Title

SPECTROCHEMICAL DETERMINATION OF STRONTIUM-TO-CALCIUM RATIO IN FOOD, MILK, CREAM, BLOOD, FECES, AND URINE OF COWS

Authors

Shalimoff, George V.
Conway, John G.
Pitzer, Ann E.

Publication Date

1958

UCRL 8013

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

BERKELEY, CALIFORNIA

DISCLAIMER

UCRL-8013

UNIVERSITY OF CALIFORNIA

Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

SPECTROCHEMICAL DETERMINATION OF STRONTIUM-TO-CALCIUM RATIO IN FOOD, MILK, CREAM, BLOOD, FECES, AND URINE OF COWS

George V. Shalimoff, John G. Conway, and Ann E. Pitzer

January 1958

Printed for the U. S. Atomic Energy Commission

SPECTROCHEMICAL DETERMINATION OF STRONTIUM-TO-CALCIUM RATIO IN FOOD, MILK, CREAM, BLOOD, FECES, AND URINE OF COWS

George V. Shalimoff, John G. Conway, and Ann E. Pitzer

Radiation Laboratory
University of California, Berkeley, California

January 1958

ABSTRACT

A dc carbon-arc spectrochemical method has been developed for the determination of strontium-to-calcium ratios in the food, milk, cream, blood, feces, and urine of cows. In this method sodium is added to the samples to produce uniformly enhanced and reproducible spectral lines in the range of 10^{-4} to 5×10^{-2} strontium-to-calcium ratio. Results with a precision of ± 12% of analysis of the food and products of three cows are included.

SPECTROCHEMICAL DETERMINATION OF STRONTIUM-TO-CALCIUM RATIO IN FOOD, MILK, CREAM, BLOOD, FECES, AND URINE OF COWS

George V. Shalimoff, John G. Conway, and Ann E. Pitzer

Radiation Laboratory
University of California, Berkeley, California

January 1958

I. INTRODUCTION

The development of a spectrographic technique for the determination of strontium-to-calcium ratios in the products of cows resulted from the need for a method whereby these elements could be determined at the same time in the same sample with little or no chemistry. By this method results can be obtained from smaller samples containing microgram quantities of the elements. The usual chemical analytical methods -- titrimetric, colorimetric, or flame-photometric -- for alkaline earths require larger-sized samples in a chemical composition that may be difficult to obtain uniformly from the milk, cream, blood, feces, and urine, as well as the feed of cows.

Information about the strontium-to-calcium ratio allows estimation of the actual amount of strontium if a chemical determination of calcium is made. Though calcium can easily be determined to 0.1%, it need only be estimated to the limits of error of the spectrographically determined ratio of strontium to calcium, provided, of course, the strontium is not present to such an extent as to make the result of the chemical determination of calcium seem high.

Fallout information for Sr^{90} is presented as sunshine units, which are ratios of Sr^{90} disintegrations per gram of calcium. Thus a knowledge of the elemental strontium-to-calcium ratio allows correlation with existing radioactive Sr^{90}-to-calcium ratios to give the more significant ratio of Sr^{90} to total strontium.

II. PRELIMINARY EXPERIMENTS

Routine spectrographic analysis by copper-spark emission of skim milk and blood samples that could be conveniently handled indicated strontium-to-calcium ratios on the order of 10^{-4} to 5×10^{-2}. The amounts of strontium were in the range of 5×10^{-3} μg to 10^{-2} μg; amounts of calcium were 1 to 20 μg.

A dc arc method was chosen because it allowed photometry without background corrections of calcium and strontium lines over a wide range of concentration ratios of the samples.

When synthetic samples with constant ratios of strontium to calcium but with varying relatively small amounts of strontium and calcium were run, the line-intensity ratio was not constant. This is shown in Fig. 1, Curve A. This indicated a matrix effect dependent upon the absolute amount of material present and was observed before.[1,2] When samples with constant ratios of strontium to calcium but with varying relatively large amounts of strontium and calcium were run, the intensity ratio did not change much, indicating that enough material was present to cause the total matrix effect (Fig. 2, Curve A).

Because this effect was observed with samples made of pure strontium and calcium salts, it was expected to occur with the unknown samples as well. It became a problem to find some agent that could be added to all samples and that would buffer the matrix effect and suppress the dependence of strontium and calcium intensities upon each other, especially at small concentrations.

It was observed in the spectra of milk and blood samples that significant amounts of magnesium and sodium were present in addition to the organic material. Synthetic strontium and calcium were prepared with large excesses of magnesium, sodium, and lucite, substituting for the organic material found in the cow's products. Spectra of these samples show no apparent effect of magnesium or lucite on the strontium- and calcium-line intensities. Inclusion of 50 to 100 μg sodium in the samples not only markedly enhances the strontium and calcium intensities (Fig. 2, Curve B) but also overcomes the fluctuation of the intensity ratio when small amounts of strontium and calcium are used (Fig. 1, Curve B).

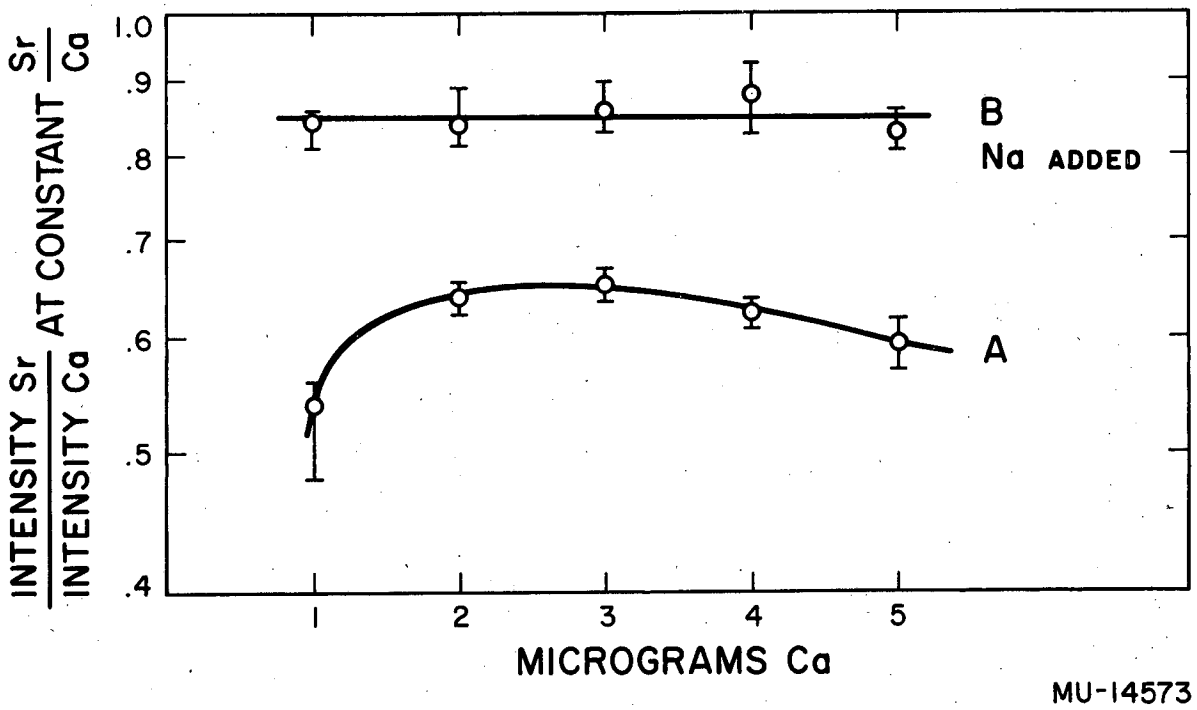

Fig. 1. Effect on intensity ratio of adding sodium to samples containing small amounts of calcium.

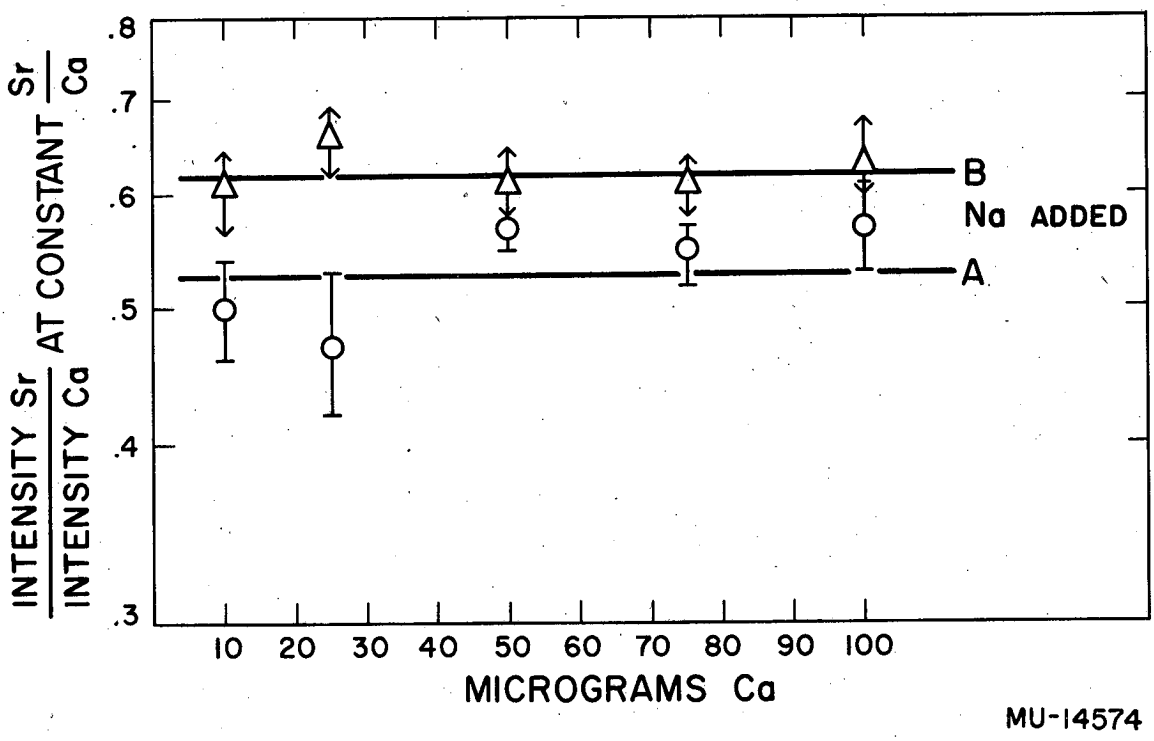

Fig. 2. Effect on intensity ratio of adding sodium to samples containing large amounts of calcium.

This enhancement of line intensities with added sodium was also found in the skim milk samples, but not with the blood samples, which already contain lesser amounts of sodium. Although there was no difference in line intensities whether 50 or 100 μg sodium was added, it was decided to add 100 μg sodium to all samples and standards. Conflicting explanations have been proposed for the action of buffers during excitation which leads to reproducible results; however, the lack of understanding does not prevent the utilization of these agents when necessary.

III. EXPERIMENTAL PROCEDURE

Apparatus and Conditions

Spectrograph:	Baird Associates Eagle-mount spectrograph with 3-meter grating.
	Linear dispersion: 5.6 A/mm.
Electrodes: Cathodes:	1/8-inch-diameter graphite, point-shaped.
Anodes:	1/4-inch-diameter graphite, flat surface and 1-mm crater. Flat-surfaced electrodes were coated with an acetone-lucite mixture to reduce the porosity of the electrode.
Exposure conditions:	Spectral region: 3640 to 5040 A
	Slit width: 25 microns
	Slit length: 20 mm
	Filter: glass plate
Excitation:	1 min dc arc at 3 amp.
Photographic plate:	Eastman Kodak IV-O, emulsion calibrated by step sector method.
Plate processing:	3 min Kodak D-19 developer,
	10 sec acetic acid stop bath,
	3 min Kodak Rapid Liquid Fixer.
Densitometer:	A.R.L. Dietert Projector Comparator equipped with Leeds and Northrup recorder.
Spectral lines:	Sr: 4607.33 A
	Ca: 4585.87 A for 10^{-4} to 10^{-2} Sr/Ca region
	Ca: 4298.99 A for 5×10^{-3} to 5×10^{-2} Sr/Ca region.

Standard Preparation

Weighed amounts of selected reagent-grade NaCl, $SrCl_2$, and $CaCO_3$ were dissolved in dilute HCl. Sodium chloride reagent shown by spectrographic analysis to have no calcium or strontium impurity was chosen. Similarly, strontium salts free from calcium and calcium salts free from strontium impurity were selected.

Appropriate micropipet aliquots containing microgram quantities of strontium and calcium and 100 μg sodium were slowly evaporated on the graphite electrodes.

Sample Preparation

All samples were obtained from cows grazing in pasture at the Agricultural Station of the University of California at Davis, California.

Ten microliters of skim milk was slowly evaporated on the electrode to which 100 μg sodium had been added.

About 100 microliters of blood was slowly evaporated on the electrodes. The blood samples bubbled and formed a large thin-shelled residue; however, slow evaporation yielded a residue that was easily and evenly excited.

The cream samples were much more difficult to handle. Because of the high butterfat content, the cream sample simply melted when evaporation was attempted. The sample eventually charred and stuck to the electrode in a usable fashion. About 1/4 cc sample was needed. Later it was found much easier to dry ash the cream sample in a platinum crucible and place the residue in a very shallow cup electrode. Which method was used made no difference in the error, although the dry-ash method was more convenient.

The feed, feces, and urine samples were supplied in a dry ash form. Samples weighing 10 grams were carefully ground with a mortar and pestle, placed in a 10-ml volumetric flask, and made to volume with reagent-grade acetone. A 100-μl aliquot of the shaken slurry was found to contain sufficient material to place on the electrode and burn reproducibly.

Working Curves

Analytical working curves are made for the two concentration ranges (Fig. 3). Sectored portions of the analytical lines that had little or no background were read. As many line pairs as possible in the sectored spectra

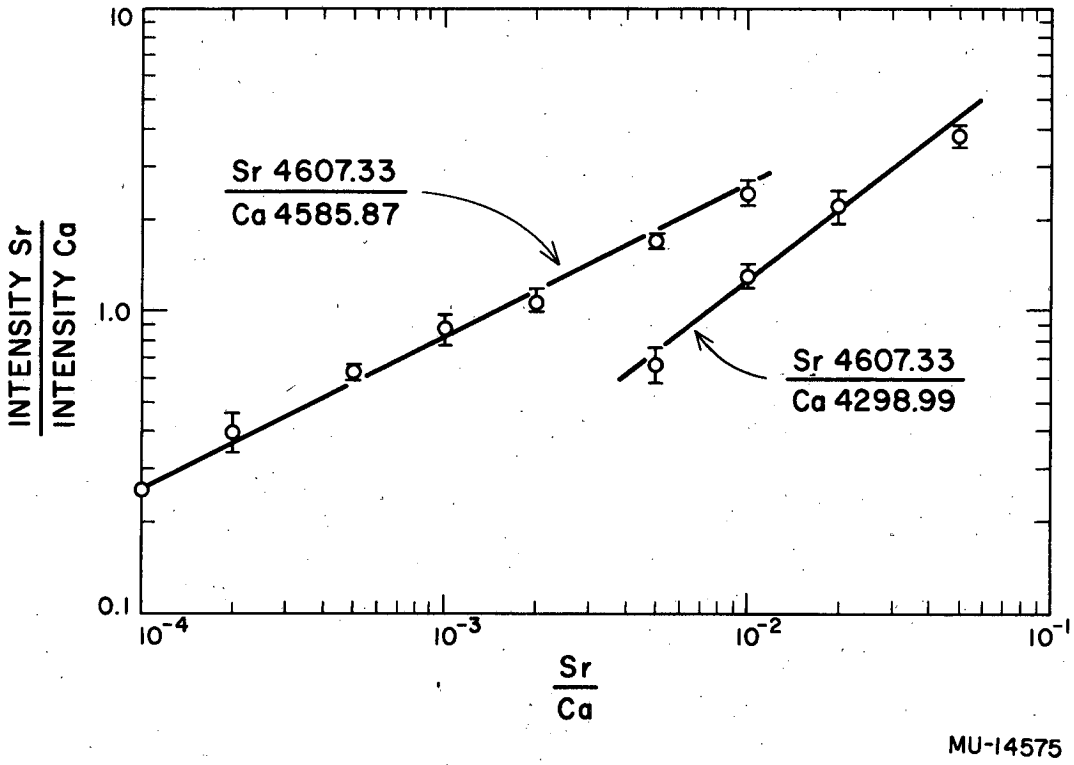

Fig. 3. Analytical working curves for two concentration ranges of strontium-calcium mixture.

were read in the same sample, although intensity ratios are derived from lines with the same step number. By use of the emulsion-calibration curve, transmittances of the line pair are converted to an intensity ratio which, in turn, is converted to a concentration ratio of strontium to calcium from the analytical working curve.

IV. RESULTS

The results of analysis of three cows' products and their feed is given in Table I. The column headed "Number of values" indicates the number of ratios obtained from various steps of the sectored lines of at least two different samples.

With this method only a limit was obtained for urine samples.

The percent deviation of the values obtained from two samples of each type indicates the reproducibility of the results. An over-all precision of the many determinations by this method is set at ± 12% of the ratio being estimated. Although the calcium and strontium have not been determined chemically or by any other method by which the results may be compared, it is felt the accuracy should be on the same order as the precision.

ACKNOWLEDGMENTS

We wish to thank Dr. Hardin B. Jones and Margaret R. White of Donner Laboratory, University of California, for their suggestion and encouragement of this investigation and for the samples that they provided.

This work was performed under the auspices of the U. S. Atomic Energy Commission.

LITERATURE CITED

1. Fast, C. and Rud Nielsen, J., J. Opt. Soc. Am. 37, 614-622 (1947).
2. Turekian, K. K., Gast, P. W., and Kulp, J. L., Spectrochem. Acta 9, 40-46 (1957).

Table I

Ratios of strontium to calcium in products and feed of three different cows

Sample	Sr/Ca	Average deviation	± % Deviation	Number of values
Cow No. 89				
Skim milk	7.8×10^{-4}	± 1.2	15	4
Serum	5.9×10^{-3}	± 0.8	12	5
Cream	1.0×10^{-3}	± 0.2	16	6
Feces	1.1×10^{-2}	± 0.1	9	7
Urine	$> 10^{-1}$			2
Cow No. 50				
Skim milk	1.9×10^{-3}	± 0.1	6	4
Serum	1.7×10^{-2}	± 0.2	11	5
Cream	1.5×10^{-3}	± 0.1	9	6
Feces	1.2×10^{-2}	± 0.1	8	8
Urine	$> 10^{-1}$			2
Cow No. 54				
Skim milk	4.6×10^{-4}	± 0.2	5	2
Serum	3.0×10^{-3}	± 0.2	7	6
Cream	---			
Feces	1.1×10^{-2}	± 0.1	9	8
Urine	$> 10^{-1}$			2
Pasture grass	1.4×10^{-2}	± 0.1	8	6
Alfalfa leaf	7.9×10^{-3}	± 0.5	6	6
Alfalfa and hay	9.9×10^{-3}	± 1.1	12	8
Grain mixture	2.3×10^{-2}	± 0.3	13	4