INTERFERENCE STUDIES IN THE DETERMINATION OF SODIUM, POTASSIUM, CALCIUM, AND MAGNESIUM IN NATURAL WATERS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY [1]

by

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Atomic absorption is a sensitive and rapid method for measuring sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg) in rainfall, runoff and impounded waters. The technique is relatively simple because little sample preparation is required.

Much of the early literature on atomic absorption emphasized the simplicity of the method and its freedom from interferences. It is now generally recognized, however, that certain interferences do exist. Recently, Pickett and Koirtyohann (15) [3], Slavin (20), and Angino and Billings (3) discussed the various types of interference (chemical; spectral, including molecular absorption; and ionization) and their relative significance in atomic absorption.

Chemical interferences result from chemical combination of the element of interest with other elements or compounds in the flame. This results in fewer ground state atoms and a negative error in absorption. The alkaline earths are particularly subject to this type of interference using the low temperature flames, e.g. air-H_2, and to a lesser extent in air-acetylene; forming compounds with sulfur, aluminum, phosphorus, silicon, and oxygen. This interference is usually controlled by adding a "protective agent" such as lanthanum (La) or strontium (Sr), or by using the hotter nitrous oxide-acetylene flame (14).

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[3] Numbers in parentheses refer to Literature Cited--at the end of the report.

Atomic absorption spectrophotometry is relatively free from spectral interferences. A few exceptions are outlined by Pickett and Koirtyohann (15). Spectral interferences can also occur when using multielement hollow cathode lamps (11). Molecular absorption, a special type of spectral interference, can occur when determining certain trace elements in high-salt solutions (6, 3, 20). The interfering molecular species, e.g., CaOH and SrOH, absorb some of the light passing through the flame (12, 13). The result is a positive error in measurement. The interference is eliminated or reduced by using the nitrous oxide-acetylene flame (20). No molecular absorption effects have been noted on the analytical lines of Na, K, Ca, and Mg (6).

Many elements, especially the alkali metals, are appreciably ionized at the temperature of the air-acetylene flame. Ionization results in fewer atoms remaining in the ground state available for absorption measurement. If other elements are present that can supply free electrons, the number of ions returned to the ground state increases. This results in an increase in absorption, or positive error (ionization error).

Ionization interferences in the determination of the alkali and alkaline earth metals have been reported by numerous authors, but in many cases, with little supporting evidence. The literature reports several discrepancies regarding the potential interferences and their quantitative effects. Since some of the conflicting data can probably be attributed to differences in instrumentation and operating parameters, especially flame parameters, the analyst should make his own interference tests. This report is concerned with the ionization interferences of Na, K, Ca, and Mg on each other in the analysis of natural waters.

MATERIALS AND METHODS

The experimental approach to the interference studies is outlined in Table 1. Generally, absorbance measurements of the element under investigation were made at interfering element concentrations of 0, 4, 10, 20, 50, 100, 200 and 500 ppm. These absorbance values were then compared to the absorbance values obtained at zero interfering element concentration. The change in absorbance (ΔA) caused by the interfering element was converted to an apparent change in concentration (ΔC) using the standard curve (absorbance vs. concentration). The quantitative effect of the interfering element is expressed as an error term, calculated from the following relationship:

$$\% \text{ Error} = \frac{\Delta C}{C_o} \times 100 \qquad (1)$$

where C_o represents the true concentration of the element being analyzed.

Table 1.--Interference studies conducted in water using atomic absorption spectrophotometry.

Element Analyzed	Concentration of Element Analyzed (ppm)	Interfering Elements	Interfering Element Concentration (ppm)
Na	0	K, Ca, Mg	0-500
Na	1	K, Ca, Mg	0-500
Na	3	K, Ca, Mg	0-500
K	0	Na, Ca, Mg	0-500
K	2	Na, Ca, Mg	0-500
K	5	Na, Ca, Mg	0-500
Ca	0	Na, K, Mg	0-500
Ca	8	Na, K, Mg	0-500
Mg	0	Na, K, Ca	0-500
Mg	1	Na, K, Ca	0-500

All absorbance measurements were made with a Perkin-Elmer Model 303 spectrophotometer equipped with a digital concentration readout (DCR1) [4/]. The operating parameters for the spectrophotometer are given in Table 2 (2). All measurements were made with an air-acetylene premixed flame using a Boling (three-slot) burner (22). Standard and test solutions were prepared as chlorides from reagent-grade chemicals. The DCR was adjusted to zero absorbance with distilled water at the beginning of the analyses. Standard solutions were analyzed periodically during each set of test solutions to confirm the overall stability of the instrumentation.

RESULTS AND DISCUSSION

The results of the interference studies are discussed briefly for each element in the subsequent sections.

Sodium

K, Ca, and Mg enhance the absorption of Na, resulting in substantial positive errors (Figures 1 and 2). The order of interference is K>>Mg>Ca. The errors determined at 1 ppm Na are almost twice those determined at 3 ppm Na. This indicates that the errors in measurement are functions of both the Na concentration and the interfering ion concentration. Errors of 5 to 15% will be encountered frequently in the measurement of Na in fresh waters.

Our findings contradict the conclusions of several other workers. Fishman and Downs (10) reported that none of the cations in normal amounts in fresh water interferes with Na determinations. Similar results on sea water were reported by Billings and Harriss (7). Robinson (17) found no ionization interference on 10 ppm Na by 5000 ppm of K or Li. Rubeska et al. (18) reported no interference on Na absorption by up to 3000 ppm K in the study of Na in limestones. They reported, however, that Ca affected the slope of the curve by altering the release of Na in the flame. Sanui and Pace (19) reported that K enhanced the absorption of Na, but this interference could be eliminated in the presence of 4mM cesium (532 ppm Cs).

4/ Trade names and company names are included for the benefit of the reader and do not infer any endorsement or preferential treatment of the product listed by the USDA.

Table 2.--Operating parameters for the Perkin-Elmer 303 atomic absorption spectrophotometer (2).

Element	Concentration range (ppm)	Wavelength (Å)	Grating	Filter	Slit	Source	Lamp Current (ma)	Flame
Na	0-3	5890	Visible	No	3	Arc Discharge	700	Oxidizing
K	0-5	7665	Visible	Yes	4	Arc Discharge	350	Oxidizing
Ca	0-10	4227	Visible	No	4	Hollow Cathode	10	Reducing
Mg	0-2	2852	Ultra-violet	No	5	Hollow Cathode	6	Reducing

Potassium

K absorption is enhanced by Na, Ca, and Mg (Figures 3 and 4). The interference caused by Ca and Mg will frequently result in errors of 5 to 10% in the analysis of runoff waters from humid regions. The interference by Na is much greater, causing errors of 10 to 20% depending on the concentration of K, at relatively low levels of Na (10-25 ppm). Errors > 20% may be encountered in the measurement of K in runoff waters from saline soils.

The results of our studies with K are in agreement with those of other workers. Fishman (9) reported that in natural waters only Na interferes in the determination of K. This is an ionization interference as noted by Willis in 1960 (24). Billings and Harriss (7) observed the interference of Na on K determinations in sea water. According to Slavin (20), Baker and Garton (4) showed that K absorption is enhanced by the alkali metals -- Na, Rb, and Cs. Sanui and Pace (19) reported that the absorption of K is not affected by varying amounts of Na in the presence of 4mM Cs.

The ionization interference of Ca and Mg on the determination of Na and K has apparently received little attention.

Calcium and Magnesium

Ca and Mg standard and test solutions contained 1% lanthanum (La) in 5% (v/v) HCl. The La-HCl solution was used in these experiments since it is required in the analysis of natural waters to reduce the interference of pH (5), and the chemical interferences due to sulfate, aluminate, phosphate, and silicate (25).

Ca absorption is enhanced slightly by Na (Figure 5), but the error is < 4% using the recommended reducing flame (2, 21). Using an oxidizing flame, positive errors up to 8% were obtained at a Na concentration of 500 ppm. K and Mg showed no significant interference (± 1%) at concentrations up to 500 ppm.

There is little agreement among authors about the interference of Na and K on Ca absorption (8,23,25,21). Enhancement has been reported to range from "almost negligible" to about 20% (20). Platte and Marcy (16) reported no interference on 1 ppm Ca by 1000 ppm of Na or Mg. In a study of natural waters, Fishman and Downs (10) found no interference on Ca absorption by 500 ppm each of Na or K. Slavin et al. (21) reported that the enhancement of Ca absorption caused by Na could be reduced, and almost avoided, by using a fuel-rich flame and working higher in the flame.

The presence of 500 ppm Na, K, or Ca did not affect significantly the absorption of Mg (Figure 6). This is in agreement with the results reported by Allan (1), Platte and Marcy (16), and Fishman and Downs (10).

Reduction of Ionization Errors

Three methods are available to the analyst to reduce or eliminate ionization interference effects: (1) approximately equal amounts of the interfering elements in the samples can be added to the standards; (2) since there is frequently a large plateau region in which the absorbance is essentially constant with increasing concentrations of the interfering element, enough of the interfering element can be added to both standards and samples to put the concentration within the plateau--about 200 to 1000 ppm; or (3) an easily ionizable metal, not of analytical interest, can be added to both the standards and unknown samples to suppress the ionization of the element(s) to be analyzed. Methods 1 and 2 are used frequently, although Method 2 is not always applicable. Note the absence of a definite Na plateau in Figures 3 and 4. Method 3 is more adaptable to routine analyses.

Because Cs has the lowest ionization potential (3.89 electron volts) of any of the metals, it is an excellent ionization suppressant. Cs in natural waters is rarely of analytical interest. Thus it is favored as an ionization suppressant in determining the alkali and alkaline earth metals in natural waters.

The results indicate that as little as 200 ppm Cs [5/] will reduce the ionization errors caused by Na, K, Ca, and Mg to about ± 2% (Figures 1,2,3,4, and 5). Cs at 200 ppm increases the sensitivity of the K determinations about 50% (Figure 7) while reducing the interferences of Na, Ca, and Mg at concentrations up to 500 ppm, to about ± 2% (Figures 3 and 4). The sensitivity of the K determinations is increased further by increasing the Cs concentration to 500 ppm (Figure 7). Only a slight increase in the sensitivity of the Na determinations is provided by Cs at 100 and 200 ppm (Figure 8).

[5/] Available as CsCl (99.97%) from K&K Laboratories, Plainview, New York.

SUMMARY

Significant ionization errors were encountered using the air-acetylene flame in determining Na, K, and Ca in natural waters. The alkali metals, Na and K, enhance the absorption of each other because of their low ionization potentials. Ca and Mg were ionized slightly in an oxidizing flame, causing an error in the determination of Na and K. The absorption of Mg was not affected significantly by the presence of 500 ppm Na, K, or Ca. As little as 200 ppm Cs reduced the ionization errors caused by Na, K, Ca, and Mg to an acceptable level (± 2%) for routine analyses. An ionization suppressant, preferably not of analytical interest, should always be added to both standard and sample solutions when analyzing samples containing variable amounts of the alkali and alkaline earth metals. This should be done even with the air-acetylene flame. It is much more important when using the hotter nitrous oxide-acetylene flame. The use of an ionization suppressant with the hotter flames is much more desirable than the alternative, using low temperature flames, with their more serious concomitant chemical interferences.

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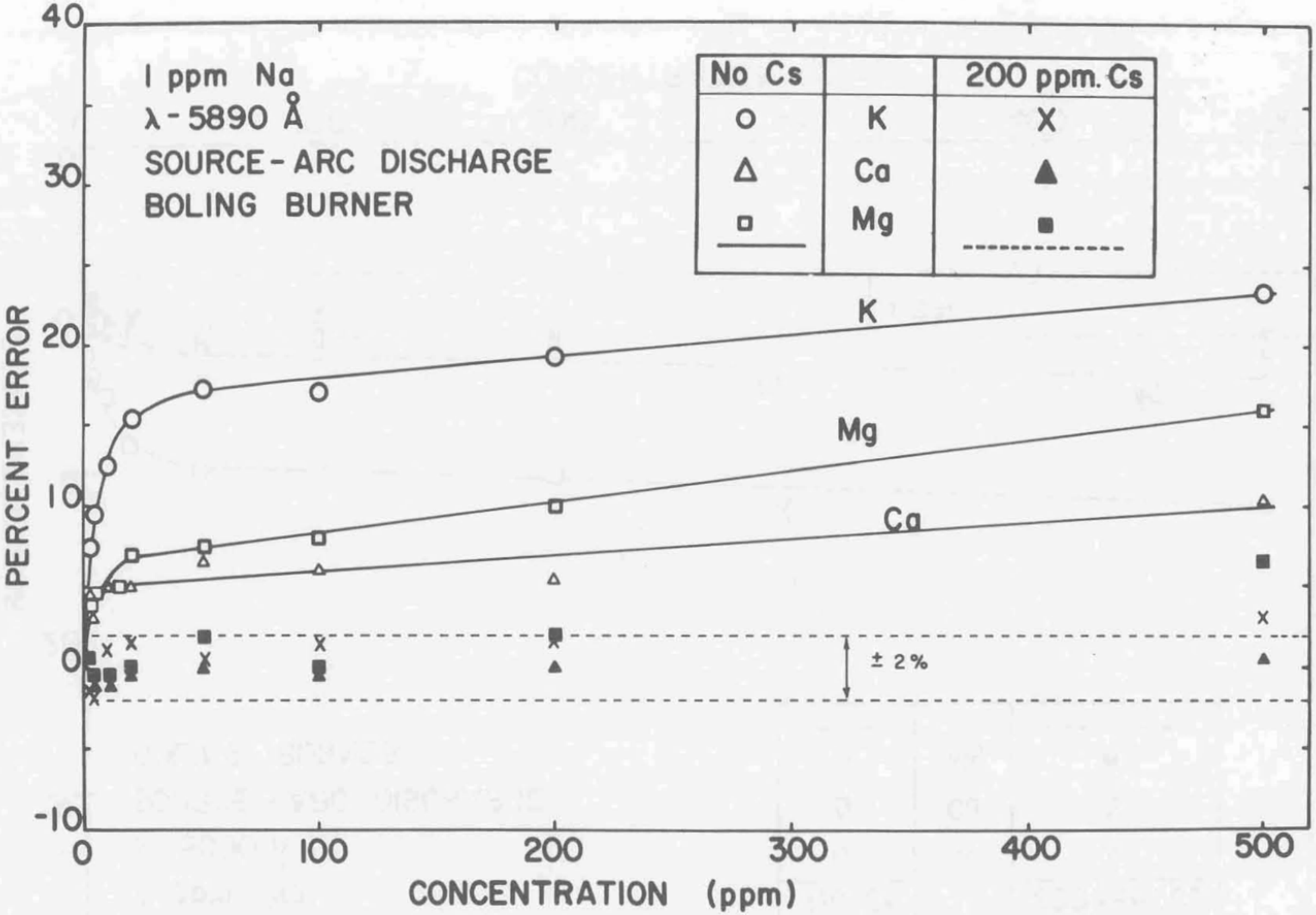

Figure 1.--Errors caused by the interference of K, Ca, and Mg in the measurement of 1 ppm Na.

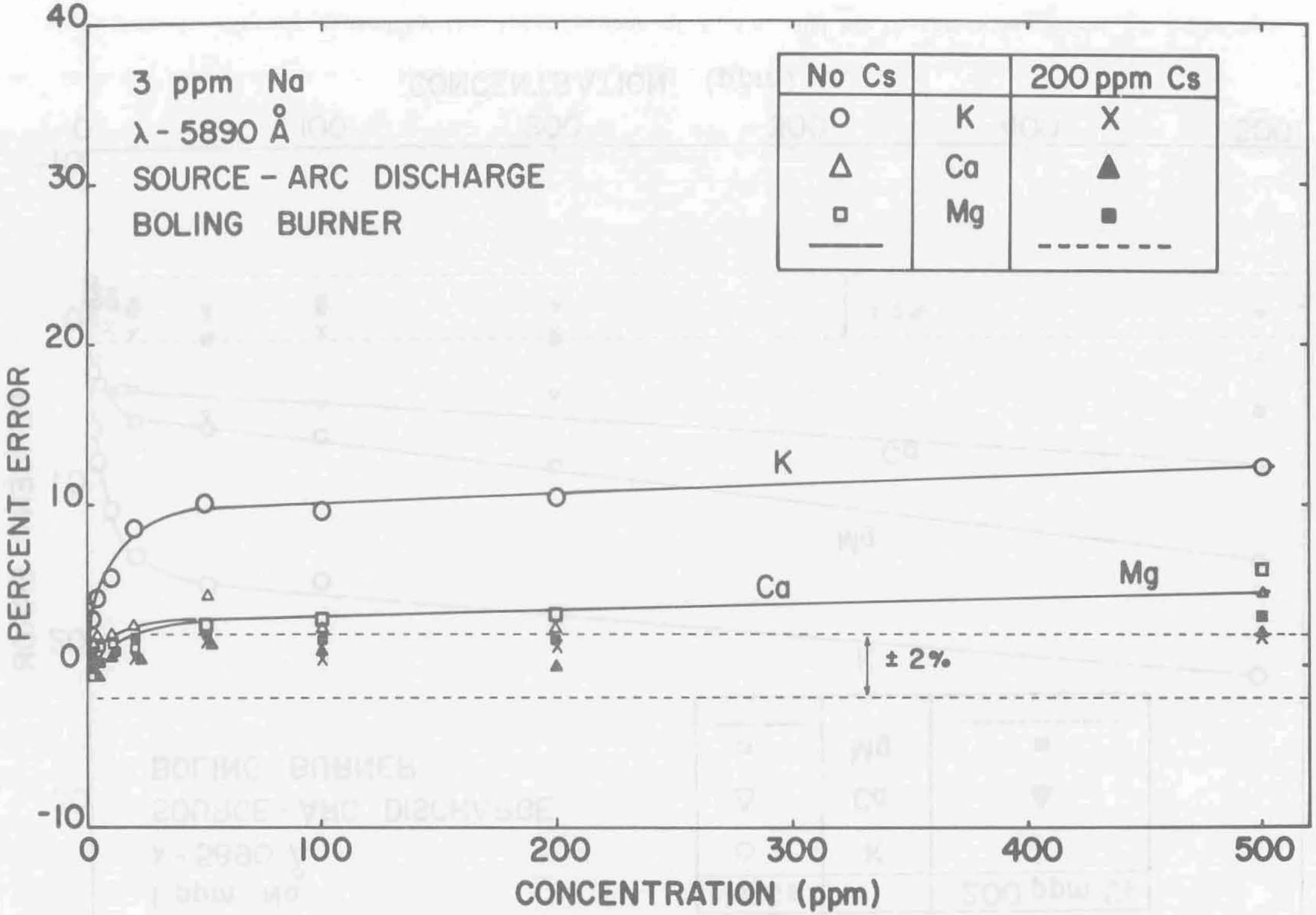

Figure 2.--Errors caused by the interference of K, Ca, and Mg in the measurement of 3 ppm Na.

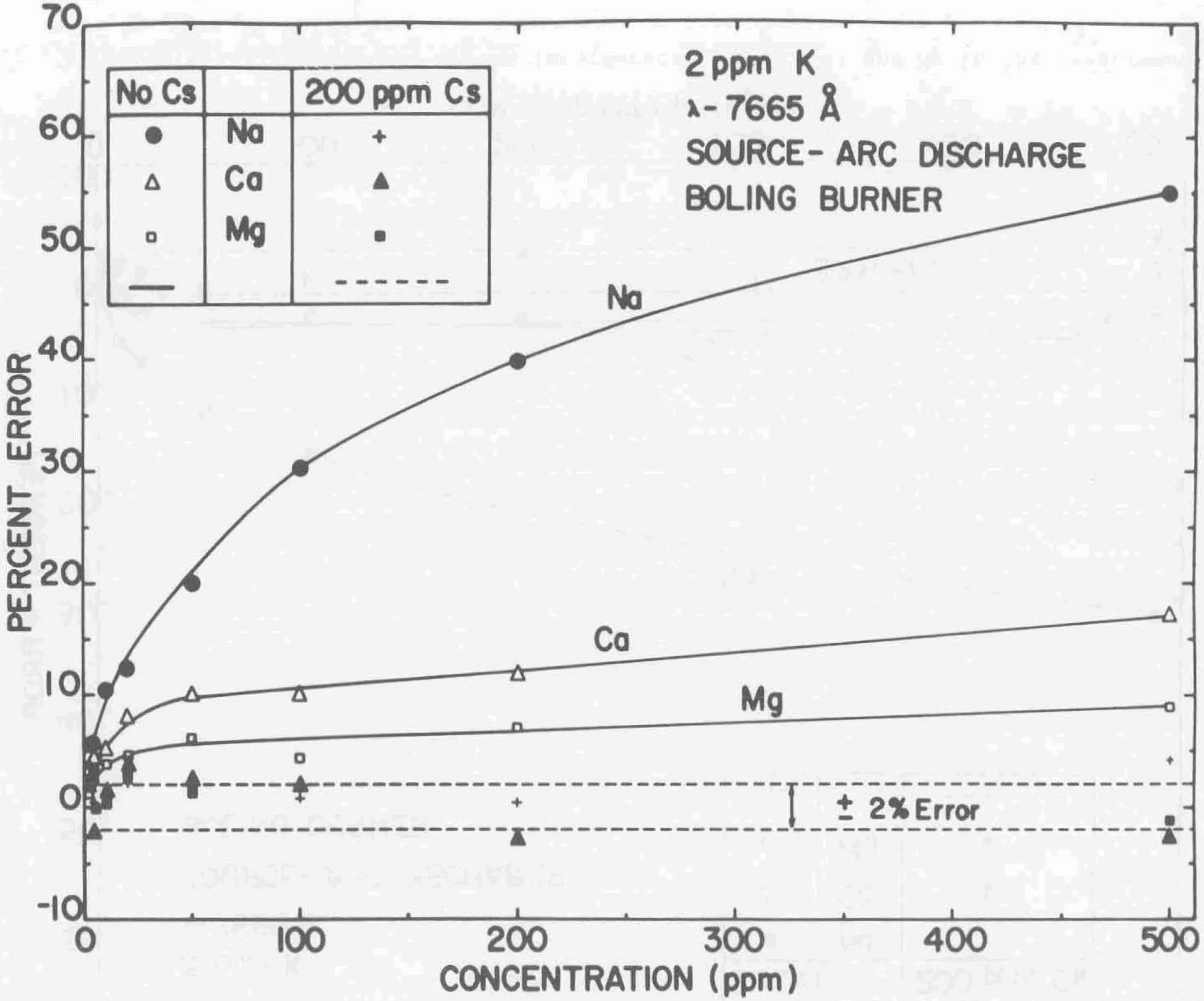

Figure 3.--Errors caused by the interference of Na, Ca, and Mg in the measurement of 2 ppm K.

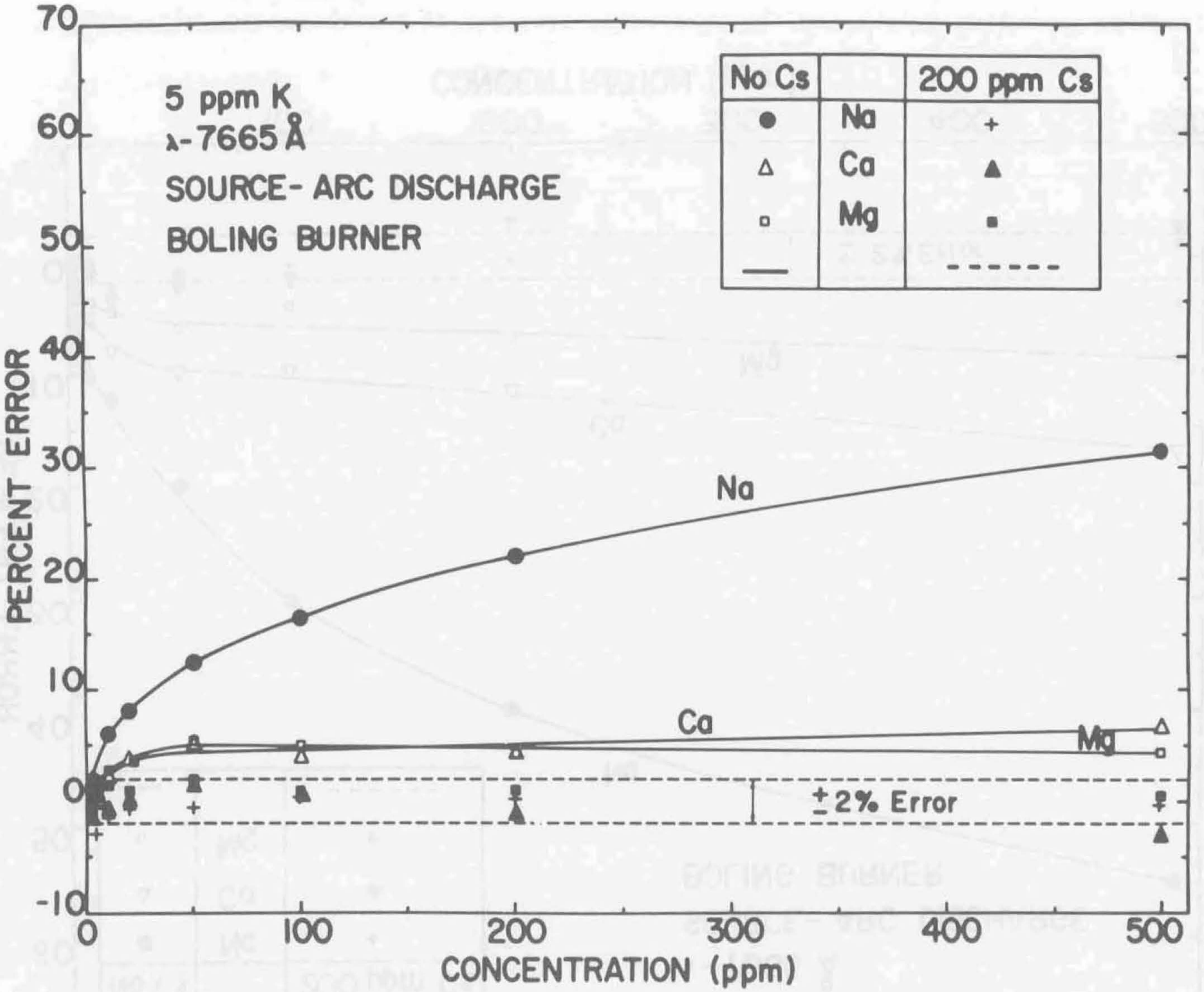

Figure 4.--Errors caused by the interference of Na, Ca, and Mg in the measurement of 5 ppm K.

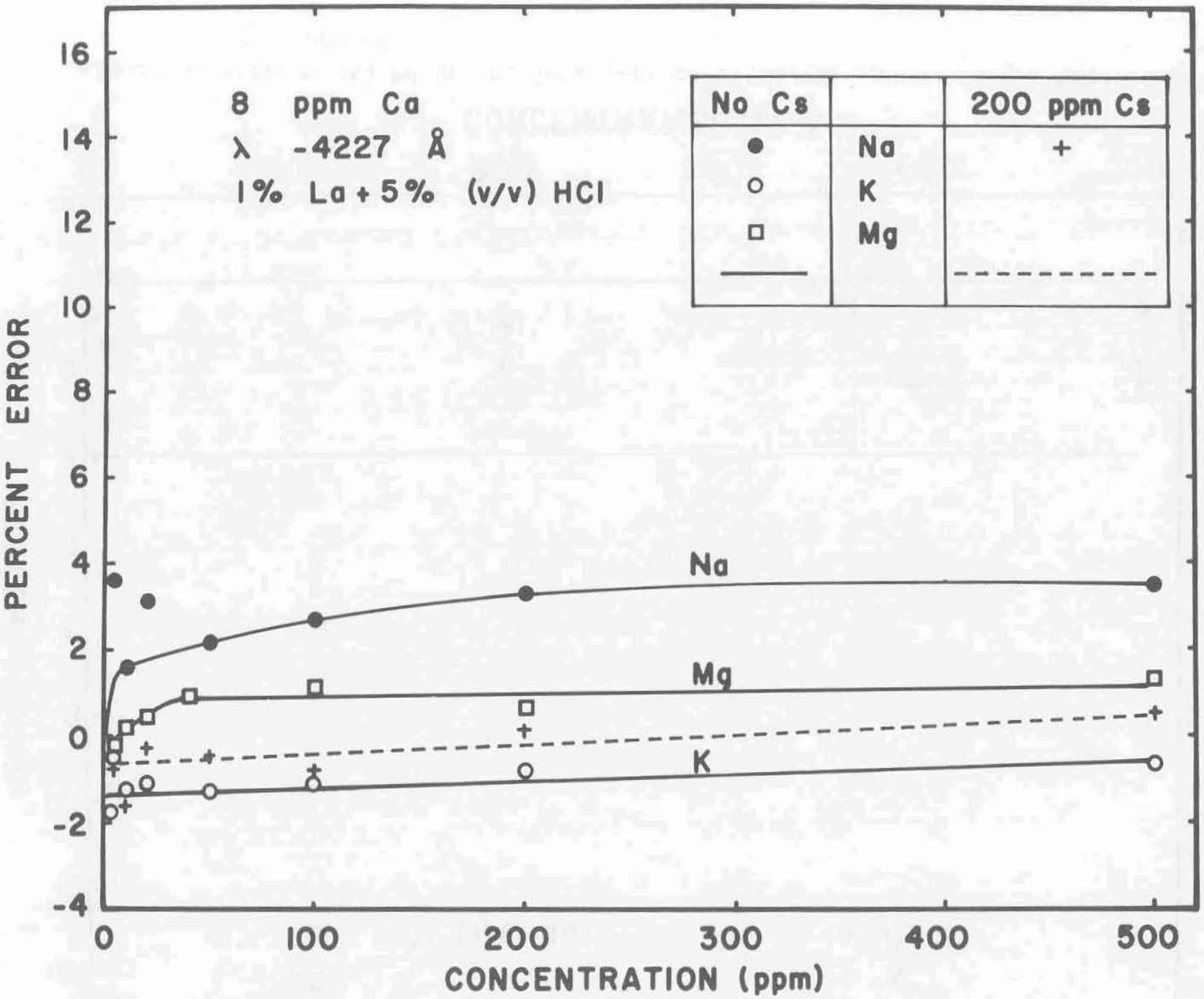

Figure 5.--Errors caused by the interference of Na, K, and Mg in the measurement of 8 ppm Ca.

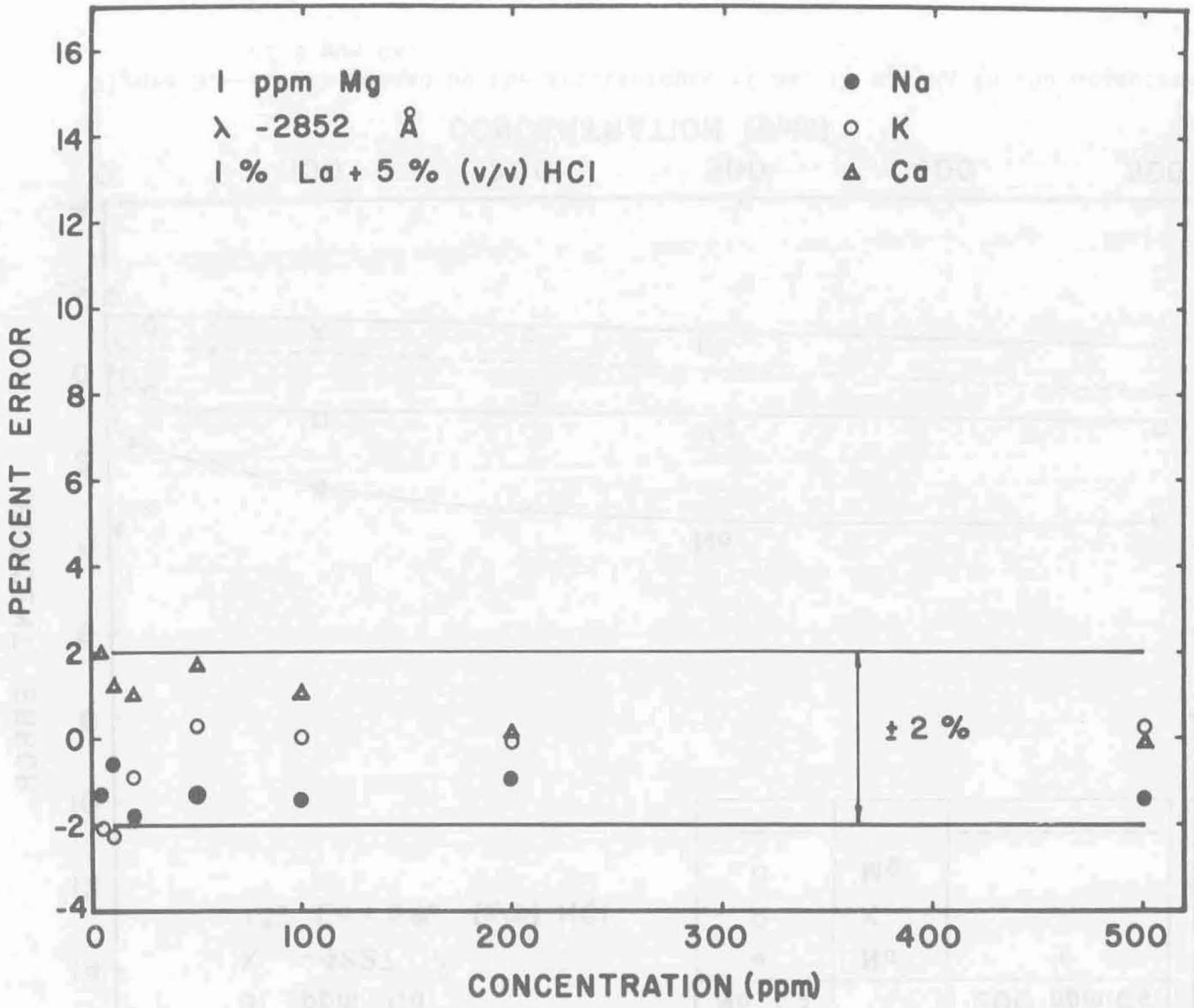

Figure 6.--Errors caused by the interference of Na, K, and Ca in the measurement of 1 ppm Mg.

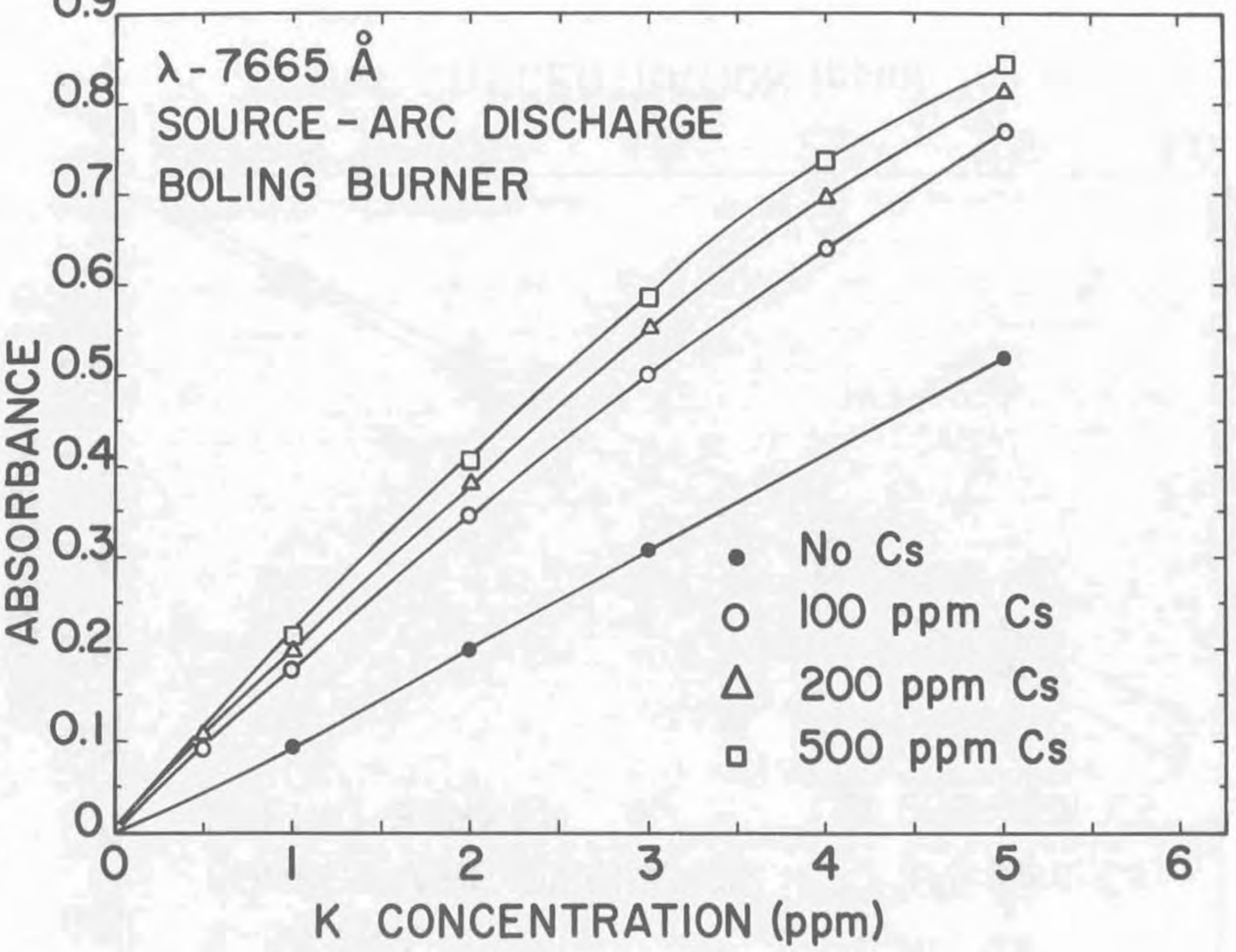

Figure 7.--Influence of Cs on the absorbance of K.

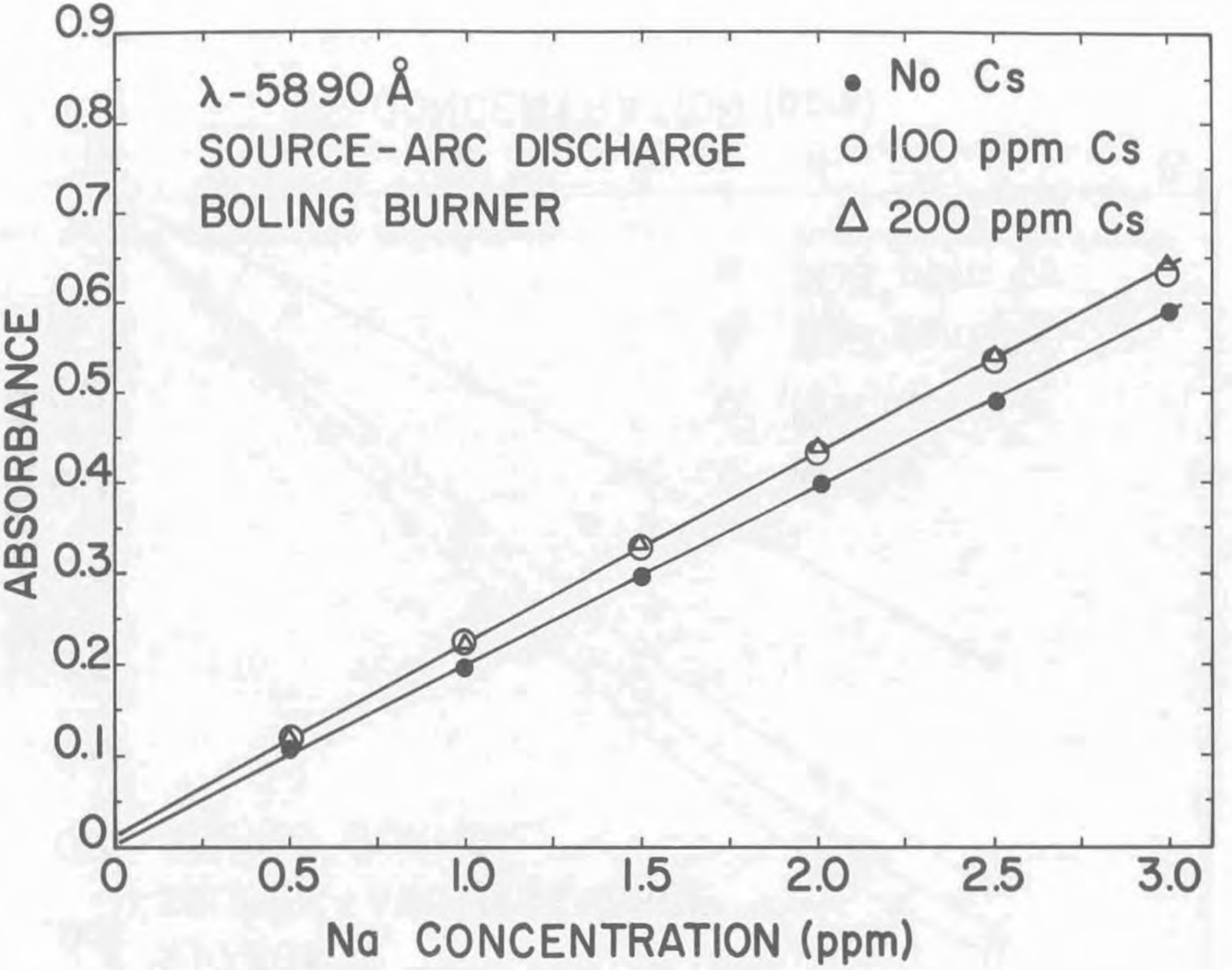

Figure 8.--Influence of Cs on the absorbance of Na.