Direct Photoelectric Spectrochemical Determination of Exchangeble Bases of Soil

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DIRECT PHOTOELECTRIC SPECTROCHEMICAL DETERMINATION OF EXCHANGEABLE BASES OF SOILS*

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It is well recognized in the field of soil science that a knowledge of the amounts and relative proportions of the exchangeable cations in the soil is indispensable in studies dealing with the chemical and physical behavior of soil or with soil fertility. While the need for more rapid methods permitting analysis of large numbers of soil samples has resulted in the development of rapid microchemical methods (11, 12) and spectrochemical procedures (5, 6, 10), the analytical procedures are time-consuming and hampered by the wide range of concentrations among the constituents. The desirability of greater rapidity and simplicity of analysis without a corresponding impairment of accuracy and precision has led to this investigation of direct photoelectric measurements of spectral radiations as an analytical procedure for the determination of the exchangeable cations of soils.

Simultaneous analysis of the calcium, magnesium, sodium, potassium, and manganese in the exchangeable base series is accomplished by combining the use of conventional spectrographic methods and instruments with the recently advocated methods of "flame photometry" (1, 2). Magnesium and manganese are analyzed with monochromators, while the analysis of calcium, sodium, potassium, and measurements of the lithium internal standard are carried out by the latter method. The purpose of this paper is to describe the procedure as presently developed and summarize the results obtained based on data using the method.

APPARATUS AND METHOD

The block diagram of Figure 1 illustrates the general arrangement of the equipment for direct photoelectric measurements of the elements in question. L indicates the position of the flame excitation source with respect to monochromators, S1 and S2, and housings, H3 and H4, arranged with holders for filters, F1 and F2. S1 and S2 are monochromators with quartz and glass optics, respectively, which have been adapted for use with phototubes housed in H1 and H2. Monochromator, S1, is set at 2852A for magnesium determinations, while monochromator, S2, is adjusted for measurement of the manganese triplet 4031-3-4A. Phototubes in housings, H3 and H4, in conjunction with suitable filter combinations, are used to measure spectral intensities of the lithium, calcium, sodium, and potassium. T is a voltage stabilizer for regulation of line voltage to rectifier circuits together with Variacs for input voltage adjustment. Power supply,

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P, consists of two conventional rectifier circuits for independent pho-
totube and meter potentials. C is a control panel containing an Ayrton
shunt for galvanometer sensitivity control and circuits for back-
ground and dark current compensation. Meter M, is a reflecting type
galvanometer having a maximum sensitivity of the order of 10^{-10}
amperes.
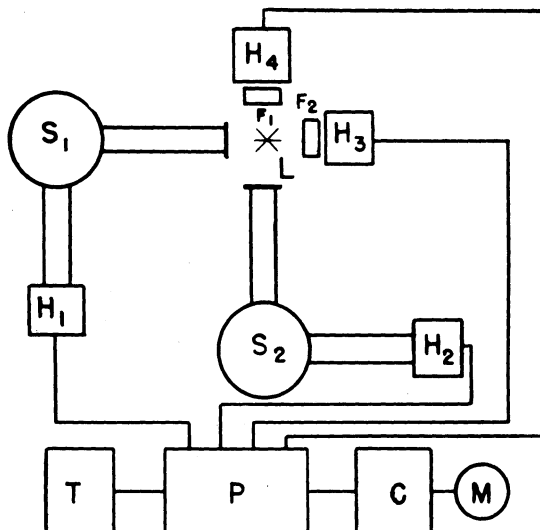
Figure I.   General Arrangement of Equipment for Simultaneous
Direct Photoelectric Determination of Spectral Intens-
ities of Exchangeable Base Elements.

S_1 Quartz optics monochromator for magnesium
determinations.

S_2 Glass optics monochromator for manganese
determinations.

H_1 H_2 H_3 H_4 Housings for photocells.

F_1 F_2 Filters for isolating spectra of lithium,
calcium, potassium, and sodium.

L   Flame source for excitation.

T   Voltage regulating transformer and variacs.

P   Rectifier power supply.

C   Control panel.

M   Galvanometer.

The spectral lines or bands for the determination of the exchangeable cations and for the lithium internal standard line, with the filter combinations used, are given in Table I.

TABLE *I*

Operating Conditions for Simultaneous Spectrochemical Analysis of Exchangeable Bases Using Flame Excitation and Direct Photoelectric Methods

Element	Spectral Isolation Region for Line	Method of Isolation of Spectra	Filter Combination Used for Flame Photometry
Lithium	6708P	Glass filters	Wratten 70 Wratten 35 Corning 9780 2 thickness light blue glass
Calcium	6182P 6203P	Glass filters	Corning 5120 Corning 9780 Corning 2412 2 thickness light blue glass
Potassium	7665P 7699P	Glass filters	Corning 2403 Corning 5850 Corning 5031
Sodium	5890P 5896P	Glass filters	Wratten 25 Corning 3387 Corning 5031
Manganese	4031P 4033P 4034P	Glass optics Monochromator	
Magnesium	2852P	Quartz optics Monochromator	

Construction of the atomizer and burner assembly is patterned after Lundegardh's (7, 8, 9) design, although somewhat simplified in detail. Air at approximately 60 pounds per square inch pressure is taken from an air line and run through a tank trap and screen filter to remove any droplets of moisture or particles of foreign matter before entering the pressure reducer used for initial pressure control. Pressure is further adjusted by a ⅛ inch needle value between the pressure reducer and an open tube mercury manometer and the atomizer assembly. Air, maintained at a pressure of 110 ± 0.2 cm. Hg, is run through the platinum-iridium jet of orfice diameter 0.5 mm. in the atomizer assembly. Acetylene is obtained from a Balbach (40 cubic feet) cylinder and its pressure is reduced by means of a conventional pressure reducer to approximately 2 pounds per square inch before further adjustment by another ⅛ inch needle value between the regulator and a water manometer. Acetylene at a pressure of 25 ± 0.1 cm. is run to the nozzle in the burner tube. The orfice diameter of the nozzle is 0.5 mm. It has also been found necessary to bubble the acetylene through a water trap to moisten the gas and

prevent clogging of the orfice in the burner tube by material depos-
ited by drying of the mist (3, 9).

The burner is so positioned that the cone of the flame is on the
optical axis of the monochromators and the lenses of the housings
for the phototubes. It is set 4 to 5 cm. from the slits of the mono-
chromators. A distance of 5 to 7 cm. separates the flame from the
filters. To obtain maximum intensity the height of the burner is
adjusted so that the tip of the blue inner cone of the flame is 10 to
15 mm. below the slits of the monochromators and openings of the
housings.

In the usual application of the air-acetylene flame to spectrochem-
ical analysis using photographic methods with Lundegardh's photo-
metric technique or an internal standard, sensitivity and reproduci-
bility are important considerations which depend on strict standard-
ization of the details of operation (3). Except for possible sensitivity
limitations of magnesium and manganese, the main requirement for
excitation of the cations in concentrations presently analyzed is a
steady flame supplied with air and acetylene at constant and repro-
ducible pressures.

Several considerations enter into the selection of a dispersing in-
strument and its adaptation to direct photoelectric measurements us-
ing flame excitation that are not influencing factors in the case of
phototube measurements using filters. The dispersive power of the
instrument must be such that the manganese triplet at 4031A can
be completely resolved from the potassium doublet 4044/7A. Although
the photomultiplier type phototubes are capable of great amplifica-
tion, a limitation in their performance for quantitative measurements
is imposed by the relatively weak spectral intensities of manganese
and magnesium in the flame and the narrow slit widths which must
be used to obtain resolution of potassium from manganese. Because
of the low intensity it is desirable to have an instrument of high
speed, an advantage inherent in the monochromator at the expense
of resolution. To utilize such an instrument, strict attention must be
paid to the construction and orientation of the slits and adjustment
of the equipment. Appreciable curvature is also present in the spec-
tral lines. Since the line in its entirety should be used to obtain maxi-
mum sensitivity, curved slits must be used if both maximum resolu-
tion and sensitivity are to be achieved. By examination of the photo-
graphic images of the spectral lines in question, it has been found
that a radius of curvature of 15 cm. is needed on the exit slit jaws.
The photographic image of the spectral lines of manganese triplet
and potassium doublet on the glass optics monochromator with an
entrance slit width of 0.10 mm. showed a linear separation of about
0.1 mm. between the two lines. It has been found that entrance and
exit slit widths of 0.10 mm. are satisfactory to isolate the potassium
radiation from the manganese determined quantitatively by the 4031A
triplet. An entrance slit width of 0.20 mm. and an exit slit width of
0.10 mm. are used on the quartz optics instrument for the determin-
ation of the magnesium at 2852A.

Choice of a photoelectric detector for analysis with the method described is limited to a device having high sensitivity. The type 931-A and 1P28 photomultiplier tubes are used for measurement of spec-
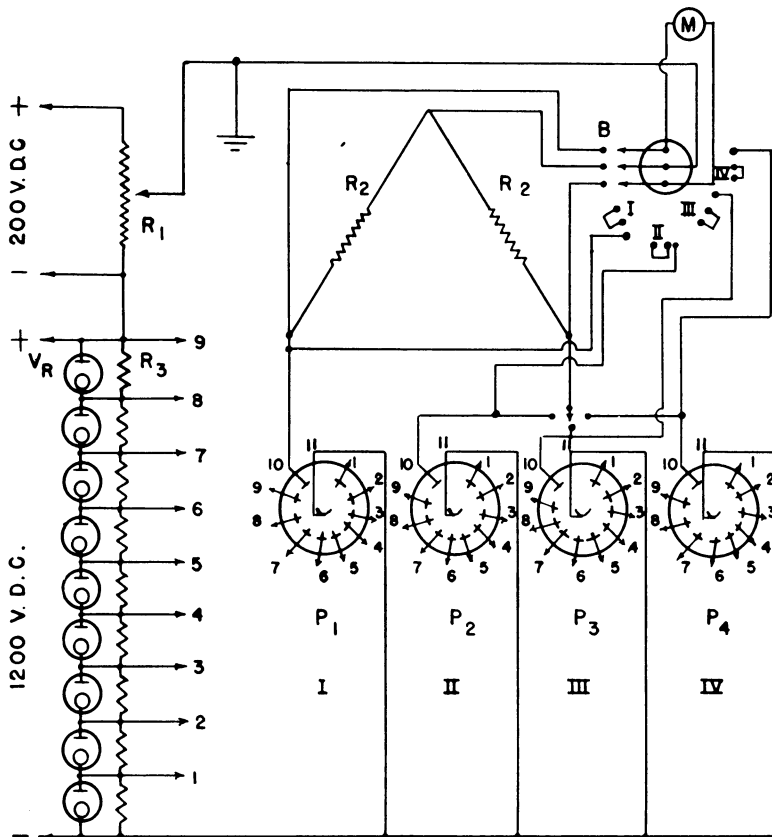

Fig. 2.   Circuit for Photomultiplier Tubes Used in Direct Measurements of Intensities. Conventional Rectifier, Filter Circuits Used for High Voltage and Meter Supply Voltage

R_1 = 20,000 ohms

R_2 = 10,000 ohms

R_3 = 50,000 ohms

$P_1 P_2 P_3 P_4$ Type 931-A or 1P28 Photomultiplier Tubes

V_R Type VR 105-30 Voltage Regulator Tubes

tral intensities. The tubes have a maximum spectral response between 3000A and 3500A with sensitivity decreasing to about 5 per cent of maximum at 6500A. With the filter arrangement, where the total photosurface may be used, sensitivity is more than adequate for both lithium and potassium, even though spectral response drops off considerably toward the longer wavelengths.

For sufficient response from the photomultiplier tubes at the lowest spectral intensities a power supply of at least 1200 volts is required. Since small changes in voltage on the stages of the photomultiplier tubes result in large changes in sensitivity, a voltage supply having a high degree of stability is essential. A schematic diagram of the application of the high voltage to the photomultiplier tubes and the method of achieving the required degree of regulation (4) is shown in Figure 2. Shown also in the diagram is the bridge circuit, with the switching arrangement permitting successive bridging of the tubes measuring the photocurrents of the lines of the unknown elements with the tube measuring the photocurrent of the internal standard line or individual tube measurements.

Consideration must be given to the characteristics and limitations of photomultiplier tubes in their applications to circuits for quantitative photoelectric measurements. Two factors, phototube fatigue and wide differences in sensitivity of individual tubes, appear to contribute most to poor repeatability of readings. Tubes must therefore be matched in so far as possible with respect to fatigue rates and sensitivity. It has been shown (4) that fatigue greatly increases with increasing current flow and is also influenced by the magnitude of the voltage between the last dynode and the anode of the tube. Intensities for the more sensitive elements are reduced such that current values of greater than 50 microamperes would not likely be exceeded for the range of concentrations to be encountered in routine soils analysis. Long exposures are avoided and fatigue effects are further minimized by keeping the plate voltage as low as possible, consistent with maintenance of current saturation at the light levels used.

PREPARATION OF ANALYTICAL STANDARDS AND CURVES

Solutions used as standards in preliminary analysis to determine reproducibility were prepared by dissolving distilled magnesium, electrolytic manganese, reagent grade calcium carbonate and lithium carbonate in concentrated hydrochloric acid. These each were made up in concentrated stock solutions for dilution and mixing. Stock solutions for potassium and sodium standards were prepared from reagent grade potassium and sodium chloride, likewise made up in concentrated stock solutions. Composition of the standard solutions is in proportions conforming to the average relative percentages found in representative groups of soils previously analyzed chemically for calcium, magnesium, potassium and sodium. Table II summarizes data on composition of solutions used as standards in prep-

aration of analytical working curves calculated on the basis that
1 ml. of solution contains the exchangeable cations of 1 gm. of soil.

TABLE *II*

Composition of Solutions Used as Standards for Preparation
of Analytical Working Curves

One Ml. solution contains exchangeable bases of 1 gm. of soil

| | Concentrations in Milliequivalents per 100 gms. of soil | | | | | Lithium Internal Standard |
Solution	Ca	Mg	K	Na	Mn	p.pm.
I	2.0	0.50	0.10	0.10	0.10	2000
II	5.0	2.0	0.20	0.30	0.50	2000
III	10.0	5.0	0.40	0.60	1.0	2000
IV	15.0	8.0	0.60	1.0	2.0	2000

In preparation of analytical curves and obtaining data on repro-
ducibility of readings, each solution was analyzed twelve times dur-
ing a five-day interval. The average bridge reading or ratio for the
twelve readings was plotted against concentration values taken from
weights of constituents converted to milliequivalent values contained
in solution. The resultant curves are shown in Figures 3, 4, and 5.

RESULTS

Results by element for repeated analysis of Solution III are shown
in detail in Table III. The average per cent deviation from the
standard for the twelve repeated analysis of Solution III for calcium
was 4.4 per cent; for magnesium, 10.0 per cent; for potassium, 2.7
per cent; for sodium, 4.4 per cent; and for manganese, 7.2 per cent.
For the 48 analysis of the standards the average deviation from the
standard was 5.1 per cent for calcium, 8.7 per cent for magnesium,
4.8 per cent for potassium, 21.6 per cent for sodium, and 24.9 per
cent for manganese. The results for the repeated analysis of the four
standard solutions are summarized in Table IV. Using the method
as presently set up, where the procedure is carried out entirely by
manual operations, it was found that the time required for the analy-
sis of the five cations in the sample was less than ten minutes; or
in terms of daily output, an equivalent of at least 240 individual chem-
ical determinations involving considerably fewer manipulations than
would be required for standard analytical procedures for the ex-
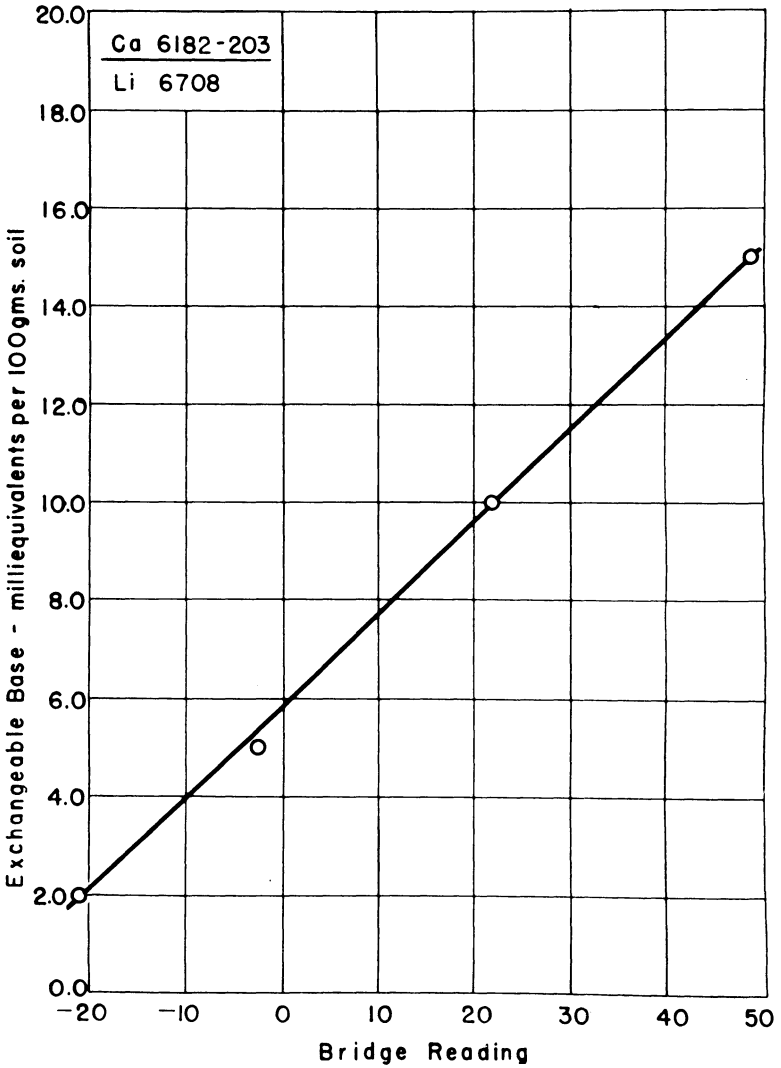changeable cations.

Fig. 3   Working Curve for Calcium

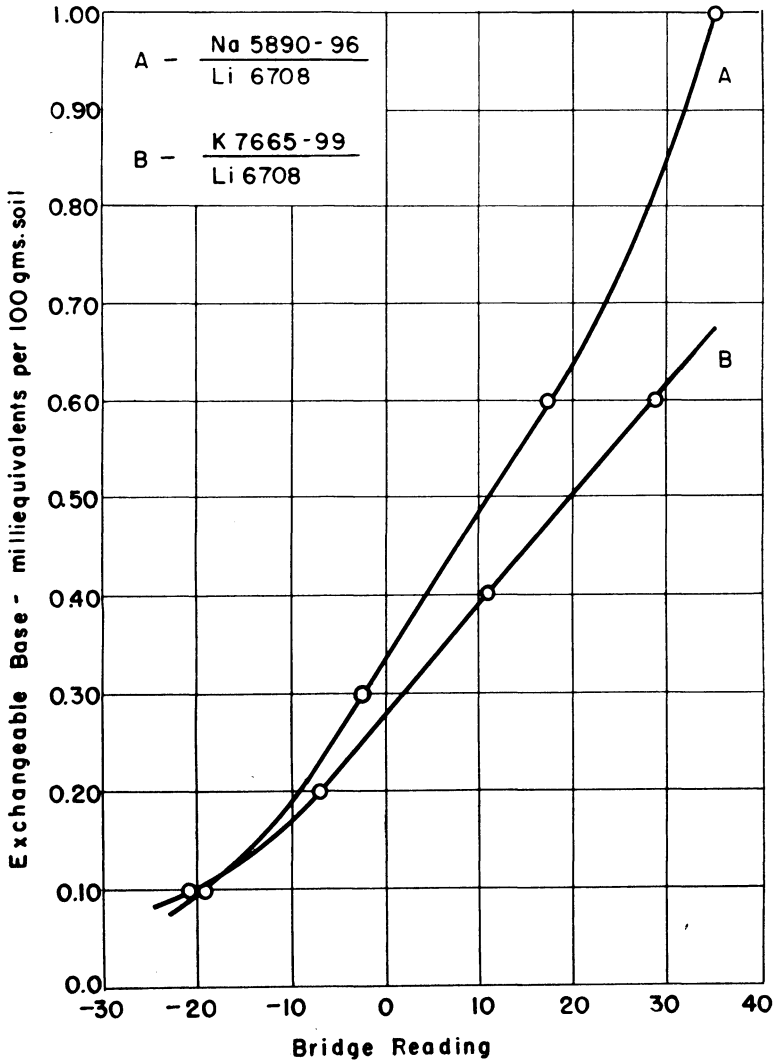Internal Standard 2000p.p.m. lithium

Fig. 4   Working Curves for Sodium & Potassium
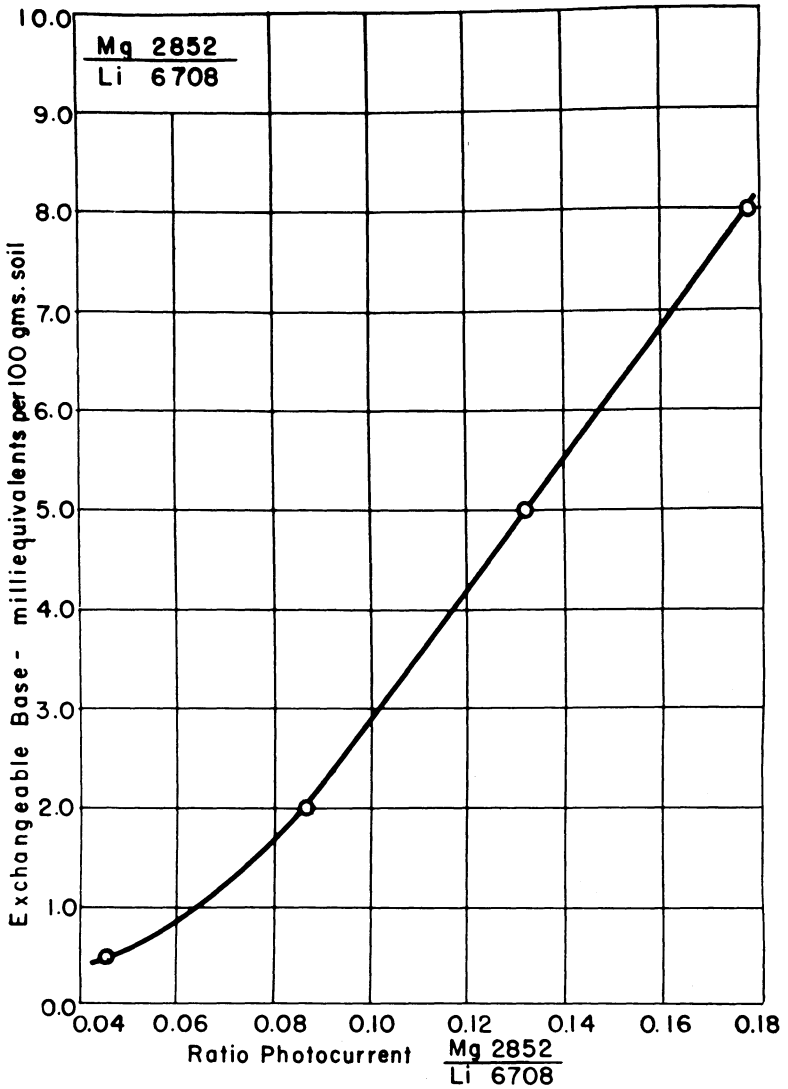
Internal Standard 2000 p.p.m. lithium

Fig. 5   Working Curve for Magnesium

Internal Standard 2000 p.p.m. lithium

TABLE III

Reproducibility of Results Obtained for Repeated Analysis of Solution III

Concentrations in Millïequivalents Per 100 Grams of Soil

Percentage Deviation from Standard

No.	Calcium			Magnesium			Potassium			Sodium			Manganese		
	Bridge Read- ing	m.e.	% Dev.	Ratio	m.e.	% Dev.	Bridge Read- ing	m.e.	% Dev.	Bridge Read- ing	m.e.	% Dev.	Bridge Read- ing	m.e.	% Dev.
1	27.5	11.0	10.0	0.0110	3.5	30.0	13.0	0.42	5.0	21.0	0.64	6.6	-23.0	9.6	4.0
2	26.0	10.8	8.0	0.0134	5.1	2.0	14.0	0.43	7.5	21.0	0.64	6.6	-23.0	9.6	4.0
3	23.0	10.2	2.0	0.0135	5.2	4.0	11.0	0.40	0.0	17.0	0.59	1.7	-17.5	11.5	15.0
4	23.0	10.2	2.0	0.0139	5.4	8.0	12.0	0.41	2.5	17.0	0.59	1.7	-15.5	12.2	22.6
5	17.5	9.2	8.0	0.0135	5.2	4.0	12.0	0.41	2.5	14.0	0.55	8.3	-19.0	11.0	10.0
6	23.0	10.2	2.0	0.0136	5.3	6.0	11.0	0.40	0.0	16.0	0.58	3.3	-21.0	10.1	1.0
7	21.0	9.8	2.0	0.0141	5.5	10.0	10.0	0.39	2.5	16.0	0.58	3.3	-21.0	10.1	1.0
8	23.0	10.2	2.0	0.0132	5.0	0.0	11.0	0.40	0.0	17.0	0.59	1.7	-19.0	11.0	11.0
9	22.5	10.1	1.0	0.0120	4.2	16.0	13.0	0.42	5.0	17.0	0.59	1.7	-22.0	9.8	2.0
10	17.0	9.1	9.0	0.0137	5.3	6.0	13.0	0.42	5.0	17.0	0.59	1.7	-22.0	9.8	2.0
11	20.5	9.7	3.0	0.0124	4.5	10.0	10.0	0.39	2.5	14.0	0.55	8.3	-23.0	9.6	4.0
12	20.0	9.6	4.0	0.0150	6.2	24.0	11.0	0.40	0.0	15.0	0.56	6.6	-24.5	8.9	11.0
Average % Deviation from Standard		4.4			10.0			2.7			4.4				7.2

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TABLE IV

Summary of Results Obtained for Repeated Analysis
of the Four Standard Solutions

Solution	Average Per Cent Deviation from Mean for Twelve Analysis of Each Solution				
	Ca	Mg	K	Na	Mn
I	4.6	11.8	4.7	8.3	56.0
II	6.7	10.2	7.7	4.7	16.5
III	4.4	10.0	2.7	4.4	7.2
IV	4.6	2.7	4.0	69.0	20.0
Average for four standards	5.1	8.7	4.8	21.6	24.9

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