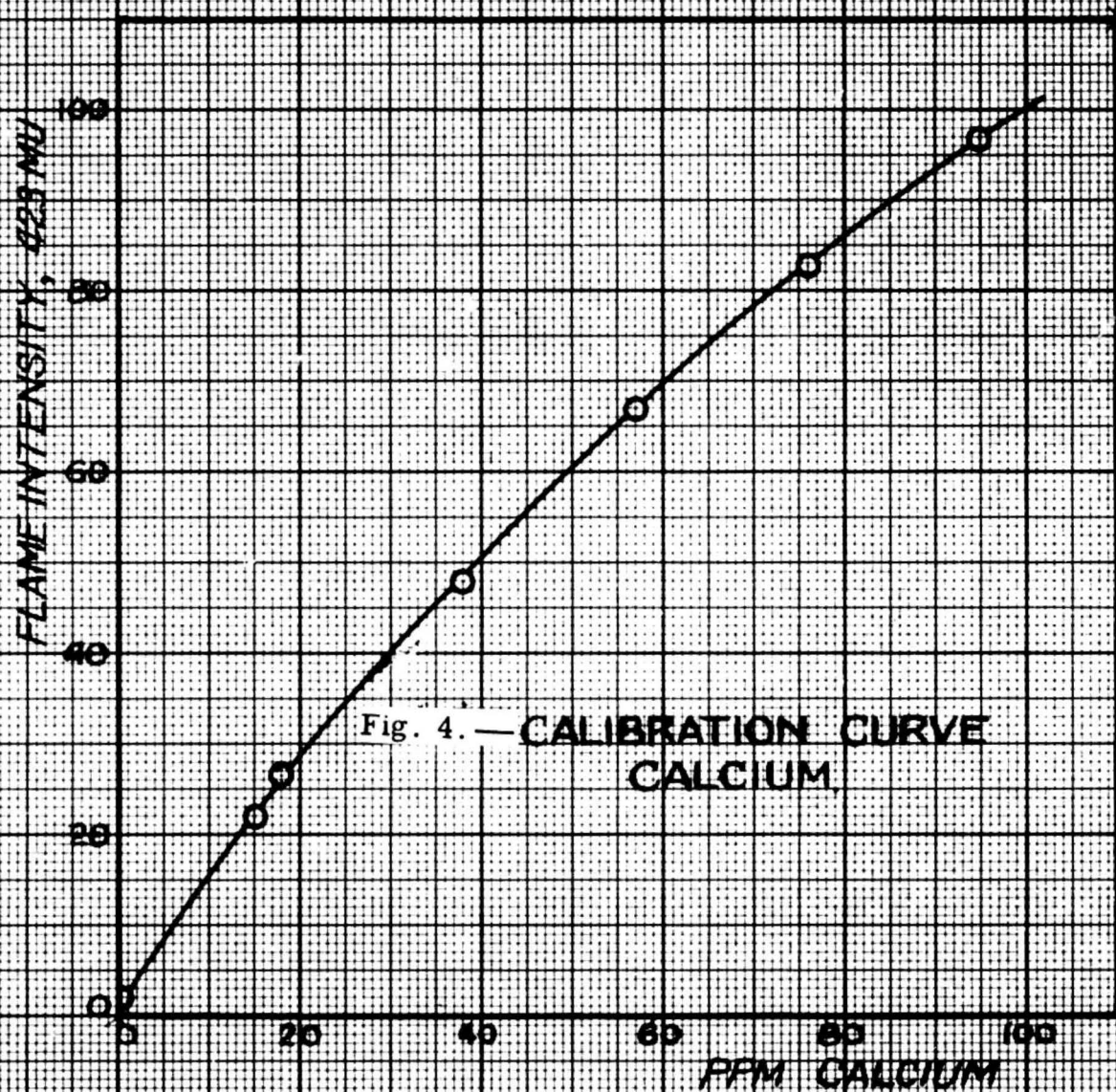


Table 2... Effect of added Na on Sr emission (461 mu)

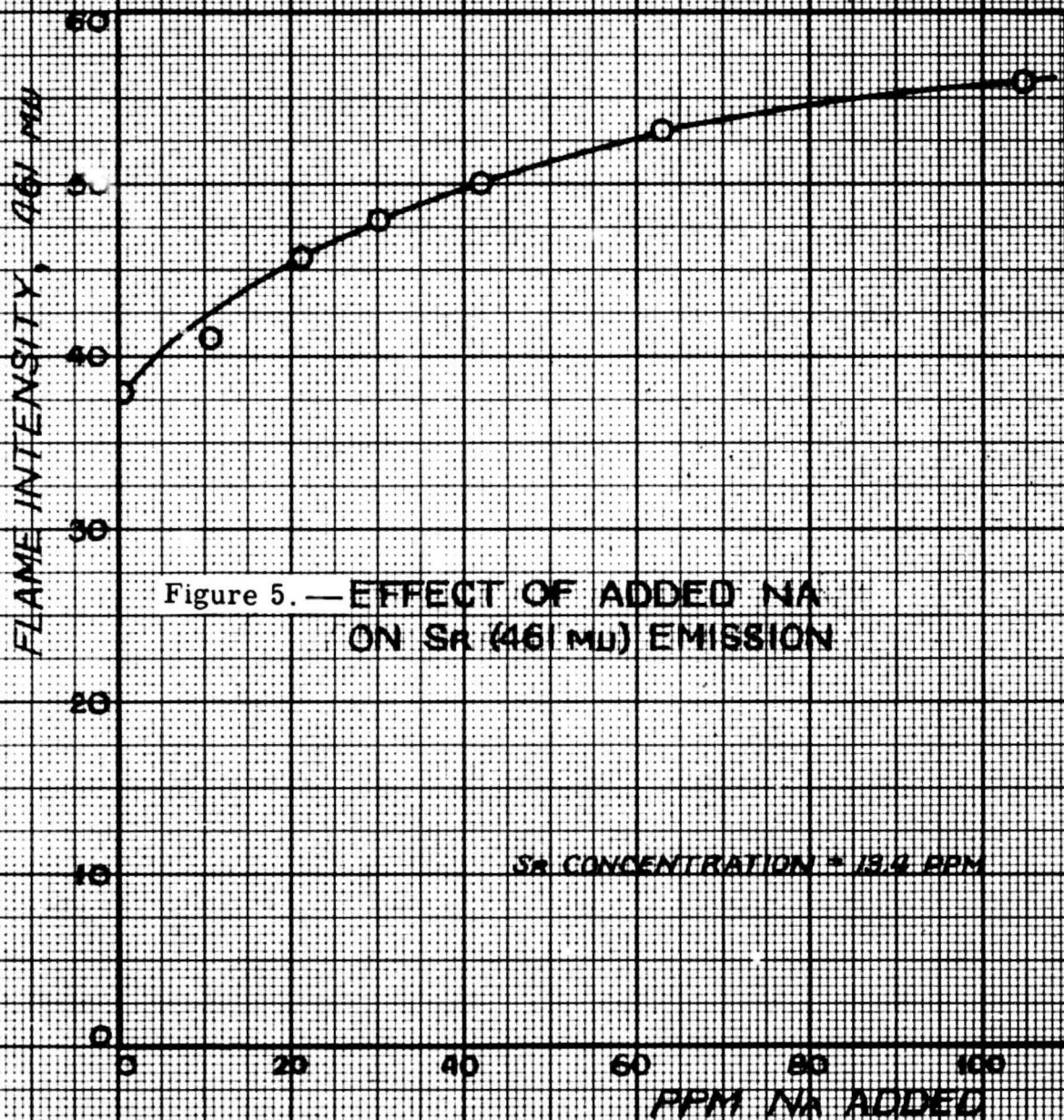
Operating data: 10 lb Oxygen, 6.0 lb Acetylene, PM tube,
22 megohm resistor

| Concentration of solution, ppm | | Relative intensity at wavelength | |
|--------------------------------|------|----------------------------------|--------|
| | | 461 mu | 459 mu |
| Na | Sr | | |
| 0.0 | 0.0 | 4.4 | 4.5 |
| 0.0 | 13.4 | 38.0 | 4.5 |
| 10.5 | 13.4 | 42.2 | 4.5 |
| 21 | 13.4 | 45.6 | 4.5 |
| 31 | 13.4 | 47.9 | 4.8 |
| 42 | 13.4 | 50.1 | 4.6 |
| 63 | 13.4 | 53.2 | 4.6 |
| 105 | 13.4 | 56.0 | 4.7 |
| 3.1 | 0.0 | 4.4 | 4.3 |
| 13.1 | 0.0 | 4.4 | 4.6 |
| 26.2 | 0.0 | 4.4 | 4.6 |
| 52.4 | 0.0 | 4.4 | 4.6 |

Table 3... Effect of added Na on Sr emission (680 mu)

| Concentration of solution, ppm | | Relative intensity at 680 mu |
|--------------------------------|------|------------------------------|
| Na | Sr | |
| 0.0 | 0.0 | 2.0 |
| 0.0 | 13.4 | 5.5 |
| 10.5 | 13.4 | 6.0 |
| 21 | 13.4 | 6.3 |
| 31 | 13.4 | 6.8 |
| 42 | 13.4 | 7.0 |
| 63 | 13.4 | 7.2 |
| 105 | 13.4 | 7.6 |
| 3.1 | 0.0 | 1.9 |
| 13.1 | 0.0 | 2.0 |
| 26.2 | 0.0 | 2.1 |
| 52.4 | 0.0 | 2.2 |

Operating data: 10 lb Oxygen, 6.0 lb Acetylene, PM tube,
22 megohm resistor



Experiment 3... The effect of added Ca (CaCl_2) on Sr emission at 461 mu. A series of standard solutions were prepared, each containing 13.4 ppm of Sr. To each was added varying amounts of Ca (CaCl_2 standard solution) up to 100 ppm Ca.

Previously, solutions containing up to 200 ppm Ca alone had shown little or no emission interference at 461 mu (Sr). 950 ppm Ca showed significant interference at 461 mu (Sr). The addition of Ca increased slightly the intensity of Sr emission above that which would have been expected as due to Ca emission alone. Table 4 and figure 6 shows the data obtained.

Table 4... Effect of added Ca on Sr emission (461 mu)

| Concentration of solution | | Relative intensity at wavelength | |
|---------------------------|--------|----------------------------------|--------|
| ppm Ca | ppm Sr | 423 mu | 461 mu |
| 0.0 | 0.0 | 3.5 | 4.3 |
| 0.0 | 13.4 | 3.6 | 20.3 |
| 9.5 | 13.4 | 21.2 | 22.1 |
| 19.1 | 13.4 | 38.3 | 23.5 |
| 28.6 | 13.4 | 62.0 | 24.8 |
| 38.1 | 13.4 | 61.1 | 26.1 |
| 57.2 | 13.4 | 93.0 | 27.4 |
| 76.2 | 13.4 | ---- | 28.1 |
| 95.3 | 13.4 | off scale | 29.1 |

Experiment 4... The effect of added KCl on emission of Sr at 461 mu. A series of standard solutions were prepared each containing 13.1 ppm of Sr. To each was added varying amounts of solid, reagent quality KCl.

The addition of a large excess of solid KCl increased the intensity of 461 mu (Sr) and also increased the intensity of background radiation measured at 459 mu. Also, it was found that the addition of solid KCl beyond a certain minimum tended to increase the intensity of emission at 461 mu (Sr) proportionally less, and that the ratio of 461 mu (Sr) to 459 (background) remained essentially constant. This is shown by the data in table 5 and also in graph 7.

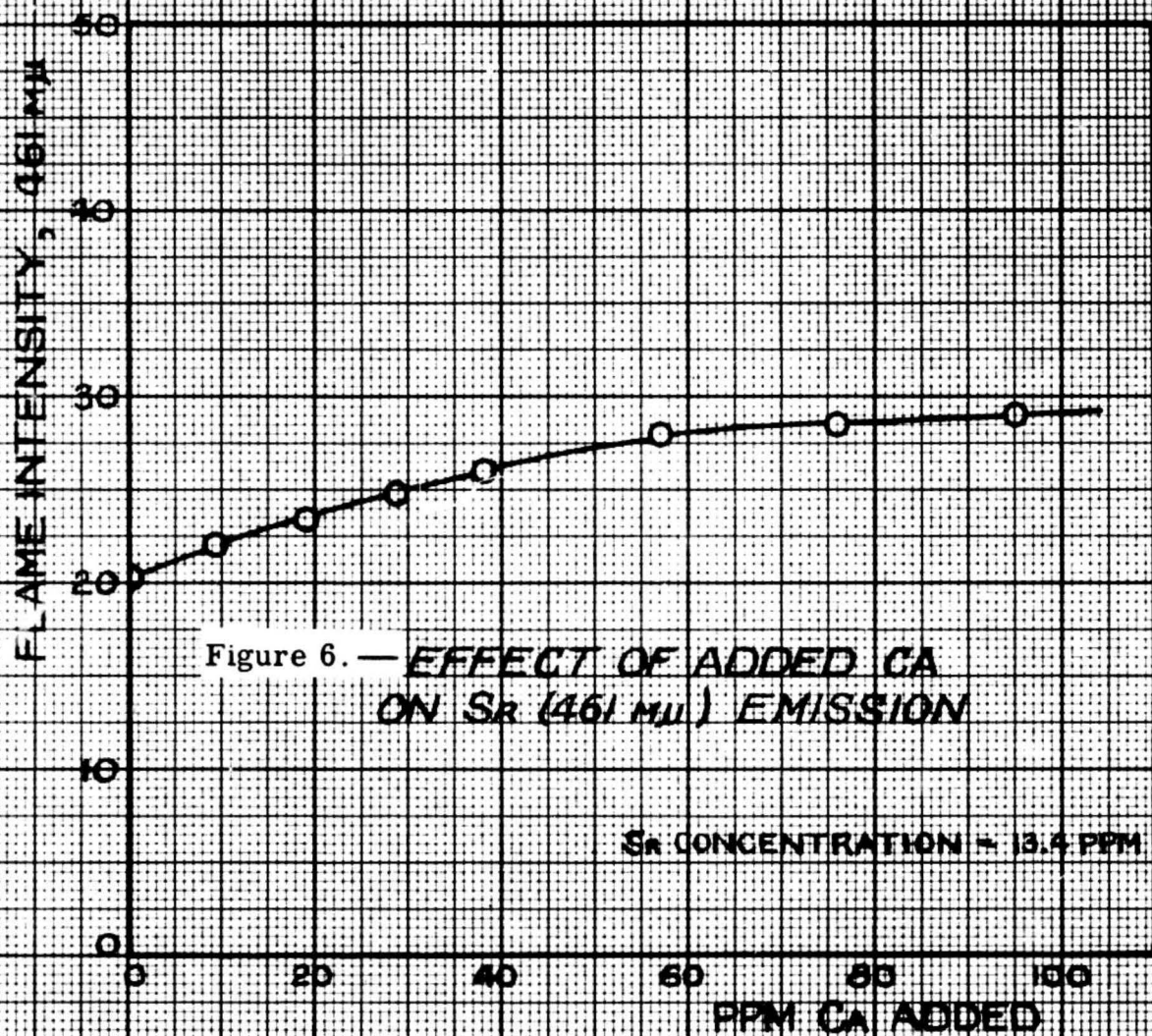


Table 5... Effect of added KCl on Sr emission (461 mu)

| Added KCl, g/100 ml | Relative intensity at | | |
|------------------------|-----------------------|--------|---|
| | 461 mu | 459 mu | |
| 0.0 | 36 | 8 | (Note) All solutions contained 13.1 ppm Sr. |
| 0.5 | 67 | 11 | |
| 1.0 | 72 | 14 | |
| 2.0 | 80 | 25 | |
| 4.0 | 85 | 29 | |
| 8.0 | 109 | 50 | |

A calibration curve was then prepared from a series of standard Sr solutions containing from 0.0 to 39.2 ppm Sr, and each containing 1.0 g of solid KCl per 100 ml of standard solution. The data are shown in table 6 and the data graphed in figure 8.

Table 6... Calibration data, Sr

| Concentration Sr, ppm | Relative intensity | | Difference (461 - 459) |
|--------------------------|--------------------|--------|---------------------------|
| | 461 mu | 459 mu | |
| 0.0 | 10.6 | 10.6 | 0.0 |
| 2.6 | 18.4 | 9.5 | 8.9 |
| 5.2 | 28.0 | 9.8 | 18.2 |
| 13.1 | 54.3 | 9.0 | 45.3 |
| 19.6 | 74.0 | 9.0 | 65.0 |
| 26.1 | 97.3 | 9.9 | 87.4 |

All samples contained 1.0 g KCl added per 100 ml.

Solutions containing 19.6 ppm Sr and Ca added up to 500 ppm of Ca. The data obtained (see table 7) showed that the added Ca had no direct effect on Sr determination when the background reading at 459 mu was subtracted from Sr emission at 461 mu. The errors are small, are completely random, and do not indicate any relationship between increased amounts of Ca and the determination of Sr.

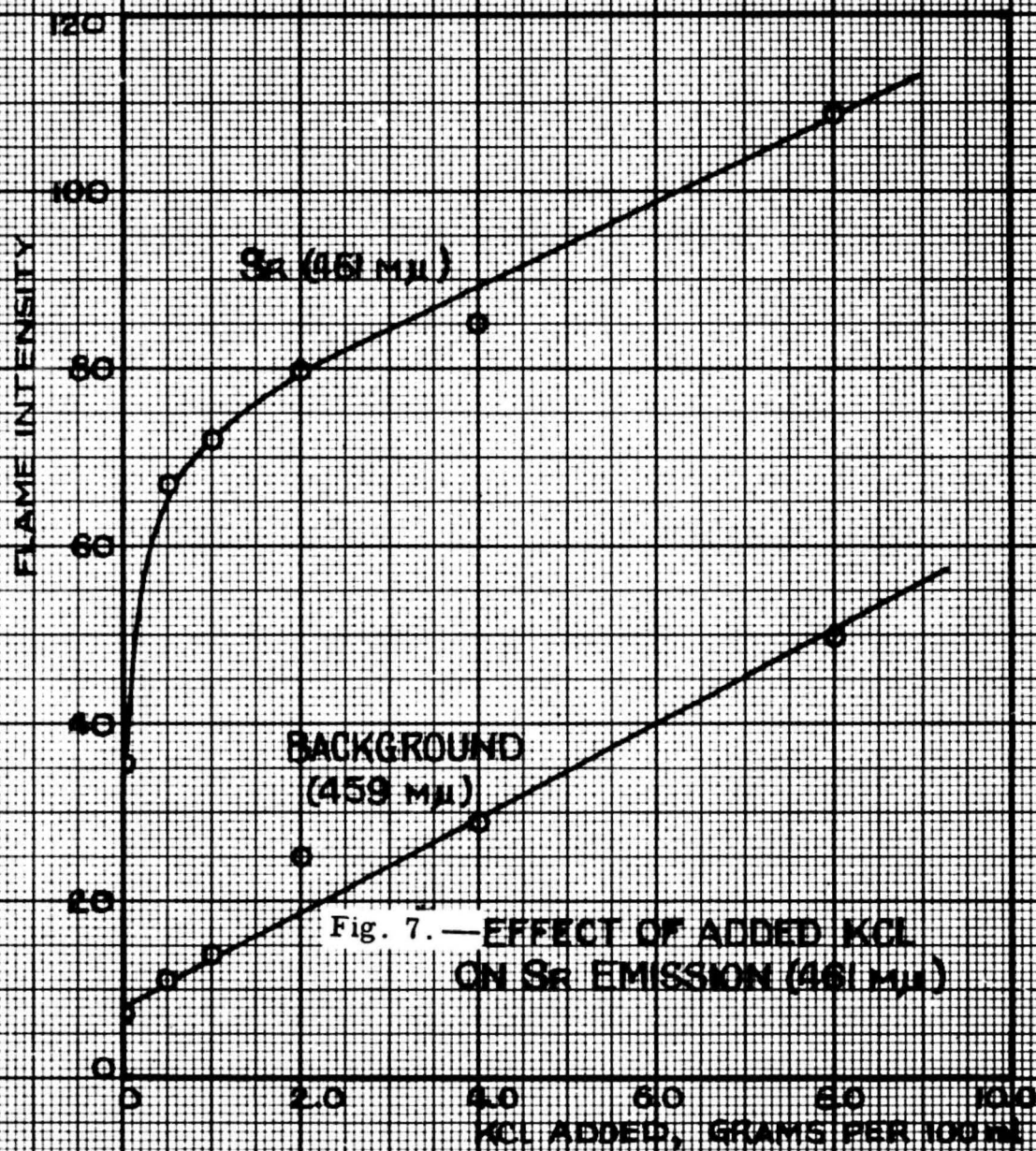


Fig. 8. — CALIBRATION CURVE
FOR
STRONTIUM

DIFFERENCE, FLAME INTENSITY, 461 MU - 459 MU

SOLUTIONS CONTAINING 1.0 G KCL
AND 0.5 G AMMONIUM CITRATE
PER 100 ML

PPM STRONTIUM

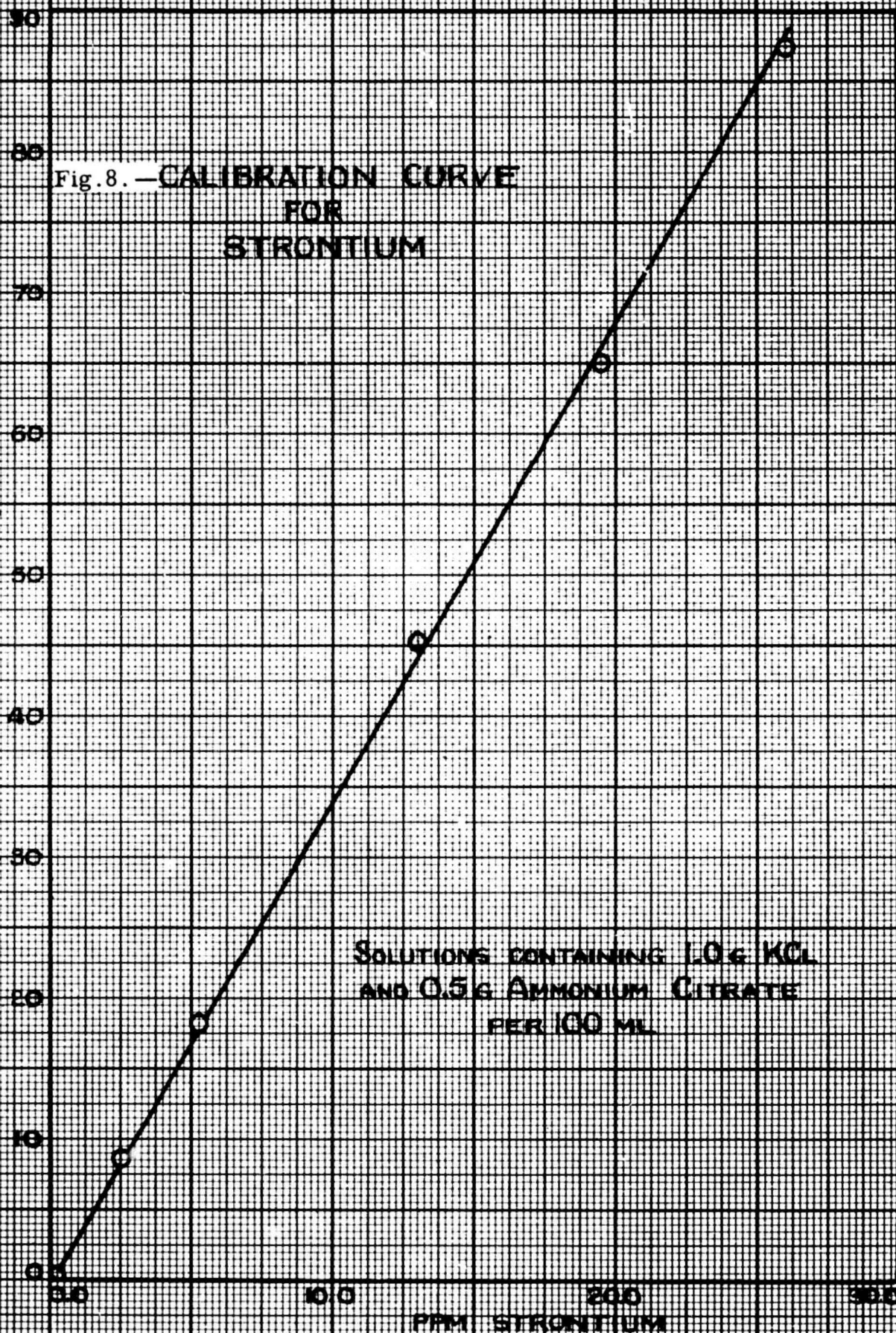


Table 7... Effect of Ca on Sr determination

| Concentration Ca, ppm | Relative intensity | | Concentration Sr, ppm | |
|--------------------------|--------------------|--------|-----------------------|-------|
| | 461 mu | 459 mu | Added | Found |
| 0.0 | 85 | 10.3 | 19.6 | 22.0 |
| 10.2 | 82 | 10.3 | 19.6 | 21.5 |
| 20.5 | 82 | 10.3 | 19.6 | 21.5 |
| 51.2 | 79 | 10.9 | 19.6 | 20.0 |
| 102 | 79 | 10.6 | 19.6 | 20.0 |
| 205 | 80 | 10.7 | 19.6 | 20.5 |
| 512 | 84 | 11.6 | 19.6 | 21.5 |

Solid $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in large excess was added to a series of standard Sr solutions, each containing 19.6 ppm Sr. It was found the Ca concentration could be increased to 5000 ppm Ca without significantly affecting the Sr determination. The results are tabulated in table 8.

Table 8... Effect of large amounts of Ca, Sr determination

| Concentration Ca, ppm | Relative intensity | | Concentration Sr, ppm | |
|--------------------------|--------------------|--------|-----------------------|-------|
| | 461 mu | 459 mu | Added | Found |
| 0.0 | 72 | 10 | 19.6 | 18.4 |
| 100 | 67 | 10 | 19.6 | 16.8 |
| 200 | 67 | 10 | 19.6 | 16.8 |
| 500 | 70 | 11 | 19.6 | 17.6 |
| 1000 | 72 | 12 | 19.6 | 17.7 |
| 2000 | 70 | 11 | 19.6 | 17.6 |
| 5000 | 78 | 18 | 19.6 | 17.7 |

A series was also run using solid K_2CO_3 instead of KCl as the added radiation buffer. Such solutions required additional acid to be added in order to prevent precipitation of CaCO_3 and other insoluble carbonates. The pH of these solutions therefore varied from about pH = 11 for those containing no Ca, to pH = 3 for those containing 500 ppm and more Ca. No consistent measurements of Sr emission could be obtained under these conditions. However, the alkaline solutions seemed to give the best results. The use of K_2SO_4 as a radiation buffer did not improve conditions.

Several types of materials were tried as additives, including NaCl, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, CuSO_4 , Na_2SO_4 , Tartaric Acid, NH_4SCN , $\text{K}_2\text{Al}_2(\text{SO}_4)_4$, and Sodium Versenate. Quite erratic results were obtained in nearly all cases. At any rate, it appeared preferable to stay with the use of KCl as the additive.

Satisfactory results were obtained when solid KCl was added in the ratio of 1.0 g of solid KCl per 100 ml of solution, and 0.5 g of ammonium citrate added per 100 ml of solution. The solution is then made alkaline to phenolphthalein with solid, reagent grade KOH. This procedure was tested with a limited number of possible interfering substances. For example, 1000 ppm of SO_4 and 460 ppm of Na did not interfere with the Sr determination. In all cases it is necessary to subtract the background reading at 459 mu from the intensity of the emission of Sr at 461 mu.

Time has not permitted complete and exact determination of the extent of interferences due to the presence of various materials in solution. Interferences were determined in an approximate way, on a "Go" or "No-go" basis by adding a considerable amount of various salts to samples of standard Sr solutions, and measuring the 461 to 459 intensity difference. The results, as shown in table 9, indicate that this technique is probably acceptable for the determination of Sr in the presence of significant amounts of other dissolved materials.

It should be pointed out that the $\text{KAl}(\text{SO}_4)_2$ practically eliminated Sr emission at 461 mu. Also, the $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, when present in fairly large amounts, depressed the Sr emission appreciably and would cause significant error.

Table 9... Effect of various substances on Sr determination

| Material added | Amount | Relative intensity | | ppm Sr | |
|--|---------|--------------------|--------|--------|-------|
| | | 461 mu | 459 mu | Added | Found |
| $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ | | | | | |
| 6 H_2O | 2.8 g/l | 44.0 | 19.3 | 7.8 | 5.7 |
| " | 1.4 g/l | 47.4 | 17.2 | 7.8 | 7.1 |
| " | 0.3 g/l | 48.2 | 16.8 | 7.8 | 7.8 |
| $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ | 1.8 g/l | 51.3 | 17.8 | 7.8 | 7.9 |
| $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ | 3.8 g/l | 19.0 | 17.2 | 7.8 | 0.3 |
| Na_2CO_3 | 2.8 g/l | 51.0 | 18.4 | 7.8 | 7.6 |
| $\text{Na}_2\text{CO}_3 + \text{NaCl}$ | 3.2 g/l | 51.0 | 19.4 | 7.8 | 7.4 |

A concentration of 2.8 g of ferrous ammonium sulfate per liter corresponds to an iron concentration of about 375 ppm. The addition of ferrous ammonium sulfate at a concentration of 0.3 g per liter (about 40 ppm Fe) did not cause any error in the Sr determination.

This procedure should be tested completely for the exact extent of interference by substances likely to be encountered in regular water analysis applications.

The procedure finally established as giving the most reliable results for Sr determination is as follows:

1. Add about 50 ml of the sample to be analyzed to a 100 ml volumetric flask or calibrated bottle.
2. Add 1.0 of high purity solid KCl and 0.5 g of reagent quality Ammonium Citrate to the sample in the flask.
3. Add three drops of phenolphthalein indicator to the sample, shake to dissolve all KCl and Ammonium Citrate added and to thoroughly mix the sample.
4. If the solution is not alkaline (pink) add solid KOH until a definite pink color is apparent.
5. Measure the relative intensities of Sr (461 mu) and background (459 mu) with the flame photometer.

The following settings were standardized for all flame photometer measurements:

Oxygen pressure: 10 lb./sq. in.
 Acetylene pressure: 5.5 lb./sq. in.
 Slit width: Not determinable on our instrument as the scale has been shifted so that the slit width readings have no meaning. However, the slit width employed was always very small, as indicated by the sharpness of the line measured, and the extreme difference in intensity readings obtained over a very short wavelength span.
 Sr line wavelength: 461 mu.
 Background wavelength selected: 459 mu.
 Photomultiplier phototube at full sensitivity.
 Load resistor: 22 megohms.

ANALYSIS OF WATER SAMPLES

Three samples supplied by Mr. C. S. Howard of the Menlo Park Laboratory were analyzed for Sr. These samples contained high concentrations of sodium, chloride, and bicarbonate, and, in one sample, sulfate also. The analysis attempt was made in the middle of our attempts to establish a standard procedure and so were not considered to be entirely reliable. The three samples showed some Sr present by the method used, but the results did not agree with analysis results previously reported.

| Sample No. | MWS | Previously Reported | |
|------------|---------|---------------------|--------|
| | | A | B |
| 1 | 0.9 ppm | 12 ppm | 20 ppm |
| 2 | 0.6 " | 3.8 " | 3.8 " |
| 3 | 0.7 " | 0 | 11 |

Five samples were submitted by Mr. John Hem of the Denver Laboratory. Although results of chemical analysis of these samples were not furnished, the data on specific conductance, which was supplied, indicated a much lower total dissolved solids content in these samples than in the California samples. These samples were analyzed for Sr. Only one of the five samples showed a detectable amount of Sr (about 0.2 ppm). It is reasonable to expect that the results of this analysis are reliable.