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# Simplified Atomic Absorption Determination of Stable Strontium in Milk and Hay


National Environmental Research Center
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# SIMPLIFIED ATOMIC ABSORPTION DETERMINATION OF STABLE STRONTIUM IN MILK AND HAY: A Comparison of Methods and Stepwise Procedure

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ABSTRACT

A highly simplified atomic absorption procedure for the determination of stable strontium in fluid milk, milk powder, and alfalfa is evaluated. A comparison is made between the atomic absorption method of additions and the standard curve method. A suggested stepwise procedure is given.

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## ACKNOWLEDGMENTS

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## INTRODUCTION

Flame emission spectrophotometry and atomic absorption spectrophotometry procedures are currently used for the determination of stable strontium in biological materials. Flame emission spectrophotometry involves the separation and removal of interfering ions by precipitation and ion exchange procedures (1, 2). Atomic absorption procedures usually involve the removal of phosphate by anion exchange resin. Calcium and phosphate together in solution seriously depress absorption of the 4607 Å strontium resonance line, but neither calcium nor phosphate alone produces serious depression (3).

This report describes in detail a very rapid and simplified procedure for determining stable strontium in milk* and livestock feed. Precipitation or ion exchange procedures are unnecessary. The stepwise procedure described here and in the Appendix was developed from principles and information reported by Trent and Slavin (4). The ash solutions are analyzed directly in the atomic absorption spectrophotometer without ion exchange resin treatment of any kind. The procedure is adaptable to the routine analysis of large numbers of samples.

To evaluate the procedure, two atomic absorption methods were compared: the standard curve procedure and the method of additions. The method of additions is described both by David (3) and Perkin-Elmer Analytical Methods for Atomic Absorption Spectrophotometry (5).

*The powdered and reconstituted milk samples were prepared and supplied by the Analytical Quality Control Service, Northeast Radiological Health Laboratory, U.S.P.H.S., Winchester, Massachusetts, as part of their program.

# MILK ANALYSIS

## SAMPLE PREPARATION

A batch of whole, dry, powdered milk used in ice cream manufacture was purchased by the Analytical Quality Control Service. The milk powder with nothing added provided one sample for analysis. A second milk sample was prepared by reconstituting the milk powder with distilled water so that 6.06 ml of reconstituted milk contained one gram of milk powder. Strontium nitrate was added to the reconstituted milk at a level of 0.0040 mg strontium per gram of milk powder.

## PREPARATION OF ASH SOLUTION

Fifteen grams of milk powder was added to each of three porcelain crucibles. The samples were placed into a muffle furnace and the temperature was raised about 40° C each hour until 450° C was reached. The samples were then ashed for 18 hours. The ashes were transferred to small beakers and the crucibles washed with 5 ml of 6 N HCl. The crucibles were washed twice more with small amounts of 6 N HCl and all washings were added to the beakers. The beakers were evaporated to dryness on a steam bath and the residue redissolved in 6 N HCl. The beakers were again evaporated to dryness. The residues were dissolved in 10 ml of 1.0 N HCl and filtered warm through Whatman No. 42 filter paper into 100 ml volumetric flasks. The filter paper was washed with small volumes of hot water, until the flasks were not quite full. The flasks were allowed to cool and diluted to the mark.

In the case of reconstituted milk, 115 ml of milk was pipetted into each of three porcelain crucibles, then five milliliters of glacial acetic acid was added to each. The crucibles were placed in a drying oven set at about 80° C for about three days. Then the temperature was gradually raised to about 115° C and the milk held until as dry as possible. The crucibles were then placed in a cold muffle furnace and the temperature was brought up to about 150° C. The temperature was then raised about 40° C each hour until about 450° C was reached. The ash solutions were prepared in the same way as described previously for the milk powder. It was found that the ashing procedure described was

not entirely satisfactory since there was a small amount of carbonaceous material remaining. This procedure was therefore modified when the alfalfa pellets were ashed and is described in that section.

## ATOMIC ABSORPTION ANALYSIS

Two methods of atomic absorption analysis were used for each ash solution. In the first procedure, standard solutions were prepared and analyzed on the atomic absorption spectrophotometer, their absorbances plotted, and a working curve was drawn. The second procedure employed the method of additions. Both analyses were done on the same day and the analyses of the ash solutions were repeated on another day.

### Standard Curve Procedure

A blank and standards were made up in 25 ml volumetric flasks as follows: solutions were made up containing 0.00, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, and 0.40 ppm strontium. To each flask was added 5 ml of 5.0% lanthanum solution as lanthanum oxide, 2.5 ml of a solution of NaCl containing 5 mg Na per ml, and 5 ml of 0.1 N HCl solution.

Each ash solution was run in triplicate each day. Two milliliters of ash solution was pipetted into a 10 ml volumetric flask. Two milliliters of 5% lanthanum stock solution was added and the flasks filled to the mark. These samples were ready for atomic absorption analysis.

### Method of Additions

For a single determination using the method of additions, two milliliters of ash solution was pipetted into each of five 10 ml volumetric flasks. Additions of strontium were made to the flasks as follows: zero, 0.05, 0.10, 0.15, and 0.20 ppm. Two milliliters of 5 per cent lanthanum stock solution was added and the flasks filled to the mark. These solutions were then ready for atomic absorption analysis.

## ATOMIC ABSORPTION INSTRUMENTATION

The samples were analyzed in a Perkin-Elmer Atomic Absorption Spectrophotometer Model-303 equipped with a three-slot Boling burner head.

The instrument settings described in the Perkin-Elmer Instrument

Manual (5) were used with one exception. The range was set at visible, the slit at 4, and the wavelength at 4607 Å with the instrument scale setting at about 230. As described by Trent and Slavin (4) the hollow cathode lamp was set at 16 ma instead of 10 ma. A scale expansion setting of ten was used for all the milk analyses. It was necessary to use the time response control at all times.

The lamp current setting was higher than that usually recommended for the strontium hollow cathode tube. This allowed a minimum gain setting which resulted in minimum noise. The gain was set at approximately 5 scale divisions to the left of center, or the needle of the energy meter was just within the left hand portion of the black region of the scale.

The same blank was used to zero the instrument in both methods. The instrument absorption readings were converted to absorbance. The results of the milk analyses are shown in Tables 1, 2, 3, and 4.

TABLE 1. STABLE STRONTIUM IN MILK POWDER BY ATOMIC ABSORPTION USING A STANDARD CURVE*

| Ash Solution | Sub Sample | Powder $10^{-3}$ mg/g | Ash $10^{-2}$ mg/g |
|---|---|---|---|
| | First Trail | | |
| | 1 | 4.97 | 6.065 |
| 1 | 2 | 4.84 | 5.915 |
| | 3 | 4.97 | 6.065 |
| | Average | 4.93 | 6.015 |
| | 1 | 5.47 | 6.680 |
| 2 | 2 | 4.95 | 6.045 |
| | 3 | 5.19 | 6.344 |
| | Average | 5.21 | 6.356 |
| | 1 | 5.20 | 6.344 |
| 3 | 2 | 5.20 | 6.344 |
| | 3 | 5.48 | 6.680 |
| | Average | 5.29 | 6.456 |
| First Trial Average | | 5.14 | 6.276 |
| | Second Trial | | |
| | 1 | 5.00 | 6.102 |
| 1 | 2 | 5.00 | 6.102 |
| | 3 | 5.03 | 6.140 |
| | Average | 5.01 | 6.113 |
| | 1 | 4.89 | 5.971 |
| 2 | 2 | 4.89 | 5.971 |
| | 3 | 4.92 | 6.008 |
| | Average | 4.90 | 5.983 |
| | 1 | 4.87 | 5.934 |
| 3 | 2 | 4.84 | 5.896 |
| | 3 | 4.89 | 5.964 |
| | Average | 4.86 | 5.931 |
| Second Trial Average | | 4.92 | 6.009 |

*Final average of milk powder determined by standard curve method.

$5.033 \times 10^{-3}$ mg/g powder
Standard deviation $\pm$ $0.198 \times 10^{-3}$
Coefficient of variation 3.9340
$6.1428 \times 10^{-2}$ mg/g ash
Standard deviation $\pm$ $0.241 \times 10^{-2}$

TABLE 2. STABLE STRONTIUM IN MILK POWDER BY ATOMIC ABSORPTION USING THE METHOD OF ADDITIONS*

| Ash Solution | Sub Sample | Powder $10^{-3}$ mg/g | Ash $10^{-2}$ mg/g |
|---|---|---|---|
| | First Trial | | |
| | 1 | 4.78 | 5.850 |
| 1 | 2 | 4.78 | 5.840 |
| | 3 | 5.37 | 6.551 |
| | Average | 4.98 | 6.073 |
| | 1 | 5.53 | 6.754 |
| 2 | 2 | 5.07 | 6.194 |
| | 3 | 5.20 | 6.344 |
| | Average | 5.19 | 6.431 |
| | 1 | 5.57 | 6.792 |
| 3 | 2 | 5.45 | 6.643 |
| | 3 | 4.87 | 5.934 |
| | Average | 5.29 | 6.456 |
| First Trial Average | | 5.16 | 6.321 |
| | Second Trial | | |
| | 1 | 4.81 | 5.878 |
| 1 | 2 | 4.97 | 6.065 |
| | 3 | 5.03 | 6.140 |
| | Average | 4.94 | 6.028 |
| | 1 | 5.41 | 6.605 |
| 2 | 2 | 5.53 | 6.754 |
| | 3 | 5.35 | 6.530 |
| | Average | 5.43 | 6.630 |
| | 1 | 4.99 | 6.084 |
| 3 | 2 | 5.42 | 6.605 |
| | 3 | 5.45 | 6.643 |
| | Average | 5.28 | 6.444 |
| Second Trial Average | | 5.22 | 6.367 |

*Final average of milk powder determined by method of additions:

$5.198 \times 10^{-3}$ mg/g powder
Standard deviation $\pm$ $0.284 \times 10^{-3}$
Coefficient of variation 5.4636
$6.3442 \times 10^{-2}$ mg/g ash
Standard deviation $\pm$ $0.346 \times 10^{-2}$

TABLE 3. STABLE STRONTIUM IN RECONSTITUTED POWDERED MILK BY ATOMIC ABSORPTION USING A STANDARD CURVE*

| Ash Solution | Sub Sample | Milk $10^{-3}$ mg/ml | Ash $10^{-2}$ mg/g |
|---|---|---|---|
| | First Trial | | |
| 1 | 1 | 1.56 | 10.14 |
| | 2 | 1.54 | 10.03 |
| | 3 | 1.54 | 10.06 |
| | Average | 1.55 | 10.07 |
| 2 | 1 | 1.52 | 9.909 |
| | 2 | 1.52 | 9.909 |
| | 3 | 1.51 | 9.880 |
| | Average | 1.52 | 9.90 |
| 3 | 1 | 1.48 | 9.425 |
| | 2 | 1.48 | 9.425 |
| | 3 | 1.54 | 9.796 |
| | Average | 1.50 | 9.55 |
| First Trial Average | | 1.52 | 9.84 |
| | Second Trial | | |
| 1 | 1 | 1.51 | 9.86 |
| | 2 | 1.51 | 9.86 |
| | 3 | 1.55 | 10.09 |
| | Average | 1.53 | 9.94 |
| 2 | 1 | 1.55 | 10.14 |
| | 2 | 1.55 | 10.11 |
| | 3 | 1.54 | 10.09 |
| | Average | 1.55 | 10.11 |
| 3 | 1 | 1.49 | 9.51 |
| | 2 | 1.49 | 9.48 |
| | 3 | 1.51 | 9.65 |
| | Average | 1.52 | 9.55 |
| Second Trial Average | | 1.52 | 9.87 |

*Final average of reconstituted milk powder using the standard curve method:

$1.5214 \times 10^{-3}$ mg/ml of reconstituted milk
Standard deviation $\pm$ $0.025709 \times 10^{-3}$
Coefficient of variation 1.6898
$9.8536 \times 10^{-2}$ mg/g ash
Standard deviation $\pm$ $0.253446 \times 10^{-2}$

TABLE 4. STABLE STRONTIUM IN RECONSTITUTED POWDERED MILK BY ATOMIC ABSORPTION USING THE METHOD OF ADDITIONS*

| Ash Solution | Sub Sample | Milk $10^{-3}$ mg/ml | Ash $10^{-2}$ mg/g |
|---|---|---|---|
| | First Trial | | |
| 1 | 1 | 1.66 | 10.82 |
| | 2 | 1.55 | 10.12 |
| | 3 | 1.61 | 10.46 |
| | Average | 1.60 | 10.47 |
| 2 | 1 | 1.68 | 10.99 |
| | 2 | 1.54 | 10.05 |
| | 3 | 1.60 | 10.45 |
| | Average | 1.61 | 10.50 |
| 3 | 1 | 1.61 | 10.28 |
| | 2 | 1.57 | 10.01 |
| | 3 | 1.54 | 9.84 |
| | Average | 1.57 | 10.04 |
| First Trial Average | | 1.60 | 10.34 |
| | Second Trial | | |
| 1 | 1 | 1.50 | 9.75 |
| | 2 | 1.52 | 9.92 |
| | 3 | 1.60 | 10.46 |
| | Average | 1.54 | 10.04 |
| 2 | 1 | 1.60 | 10.48 |
| | 2 | 1.60 | 10.45 |
| | 3 | 1.61 | 10.53 |
| | Average | 1.60 | 10.49 |
| 3 | 1 | 1.63 | 10.32 |
| | 2 | 1.67 | 10.90 |
| | 3 | 1.62 | 10.53 |
| | Average | 1.64 | 10.60 |
| Second Trial Average | | 1.59 | 10.38 |

*Final averages of reconstituted milk powder using method of additions:

$1.5954 \times 10^{-3}$ mg/ml reconstituted milk
Standard deviation $\pm$ 0.050497 $\times 10^{-3}$
Coefficient of variation 3.1652
$10.3533 \times 10^{-2}$ mg/g ash
Standard deviation $\pm$ 0.353802 $\times 10^{-2}$

Accuracy

Strontium content of reconstituted milk is higher than that of milk powder by 0.0040 mg/g of powder as supplied by the Analytical Quality Control Service. The reconstituted milk was made up so that 6.06 ml of milk was equivalent to one gram of powder and one ml of milk was equivalent to 0.16501 gram of powder.

Standard curve method

$5.033 \times 10^{-3}$ mg Sr/g powder
$1.5214 \times 10^{-3}$ mg Sr/ml of reconstituted milk
$9.2196 \times 10^{-3}$ mg Sr/g powder of the reconstituted milk

$9.220 \times 10^{-3}$ minus $5.033 \times 10^{-3} = 4.187 \times 10^{-3}$ mg Sr/g
$4.187 \times 10^{-3}$ minus $4.0 \times 10^{-3} = 0.187 \times 10^{-3}$ mg/g high

Method of additions

$5.198 \times 10^{-3}$ mg Sr/g powder
$1.5954 \times 10^{-3}$ mg Sr/ml reconstituted milk
$9.668 \times 10^{-3}$ mg Sr/g powder of the reconstituted milk

$9.668 \times 10^{-3}$ minus $5.198 \times 10^{-3} = 4.470 \times 10^{-3}$
$4.470 \times 10^{-3}$ minus $4.0 \times 10^{-3} = 0.470 \times 10^{-3}$ mg/g high

## ALFALFA PELLETS ANALYSIS

### PREPARATION OF SAMPLES AND ASH SOLUTIONS

Twelve grams of alfalfa pellets was weighed into each of six porcelain crucibles. Into three of the crucibles, 0.60 mg of strontium as strontium carbonate solution was pipetted directly onto the pellets. The crucibles were placed in a drying oven to evaporate the added strontium carbonate solution.

The six samples were placed in a cold muffle furnace and ashed for about 18 hours at about 450° C. The crucibles were allowed to cool and the ash moistened with distilled $H_2O$. Ten milliliters of 6.0 N $HNO_3$ was added to each sample and the contents stirred carefully. The crucibles were then taken to dryness on a steam bath, returned to a cold muffle furnace and ashed overnight at about 450° C. They were cooled and weighed.

Five milliliters of 6.0 N HCl was added to each crucible and the contents were evaporated to dryness on a steam bath. Five milliliters of 6.0 N HCl was added to each crucible and evaporated on a steam bath a second time. Ten milliliters of 1.0 N HCl was added and the crucibles heated on a steam bath. The contents of each crucible were filtered while hot through Whatman No. 42 filter paper into 250 ml volumetric flasks. A Pasteur pipette was used to transfer the contents from the crucibles to the filter paper. The crucibles and filter paper were washed well with hot water with the aid of a Pasteur pipette.

Fifty milliliters of 5 per cent lanthanum solution was added to each flask. The flasks were allowed to cool and made up to the mark with distilled water.

### ATOMIC ABSORPTION ANALYSIS AND INSTRUMENTATION

As in the case of milk, the alfalfa ash solutions were analyzed by the standard curve method and by the method of additions. One determination of each ash solution was made by each method on each of three different days.

#### Standard Curve Procedure

Since there was a 0.60 mg difference between the ash solutions

containing alfalfa only and those containing added strontium, separate standard curves had to be run for each.

For the analysis of alfalfa only, standards were made up in 25 ml volumetric flasks containing 0.0, 0.5, 1.0, 1.5, 2.0, and 2.5 ppm strontium. For the analysis of alfalfa with added strontium, the standards were made up to contain 1.0, 2.0, 3.0, 4.0, and 5.0 ppm strontium. To each flask was added 5 ml of 5 per cent lanthanum solution, 2.5 ml of a solution of NaCl containing 5.0 mg sodium per ml, and 1.0 ml of 1.0 N HCl.

The ash solutions were analyzed directly as prepared in the 250 ml volumetric flasks with no further preparation. The instrument settings were similar to those described in the milk analysis except that the scale expansion was set at "five" for the untreated alfalfa pellets and "two" for the alfalfa pellets with added strontium.

Method of Additions

It was necessary to use a separate series of additions for the alfalfa pellets alone and the alfalfa pellets with added strontium. In either case, 5.0 ml of ash solution was pipetted into five 10 ml volumetric flasks, then 0.00, 0.2, 0.4, 0.6 and 0.8 ppm of strontium was added to the flasks containing untreated alfalfa ash solution. The flasks containing alfalfa with added strontium ash solution had 0.00, 0.5, 1.0, 1.5, and 2.0 ppm of strontium added. One milliliter of 5 per cent lanthanum solution was added to all volumetric flasks and then made to volume with distilled water.

The standard curve method blank was used to zero the instrument. The atomic-absorption spectrophotometer scale expansion was set at "five" for the untreated alfalfa and "two" for the alfalfa with added strontium. The time response control was used at all times. The results are shown in Tables 5a, 5b, 6a, and 6b.

TABLE 5a. STABLE STRONTIUM IN UNTREATED ALFALFA PELLETS BY ATOMIC ABSORPTION USING A STANDARD CURVE

| Ash Solution | Day | Alfalfa mg/12 g | Ash mg/g |
|---|---|---|---|
| 1 | 1 | .2475 | .2150 |
| | 2 | .2500 | .2172 |
| | 3 | .2400 | .2085 |
| | Average | .2458 | .2136 |
| 2 | 1 | .2750 | .2428 |
| | 2 | .2500 | .2207 |
| | 3 | .2425 | .2141 |
| | Average | .2558 | .2259 |
| 3 | 1 | .2500 | .2194 |
| | 2 | .2525 | .2216 |
| | 3 | .2425 | .2128 |
| | Average | .2483 | .2179 |
| Final average | | .2500 | .2191 |
| Standard deviation | | .01031 | .009798 |
| Coefficient of variation | | 4.1240 | |

TABLE 5b. STABLE STRONTIUM IN ALFALFA PELLETS WITH ADDED STRONTIUM BY ATOMIC ABSORPTION USING A STANDARD CURVE

| Ash Solution | Day | Alfalfa mg/12 g | Ash mg/g |
|---|---|---|---|
| 1 | 1 | .8500 | .7408 |
| | 2 | .8475 | .7386 |
| | 3 | .8375 | .7299 |
| | Average | .8450 | .7364 |
| 2 | 1 | .8475 | .7480 |
| | 2 | .8425 | .7436 |
| | 3 | .8300 | .7326 |
| | Average | .8400 | .7414 |
| 3 | 1 | .8225 | .7130 |
| | 2 | .8125 | .7044 |
| | 3 | .7975 | .6914 |
| | Average | .8108 | .7031 |
| Final average | | .8319 | .7270 |
| Standard Deviation | | .01806 | .01954 |
| Coefficient of variation | | 2.1709 | |

TABLE 6a. STABLE STRONTIUM IN UNTREATED ALFALFA PELLETS BY ATOMIC ABSORPTION USING METHOD OF ADDITIONS

| Ash Solution | Day | Alfalfa mg/12 g | Ash mg/g |
|---|---|---|---|
| 1 | 1 | .2495 | .2168 |
| | 2 | .2550 | .2215 |
| | 3 | .2600 | .2259 |
| | Average | .2548 | .2214 |
| 2 | 1 | .2400 | .2119 |
| | 2 | .2500 | .2207 |
| | 3 | .2585 | .2282 |
| | Average | .2495 | .2203 |
| 3 | 1 | .2500 | .2194 |
| | 2 | .2590 | .2273 |
| | 3 | .2515 | .2221 |
| | Average | .2535 | .2229 |
| Final Average | | .2526 | .2215 |
| Standard Deviation | | .006317 | .005214 |
| Coefficient of variation | | 2.5008 | |

TABLE 6b. STABLE STRONTIUM IN ALFALFA PELLETS WITH ADDED STRONTIUM BY ATOMIC ABSORPTION USING METHOD OF ADDITIONS

| Ash Solution | Day | Alfalfa mg/12 g | Ash mg/g |
|---|---|---|---|
| 1 | 1 | .8600 | .7495 |
| | 2 | .9000 | .7844 |
| | 3 | .8950 | .7800 |
| | Average | .8850 | .7713 |
| 2 | 1 | .9000 | .7944 |
| | 2 | .8650 | .7635 |
| | 3 | .8900 | .7855 |
| | Average | .8850 | .7811 |
| 3 | 1 | .8550 | .7412 |
| | 2 | .8450 | .7326 |
| | 3 | .8450 | .7326 |
| | Average | .8483 | .7355 |
| Final Average | | .8728 | .7626 |
| Standard Deviation | | .02333 | .02435 |
| Coefficient of variation | | 2.6730 | |

Accuracy

Six crucibles contained 12 g of alfalfa pellets. Into three of the crucibles 0.60 mg of strontium was added.

Standard Curve Method

0.8319 mg Sr/12 g pellets with added strontium

0.2500 mg Sr/12 g untreated pellets

0.5819 mg Sr Recovered

Method of Additions

0.8728 mg Sr/12 g pellets with added strontium

0.2526 mg Sr/12 g untreated pellets

0.6202 mg Sr Recovered

## DISCUSSION

This simplified stable strontium procedure, employing either the standard curve method or method of additions, facilitates the analysis of large numbers of samples. However, to obtain satisfactory results with this procedure, strict adherence to details is essential. Since low levels of strontium are present in both the ash and standard solutions, it is important that the standards and final sample solutions be carefully prepared. It is also important that the null meter needle be set at mid-position accurately and frequently with the zero control. Difficulty was experienced "zeroing-in" the null meter when the milk was analyzed due to the scale expansion of ten. Following the milk analysis and preceeding the alfalfa analysis, the instrument was updated and the 3-turn zero control was replaced by a 10-turn zero control. This alleviated the difficulty considerably.

The three-slot "Boling" burner head provided a wider flame which improved absorbance and increased detection limits considerably. This greatly facilitated the detection of strontium in biological materials at trace levels.

A statistical comparison was made between the standard curve method and the method of additions. An "F" test for differences between two variances showed a significant difference between the two methods in the case of the reconstituted milk only, at 1.0% ($p<0.01$) (6). Hence for practical purposes, experimental evidence indicates that a difference was not detected between methods.

## REFERENCES


1. Krieger, Herman L., Velten, Richard J., Burmann, Franz J., Radionuclide Analysis of Environmental Samples. A Laboratory Manual of Methodology. Robert A. Taft Sanitary Engineering Center Technical Report R59-6. Revised 1966.
2. Porter, C. H., Augustine, R. J., Matusek, J. M. and Carter, M. W., Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples. Environmental Health Series, U. S. Public Health Service Publication No. 999-RH-10, January 1965.
3. David, J., Determination of Strontium in Biological Materials and Exchangeable Strontium in Soils by Atomic-Absorption Spectrophotometry. Analyst 87:576-85, 1962.
4. Trent, Dorothy and Slavin, Walter, Factors in the Determination of Strontium by Atomic Absorption Spectrophotometry with Particular Reference to Ashed Biological Samples. Atomic Absorption Newsletter No. 22, July 1964. Perkin-Elmer Corporation, Norwalk, Connecticut.
5. Analytical Methods for Atomic Absorption Spectrophotometry. Perkin-Elmer Corporation, Norwalk, Connecticut.
6. Pearson, E. S. and Hartley, H. O., Biometrika Tables for Statisticians. Vol. 1, Third Edition, Cambridge University Press, London, 1966, Pages 66-67, 202.

# APPENDIX

## Suggested Stepwise Procedure

## APPENDIX

## SUGGESTED STEPWISE PROCEDURE

### I. PREPARATION OF ASH SOLUTION

1. Weigh or pipette a sample into suitable porcelain crucibles. Do not use crucibles in which the porcelain glaze is worn. The sample should yield about one gram of ash. Fifteen grams of milk powder, 150 milliliters of fluid milk, or 12 g of alfalfa are sufficient. Add 5 ml of glacial acetic acid to the fluid milk. Proceed to step I-3, except for fluid milk. If fluid milk is used proceed to step I-2.

2. (Fluid Milk Only)
Place crucibles in drying oven set at about 80° C for about three or four days. Then raise the temperature gradually until about 115° C is reached. Hold milk in drying oven until as dry as possible. Proceed to step I-3.

3. Place milk samples in a cold muffle furnace with the temperature set at 150° C. After 150° C is reached, raise the temperature about 40° C each hour until 450° C is attained. The crucibles are held at 450° C for 18 hours. Crucibles containing hay samples may be placed in a cold muffle furnace and the temperature brought directly up to 450° C and held for 18 hours.

4. The crucibles are allowed to cool and the ash is moistened with distilled water. Pipette 10 milliliters of 6.0 N $HNO_3$ slowly and carefully into each crucible and mix gently.

5. Place crucibles on a steam bath and evaporate to dryness.

6. Return crucibles to a cold muffle furnace and ash at 450° C overnight.

7. Cool and weigh.

8. Add 5 ml of 6.0 N HCl to each crucible and evaporate to dryness on a steam bath.

9. Repeat step 8.

10. Take up residues in 10 ml of 1.0 N HCl and heat crucibles on steam bath.

11a. (Milk only) Filter contents of crucibles while warm through Whatman No. 42 filter paper into 100-ml volumetric flasks. Use

a Pasteur pipette to transfer the crucible contents to the filter paper. Rinse crucibles several times with small quantities of hot water and transfer the rinsings to filter paper. Wash filter paper with small volumes of hot water until the flasks are not quite full. Cool and dilute to mark.

11b. (Hay only) Treat the crucibles containing hay ash the same as milk ash with the following exceptions: Filter the contents of each crucible while hot into 250-ml volumetric flasks. Wash the crucibles and filter paper with hot water until flasks are about one-half full. Add 50 ml of 5.0% lanthanum solution to each flask. Allow to cool and dilute to mark. The hay ash solutions are ready for atomic absorption analysis by the standard curve method without further treatment.

## II. STANDARD AND ATOMIC ABSORPTION SOLUTIONS. MILK ANALYSIS

### Standard Curve Method

Prepare 25-ml standard solutions containing 0.0 (blank), 0.1, 0.15, 0.20, 0.25, 0.30, 0.35, and 0.40 ppm strontium as follows:

1. To each of eight 25-ml volumetric flasks add the following volumes of strontium solution containing 0.01 mg strontium per milliliter.

| PPM | ml of Std. Soln. |
|---|---|
| 00.0 (Blank) | 0.000 |
| 0.1 | 0.250 |
| 0.15 | 0.375 |
| 0.20 | 0.500 |
| 0.25 | 0.625 |
| 0.30 | 0.750 |
| 0.35 | 0.875 |
| 0.40 | 1.00 |

2. Add 5 ml of 5.0 per cent lanthanum solution.
3. Add 2.5 ml of sodium chloride solution containing 5.0 mg sodium per milliliter.

4. Add 5.0 ml of 0.1 N HCl solution.

5. Dilute to volume.

Prepare final sample solutions from ash solutions for atomic absorption analysis as follows:

1. Pipette two milliliters of ash solution into a 10 ml volumetric flask.

2. Pipette two milliliters of 5.0% lanthanum solution into each flask.

3. Dilute to mark with distilled water.

Method of Additions

Each sample determination requires the preparation and atomic absorption readings of five solutions. Ten-milliliter solutions are prepared containing an aliquot of ash solution and strontium additions of zero, 0.05, 0.10, 0.15 and 0.20 ppm as follows:

1. To each of five 10-ml volumetric flasks add the following volumes of strontium solution containing 0.01 mg strontium per milliliter.

| PPM | ml of Std. Soln. |
|---|---|
| 0.00 | 0.00 |
| 0.05 | 0.05 |
| 0.10 | 0.10 |
| 0.15 | 0.15 |
| 0.20 | 0.20 |

2. Add a two milliliter aliquot of ash solution.

3. Add 2 ml of 5.0% lanthanum solution.

4. Dilute to mark.

(A blank is made up as described in the standard curve method)

III. STANDARDS AND ATOMIC ABSORPTION SOLUTIONS. HAY ANALYSIS

Stable strontium levels in the various hays and forages vary over a considerable range. Hence it will be necessary to establish strontium levels for standards according to the levels of strontium present in the samples analyzed. It is suggested that before a large number of samples are prepared for atomic absorption analysis, either by the

standard curve method or method of additions, a preliminary analysis be made on a few ash solutions to obtain an approximation of the range of strontium levels which are present. The standard curve method should be used for this. The strontium levels for standards and additions given below are intended as an example only.

Standard Curve Method

Prepare 25-ml standard solutions containing 00.0 (blank), 0.5, 1.0, 1.5, 2.0, and 2.5 ppm strontium as follows:

1. To each of six 25-ml volumetric flasks add the following volumes of strontium solution containing 0.01 mg strontium per milliliter.

| PPM | ml of Std. Soln. |
|---|---|
| 0.0 (Blank) | 0.00 |
| 0.5 | 1.25 |
| 1.0 | 2.5 |
| 1.5 | 3.75 |
| 2.0 | 5.00 |
| 2.5 | 6.25 |

2. Add 5.0 ml of 5.0% lanthanum solution.
3. Add 2.5 ml of a sodium chloride solution containing 5.0 mg of sodium per milliliter.
4. Add 1 ml of 1.0 N HCl.
5. Dilute to mark.

Final sample solution:

1. Ash solutions as prepared in the 250 ml volumetric flasks are ready for analysis without further treatment.

Method of Additions

As in the case of the milk strontium determinations, each sample requires the preparation and instrument reading of five solutions. Ten milliliter solutions are prepared containing an aliquot of ash solution and strontium additions of zero, 0.2, 0.4, 0.6, and 0.8 ppm as follows:

1. To each of five 10-ml volumetric flasks add the following volumes of strontium solution containing 0.01 mg strontium per milliliter.

| PPM | ml of Std. Soln. |
|---|---|
| 0.00 | 0.00 |
| 0.20 | 0.20 |
| 0.4 | 0.40 |
| 0.6 | 0.60 |
| 0.8 | 0.80 |

2. Add a five milliliter aliquot of ash solution.
3. Add one milliliter of 5.0% lanthanum solution.
4. Dilute to mark.

(A blank is made up as described in the standard curve method)

## IV. ATOMIC ABSORPTION SPECTROPHOTOMETRY

The procedure and instrument settings given are for the Perkin-Elmer Atomic Absorption Spectrophotometer Model-303. The instrument should be equipped with a 10-turn zero control and a time response control. The instrument settings are the same as those given in the Perkin-Elmer instrument manual (5) with some modifications. Refer to the standard conditions for strontium in the instrument manual for general operating conditions and information not given here.

1. Burner head: Equip instrument with a three-slot Boling burner head.
2. Range: Visible
3. Slit: Four
4. Wavelength: 4607 Å with the instrument scale setting at approximately 230.
5. Source: Hollow cathode lamp set at 16 ma lamp current.
6. Scale expansion: It will be necessary to use a setting of "ten" for the milk analysis. For hay analysis use either "five or two" depending on the strontium levels present.
7. Time response control: It is suggested that this control be used. The instrument operator should pick the setting which works best for each scale expansion.

8. Gain setting: The gain setting should be minimum. Set the gain so that the needle of the energy is about five scale divisions to the left of center or just within the left hand portion of the black region of the scale.

9. The blank or zero strontium standard made up for the standard curve method is used to zero the instrument for both the standard curve method and method of additions. The null meter needle should be set at mid-position accurately and frequently.

## V. CALCULATIONS

Divide the average instrument reading by the scale expansion setting to obtain absorption. Convert absorption to absorbance. The absorption should be read on the table, two places beyond the decimal, and the corresponding absorbance determined by interpolation.

### Standard Curve Method

Plot a working curve relating absorbance to concentration and determine the concentration of strontium in the final sample solution.

1. Milk

$$\frac{\text{ppm in final sample soln.}}{100} = \text{mg in 10 ml final solution or 2.0 ml aliquot}$$

$$\text{mg Sr in aliquot} \times 50 = \text{mg Sr in 100 ml ash soln. or total sample}$$

$$\frac{\text{mg Sr in sample}}{\text{sample weight}} = \text{mg per g powder}$$

$$\frac{\text{mg Sr in sample}}{\text{sample vol.}} = \text{mg per ml milk}$$

$$\frac{\text{mg Sr in sample}}{\text{ash weight}} = \text{mg per g ash}$$

2. Alfalfa

$$\frac{\text{ppm in 250 ml ash soln.}}{4} = \text{mg Sr in ash soln. or total sample}$$

### Method of Additions

An example of a method of additions working curve for an alfalfa determination is shown in Figure 1. Plot absorbance against concentrations of strontium added as shown. As described in the instrument manual (5), extrapolate the resulting straight line through zero

absorbance. The intercept on the concentration axis gives the concentration of strontium in the original sample. The working curve should be a straight line.

1. Milk

Determine concentration of strontium in final sample solution and proceed with calculations given for standard curve procedure.

2. Alfalfa

ppm in atomic absorption soln. x 2.0 = ppm in ash solution

$\frac{\text{ppm in ash solution}}{4.0}$ = mg Sr in 250 ml ash solution or total sample

VI. REAGENTS

Glacial acetic acid (fluid milk analysis)

Nitric acid: 6 N

Hydrochloric acid: 6 N, 1 N, 0.1 N

Lanthanum oxide solution, $La_2O_3$: 5.0% lanthanum. As described in the the instrument manual (5), dissolve 58.65 g of $La_2O_3$ in 250 ml of concentrated HCl. Add the acid very slowly using extreme care (REACTION IS VIOLENT) until the material is dissolved (hood is recommended). Dilute to 1000 ml with distilled water.

Stock strontium standard solution: 1000 ppm strontium as strontium carbonate. Dissolve in minimum HCl and dilute to volume.

Strontium standard solution: 0.01 milligram strontium per milliliter.

Sodium chloride solution: 5.0 milliligrams sodium per milliliter.

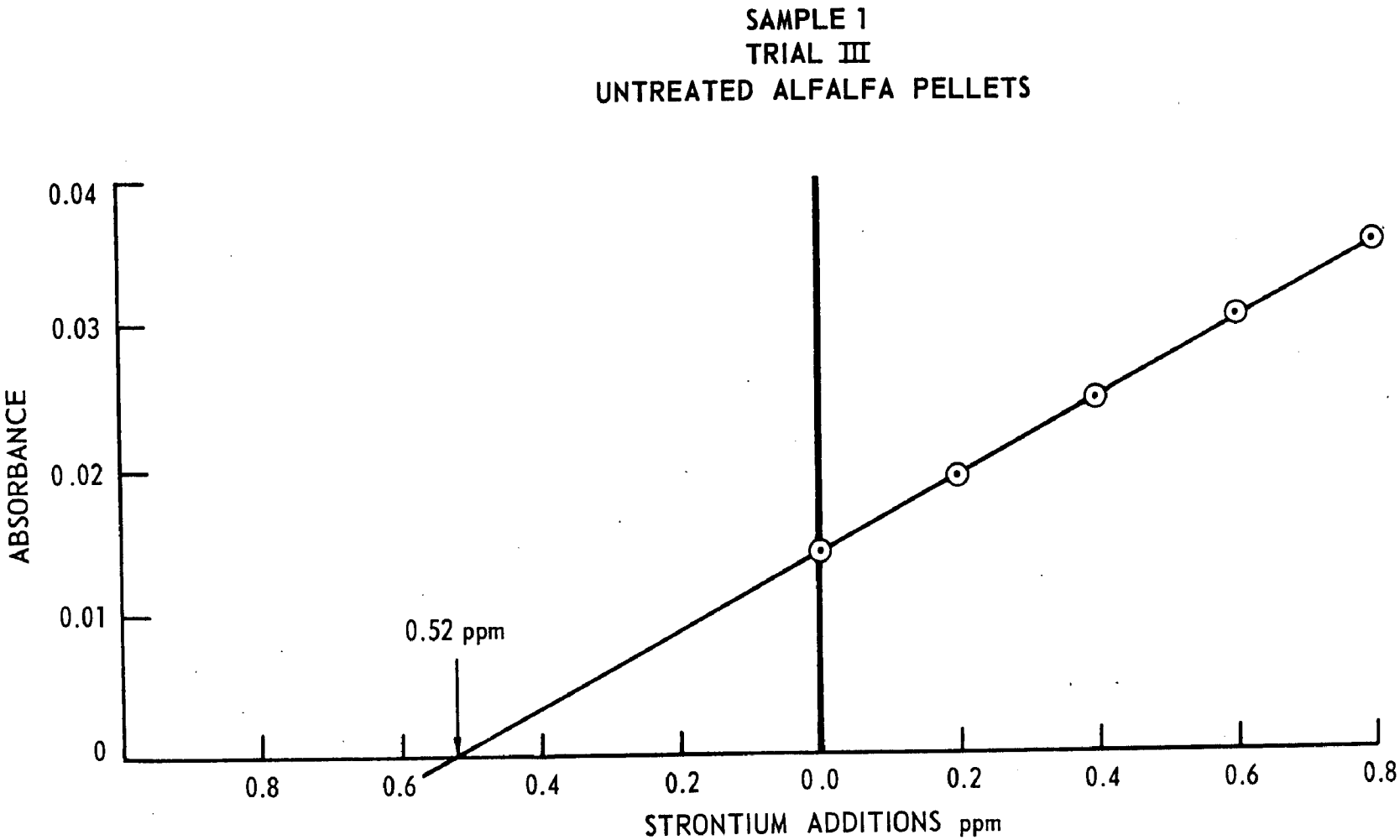


Figure 1. Working curve for an alfalfa determination by the method of additions

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16. ABSTRACT

A highly simplified atomic absorption procedure for the determination of stable strontium in fluid milk, milk powder, and alfalfa is evaluated. A comparison is made between the atomic absorption method of additions and the standard curve method. A suggested stepwise procedure is given.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
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