Atomic Absorption Analysis of Sodium, Potassium, and Calcium in Ringer's Solution

ROBERT V. SMITH* and MARK A. NESSEN

Abstract \Box A method was developed for the analysis of sodium, potassium, and calcium in Ringer's solution based on atomic absorption spectroscopy. Interelemental interference effects were investigated and are discussed. The proposed method was compared to NF procedures and offers some advantage in terms of accuracy and convenience.

Keyphrases \square Ringer's solution—sodium, potassium, calcium determination \square Interelemental interferences—sodium, potassium, calcium determination \square Atomic absorption spectroscopy—analysis \square Flame photometry—analysis

Various materials have been analyzed for their sodium, potassium, and calcium content by atomic absorption spectroscopy (AA). These include human serum (1, 2), cell membranes (3), milk (4), coal ash (5), cement (6), and plant tissue (7). One problem in measuring mixtures of elements by AA arises from frequent interference effects (*i.e.*, depression or enhancement of absorption by one or more atomic species) which are dependent on the nature of the elements present and their relative proportions. This is true with mixtures of sodium, potassium, and calcium; thus, each combination of these can present unique difficulties.

The solutions officially recognized as Ringer's solution (8) and Ringer's injection (9) are identically composed of sodium, potassium, and calcium as the chlorides. Sterility is a requisite of the latter preparation. For Ringer's solution, the NF (8) describes a newly introduced flame-photometric analysis for sodium and potassium while calcium is assayed by chelometric titration. The USP methods (9) for the cations in Ringer's injection involve three different titrimetric procedures which appear cumbersome. AA was proposed for the analysis of sodium, potassium, and calcium in Ringer's solution, anticipating that a procedure could be developed that might offer advantages over the official methods.

EXPERIMENTAL

Instruments—A Jarrell-Ash 82-270 Atomsorb atomic absorption spectrophotometer, equipped with a single-slot burner head (10-cm. pathlength) and sodium/potassium and calcium hollow cathode lamps, was used throughout. Instrumental parameters are listed in Table I. Flame photometric determinations were performed with Baird DB 4 and KY 2 flame photometers.

Reagents—Lanthanum chloride¹ (LaCl₃·6H₂O), stated purity 99.9%, and cesium chloride² (CsCl), stated purity 99+%, were used as obtained. All other reagents were ACS grade. Sodium and potassium chloride were maintained in a desiccator under vacuum.

Table I-AA Instrumental Parameters

Wavelengths (Å): Na, 5890; K, 7665; Ca, 4227 Hollow cathode lamp currents (mamp.): Na and K, 4; Ca, 5 Fuel: acetylene (flowmeter, 5; 10 psig.) Oxidizer: air (flowmeter, 22; 35 psig.)
Slit widths: monochromator entrance, 50 μ ; monochromator exit, 75 μ^a
Gain: Na. 4.2: K. 7.2: Ca. 3.8
Pathlengths: Na, 0.5 mm. ^b ; K and Ca, 10 cm. ^c

^a Instrument manufacturer's recommendations. ^b Slot burner turned 90° through light source. ^c Standard burner configuration.

Deionized water was used for all solutions; reagent solutions were kept no longer than 24 hr. in glass containers.

Stock Solutions—Solutions contained: 8.11, 8.60, and 9.10 g. NaCl/l.; 240 and 360 mg. KCl/l.; and 294 and 368 mg. $CaCl_2 - 2H_2O/l$.

Sodium Working Standards—Ten milliliters of the 8.11 and 9.10 g./l. NaCl stock solutions was diluted to 1000 ml. with water. Final dilutions were equivalent to 31.9 and 35.8 p.p.m. Na, respectively.

Potassium Working Standards—Into two 1000-ml. volumetric flasks, 10 ml. of the 8.60 g./l. NaCl stock solution was pipeted. Then 10 ml. of the 240 mg./l. KCl stock solution was added to one, and 10 ml. of the 360 mg./l. KCl stock solution was added to the other. They were made to volume with water. Resulting dilutions were equivalent to 1.26 and 1.89 p.p.m. K, respectively, plus 33.8 p.p.m. Na in each.

Calcium Working Standards—Ten milliliters each of the 8.60 g./l. NaCl stock solution was pipeted into two 100-ml. volumetric flasks. Then 10 ml. of the 294 mg./l. $CaCl_2 \cdot 2H_2O$ stock solution was added to one, and 10 ml. of the 364 mg./l. $CaCl_2 \cdot 2H_2O$ stock solution was added to the other and made to volume with water. Final dilutions were equivalent to 8.02 and 10.02 p.p.m. Ca, respectively, plus 338 p.p.m. Na in each.

Blank Solutions—Deionized water or appropriately diluted solutions containing NaCl were used.

PROCEDURES

Sodium, Potassium, and Calcium Working Curves—After optimizing the wavelengths indicated in Table I and zeroing (while aspirating blank solutions), percent A of the sodium, potassium, and calcium working standards was measured. Sodium was measured with the slot-burner turned 90° through the light source, resulting in a pathlength of 0.5 mm. Potassium and calcium were measured with the slot-burner in the standard configuration (*i.e.*, pathlength equal to 10 cm.). The A versus concentration curves were drawn for sodium, potassium, and calcium.

AA of Ringer's Solution—A 100-fold diluted Ringer's solution was measured for sodium and potassium; calcium was determined with 10-fold diluted solutions.

Comparison Analysis—Ringer's solution was analyzed for sodium and potassium by flame photometry and for calcium by EDTA titration, using hydroxy naphthol blue³ as indicator, as described in the NF XIII (8). Polysorbate 80 was used as surfactant in the flamephotometric assay; where lithium internal standard was used, a 250p.p.m. Li (as LiNO₃) solution was used in preparation of standards and in dilution of samples.

¹ Alfa Inorganics.

² Matheson Coleman and Bell.

³ Mallinckrodt Chemical Works.

Table II-Interelemental Interference Effects on the Absorption of Na, K, and Ca

Concentra K ^b	K and Ca on ation, p.p.m. Ca ^c	Na <i>A^a</i> of 33.8 p.p.m. Na ^d		Na and Ca or tration, p.p.m. Ca	n K $\overline{A^a \text{ of } 1.57}$ p.p.m. K ^d	Concentra Na	-Na and K on ition, p.p.m. K	$\begin{array}{c} \text{Ca}\\ \hline A^{\alpha} \text{ of } 8.99\\ \text{p.p.m. Ca}^{f} \end{array}$
Nil 1.04 1.57 2.09 Nil Nil Nil 1.57	Nil Nil Nil 0.0818 0.0899 0.0981 0.0899	0.30 0.30 0.30 0.30 0.30 0.30 0.30 0.30	Nil 32.1 33.8 35.6 Nil Nil Nil 33.8	Nil Nil Nil 0.0818 0.0899 0.0981 0.0899	0.10 0.11 0.11 0.10 0.10 0.10 0.10 0.10	Nil 300 400 Nil Nil 338 —	Nil Nil 12.6 18.9 15.7	0.11 0.14 0.14 0.11 0.11 0.11 0.14

^a See Table I for instrumental conditions. ^b Required to meet NF specifications: 1.30–1.80 p.p.m. (in Ringer's diluted 100×'s). ^c NF specifications: 0.082–0.098 p.p.m. (in Ringer's diluted 100×'s). ^d Median concentration of 100-fold diluted Ringer's. ^e NF specifications: 32.3–35.4 p.p.m. (in Ringer's diluted 100×'s). ^f Median concentration of 10-fold diluted Ringer's.

Table III-Analysis of Na, K, and Ca in Ringer's Solution

Ringer's		Amount Found as Percentage of Amount Declared ± Relative SD ⁴ —					
Solution	Element	AA	A^b	Bc	Titration		
1 d	Na	99.6 ± 0.9					
	K	102.5 ± 1.7					
	Ca	98.0 ± 0.0					
2 ^e	Na	101.5 ± 1.4	107.9 ± 1.4	104.0 ± 1.0			
	K	98.9 ± 1.1	104.7 ± 1.8	97.3 ± 0.8	·····		
	Ca	100.3 ± 1.0		—	100.9 ± 0.2		

^a Based on 10 determinations. ^b Without internal standard. ^c Using Li internal standard. ^d Laboratory-prepared solution. ^e Commercially obtained solution.

RESULTS AND DISCUSSION

Enhancement or depression of the absorption of sodium, potassium, and calcium because of admixture of these elements is well described in the literature (1–3, 7, 10–12). These interactions are very dependent on relative concentrations; thus, their importance in Ringer's solution or dilutions thereof had to be determined. Initial experiments indicated that linear curves (*A versus* concentration) for sodium and potassium could be generated at concentrations present in 100-fold diluted Ringer's solution (*i.e.*, about 33.8 p.p.m. Na and 1.57 p.p.m. K); Ringer's solution diluted 10 times was suitable for measuring calcium (*i.e.*, about 9 p.p.m.).

Table II lists interelemental interference effects observed with sodium, potassium, and calcium at the concentrations indicated. For each element, consideration was given to the fact that the accompanying elements could vary over the range indicated in the official compendia. As noted in Table II, potassium and calcium exert no influence on the absorption of sodium. Therefore, the reference standards for sodium only require this cation. The absorption of potassium is affected by the relatively high concentration of sodium but is not affected by the calcium present; thus, sodium must be included in the potassium reference standards. This effect and its magnitude are in accord with the results of others (7, 10, 13). Enhancement of the absorption of calcium by sodium was also observed and necessitates preparation of calcium standards containing sodium. The enhancement effects caused by alkali metals are apparently due to their ability to increase the number of atoms (of the elements being measured) in the ground state, resulting in an increase in absorption (3). Fortuitously, these enhancement effects tend to plateau over a wide range of concentrations, which allows for compensation by appropriate addition of the interfering element to reference standards.

The use of 1% lanthanum solutions (12, 13) to suppress the enhancement of potassium and calcium absorption by sodium was not successful with the solutions studied. Cesium chloride was suggested for use in counteracting the effect of sodium on potassium (3); however, it accomplishes this by causing an analogous enhancement. Thus, its use in the present application offers no advantage over simply adding sodium to potassium reference standards.

Application of the proposed method to Ringer's solution was attempted. The best results were obtained when the two-standard or sandwiching method, discussed by Ramirez-Munoz (14) and described in the *Experimental* section of this report, was used. Results of determinations on laboratory prepared Ringer's solution and a commercially available product are given in Table III. Also included in Table III are results of NF analyses of the latter. The AA method seems more accurate than the NF flame-photometric procedures for sodium and potassium. This is in contrast to the fact that AA appears to offer no advantage in accuracy over the EDTA titration method for calcium. The AA procedures overall possess similar precision to that of the NF methods, but, because they can be performed with only one apparatus, they are more convenient than the official assays and could provide savings in time.

REFERENCES

(1) J. B. Willis, Spectrochim. Acta, 16, 259(1960).

- (2) Ibid., 16, 551(1960).
- (3) H. Sanui and N. Pace, Appl. Spectrosc., 20, 135(1966).
- (4) G. K. Murthy and U. Rhea, J. Dairy Sci., 50, 313(1967)
- (5) E. L. Obermiller and R. W. Freedman, Fuel, 44, 199(1965).
- (6) T. Takeuchi and M. Saizuki, Talanta, 11, 1391(1964).
- (7) D. T. Davis, Analyst (London), 85, 495(1960).

(8) "The National Formulary," 13th ed., Mack Publishing Co., Easton, Pa., 1970, pp. 624, 625.

(9) "The United States Pharmacopeia," 18th rev., Mack Publishing Co., Easton, Pa., 1970, pp. 593, 594.

(10) W. Slavin, "Atomic Absorption Spectroscopy," Wiley, New York, N. Y., 1968, pp. 87-163.

(11) J. Ramirez-Munoz, Anal. Chem., 42, 517(1970).

(12) B. A. Dalrymple and C. T. Kenner, J. Pharm. Sci., 58, 604 (1969).

(13) J. R. Leaton, J. Ass. Offic. Anal. Chem., 53, 237(1970).

(14) J. Ramirez-Munoz, "Atomic-Absorption Spectroscopy," Elsevier, New York, N. Y., 1968, p. 313.

ACKNOWLEDGMENTS AND ADDRESSES

Received December 4, 1970, from the Division of Medicinal Chemistry, College of Pharmacy, University of Iowa, Iowa City, IA 52240

Accepted for publication February 1, 1971.

This investigation was supported in part by a Mead Johnson Laboratories grant for undergraduate research in pharmacy.

* To whom all correspondence should be addressed.