The quantitative spectrographic analysis of soils

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THE QUANTITATIVE SPECTROGRAPHIC
ANALYSIS OF SOILS

by

Ralph Abijah Goodwin

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Applied Physics

Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1939
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I. INTRODUCTION

A. Present Status of Quantitative Spectroscopy

The literature on quantitative spectroscopy describes many methods and techniques for performing an analysis. The careful reader becomes aware of the fact that there are many artificial distinctions made and careless opinions expressed. It seems not out of place, therefore, to preface this paper with a note in regard to these differences.

Harrison (6) has written that, after all, there is fundamentally only one general method of quantitative spectroscopy; the various methods that one finds described in the literature are nothing more than adaptations of this method made to fit the particular problem at hand. The general method, as described by Harrison, consists essentially of the following steps:

1. Preparation of the sample.
2. Excitation of its constituent atoms to emit light of a definite though unknown amount per atom.
3. Analysis of this light by the spectrograph.
4. Photography of these lines under controlled conditions.
5. Determination of the intensity of the light in each line.
The various "methods of analysis" differ from each other only in the way in which the above steps are carried out. For example, one reads of many devices for the excitation of the constituent atoms; in the words of Sawyer and Vincent (17), "One hears of flames, of a-c and d-c arcs, at both high and low voltages, and of condensed sparks of various voltages and frequencies--unidirectional, oscillating, and damped." One finds an even greater variation in some of the other steps.

It is difficult to state exactly what one should expect of any given method of analysis. It is equally as hard to predict whether the technique of one investigator can be profitably applied to the problems of another. Until the techniques and methods of quantitative spectroscopy are more clearly defined and until the causes of such diverse opinions are recognized and overcome, each investigator must determine the validity of his own method. Certainly, in the selection of any method, the test of the experiment is the final one.

B. Statement of Problem

The purpose of this investigation has been (1) to develop a technique for the spectrochemical analysis of soils, using a d-c carbon arc as the spectroscopic source, and (2) to determine the nature of the problems confronting a worker in this field.
procedure in conjunction with the spectrophotometric determination.

Both of these instruments are employed considerable often in solution
mixture of C, Fe, N, K, etc. and in soil solutions.

Landsdred (10) has determined C, N, K, etc. and Fe in soil

concentrated the extracts.

In terms of Generalize without losing specificity, the spectrophotometric analysis of only a few investigations have been made on agricultural

materials. Pitt (2) has reported on the application of spectro

II. THE REVIEW OF LITERATURE

Theoretical method has been successfully applied
Milbourn (12) has analyzed soils as a dry powder; the only preliminary treatment being careful grinding and sampling. He reports "a general quantitative analysis for about 45 elements --- with an accuracy of ± 20 percent." His method of analysis involved the use of a 7-1/2 ampere carbon arc, an arc gap of 1 mm., and synthetic samples, which were prepared by adding a solution of re-crystallized Borax to a mixture of two parts silica and one part alumina.

Oertel (14) investigated the possibilities of spectrographic analysis of soils using a condensed spark as the spectroscopic source. Using the internal standard method (5) and the ratio quantitative system (9) he found that the determination of any minor component of the soil was not affected by varying amounts of the other minor components nor by fairly large variations (of the order of 100 percent and greater in some cases) in the relative amounts of the major components.

Other works of interest to the soil spectroscopist are those of Rusoff, Rogers, and Gaddum (16) on the determination of copper in wire grasses, of Burnstetter, Meyers, Wilkens, and Hein (1) who analyzed some 436 samples of grasses and legumes spectrographically, of Scribner (18) on the detection of rare earths in plants, and of Konishi and Tsuge (7) on the mineral matters of certain leguminous crops.
III. EXPERIMENTAL

A. Materials

1. The spectrograph

The instrument used throughout this investigation was a Bausch and Lomb medium quartz spectrograph. With this instrument the entire spectrum between the wave lengths 2100A and 7000A is photographed on a single plate, 10 inches long.

2. Spectroscopic source and accessories

The arc stand was made in the College Instrument Shop at Iowa State College. Two upright 3/4" brass rods were mounted in a block of 1" steel and insulated from it by fiber bushings. The block of 1" steel was, in turn, mounted on a plate of 1/4" steel which could be screwed or clamped in a permanent position. The electrode supports, which were carried on the upright rods, were made of brass. They had the form of spring forks which grasped the electrodes firmly, holding them in a vertical position. The upper electrode support was mounted on a rack and pinion which was in turn mounted on a heavy brass collar. The lower electrode support was mounted directly on a similar collar. The collars were equipped with set screws and each one
was machined to fit snugly over one of the upright rods. This arrangement made repeated alignments of the spectroscopic source unnecessary. After the correct position for the arc was once determined, the arc stand was screwed to the table and the set screws on the uprights screwed tight. The electrodes could then be interchanged and brought into the correct position by means of the rack and pinion adjustment and an optical system, to be described later.

The carbon electrodes of the arc were purchased from the Dow Chemical Company, Midland, Michigan and fulfilled the highest standards for spectroscopic carbons. The electrodes were prepared, in the manner described by Duffendack and Wolfe (2), by the College Instrument Shop. The rods were cut at right angles to their length, the ends made perfectly flat and smooth, and the corners rounded off with a file. Spectroscopic examination of the electrodes after this treatment failed to show any additional impurities.

The arc was excited by means of a 500 volt storage battery. For a ballast resistance, ten cone-type heater units were wired in series with a 50 ohm rheostat and the combination placed in the circuit. The heater units were mounted on a sheet of Transite and wired so that they could be used as 10 in series or as two groups of five in parallel. In addition, each heater unit was provided with a shunt switch. With this arrangement the current through the arc could be varied from 1.9 to 10 amperes.
3. **Source of standards**

In order that there may be a record of the compounds used in the preparation of the standard solutions used in this analysis, the solutions and the source of the desired element are included in table 1.

**Table 1. Source of elements for standard solutions**

<table>
<thead>
<tr>
<th>Standard solution</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>metal</td>
</tr>
<tr>
<td>Fe</td>
<td>metal</td>
</tr>
<tr>
<td>Mg</td>
<td>metal</td>
</tr>
<tr>
<td>B</td>
<td>H₃BO₃</td>
</tr>
<tr>
<td>Ca</td>
<td>Ca Cl₂</td>
</tr>
<tr>
<td>Mn</td>
<td>MnCl₂</td>
</tr>
<tr>
<td>P</td>
<td>P₂O₅</td>
</tr>
<tr>
<td>K</td>
<td>KCl</td>
</tr>
<tr>
<td>Na</td>
<td>NaCl and NaNO₂</td>
</tr>
<tr>
<td>Mo</td>
<td>(NH₄)₆Mo₇O₂₄ • 4 H₂O</td>
</tr>
</tbody>
</table>

For a standard source of silicon, the writer is indebted to Mr. C. H. Jeglum of the Philadelphia Quartz Company, who kindly furnished a sample of sodium metasilicate which had been re-crystallized to an unusually high degree of purity.
4. Microphotometer

A Moll type microphotometer was used to measure the density of the spectrum lines. It was converted into a non-recording instrument by moving the galvanometer to a convenient place and adding an optical system which provided a light lever of about ten feet and a galvanometer scale that could be read by the operator seated by the microphotometer. The lighthouse and focusing lenses were in such a position as to prevent the operator from closely viewing the area of the place being measured. This arrangement was, of course, most inconvenient when one desired to measure a line which was near several other lines.

5. Photographic materials

Wratten and Wainwright panchromatic plates were used throughout this investigation. The plates were developed in one part of fresh Eastman D-72 and two parts of water at 18°C.

B. Method of Procedure

1. Preparation of soil solutions

The soil solutions were prepared in as simple a manner as possible. A known weight of dry soil, about 15 grams, was placed
in a beaker containing 500 cc. of solvent--water, dilute HCl or NH₄OH. The mixture was kept at room temperature and stirred frequently for about 24 hours. After being filtered, the solution was evaporated to a volume less than 100 cc. and 3.75 grams of very pure NaNO₃ dissolved in it. Finally, 5 cc. of ammonium molybdate solution, containing 0.2% Mo, was added and the volume of the solution adjusted to 100 cc. by the addition of distilled water. Variations from this procedure might well have been adopted but it seemed that the prepared solutions were sufficiently representative for this investigation. The original plan of removing the organic matter from the solutions was abandoned. Several comparisons indicated that its presence did not affect the analyses by a measurable amount.

2. Preparation of standard soil solutions

Several series of solutions were made in which the percentage composition of the elements to be determined was varied over a wide range. Sufficient Na and Mo was added to make their concentration the same in these solutions as in the soil solutions described in part 1. The composition of a typical series is given in table 2.
Table 2. Composition of standard solutions

<table>
<thead>
<tr>
<th>Solution</th>
<th>Na %</th>
<th>Mo %</th>
<th>K %</th>
<th>Al %</th>
<th>Si %</th>
<th>Fe %</th>
<th>Mg %</th>
<th>Ca %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.25</td>
<td>.01</td>
<td>.05</td>
<td>.05</td>
<td>.005</td>
<td>.05</td>
<td>.05</td>
<td>.05</td>
</tr>
<tr>
<td>B</td>
<td>1.25</td>
<td>.01</td>
<td>.01</td>
<td>.01</td>
<td>.001</td>
<td>.01</td>
<td>.01</td>
<td>.01</td>
</tr>
<tr>
<td>C</td>
<td>1.25</td>
<td>.01</td>
<td>.005</td>
<td>.005</td>
<td>.0005</td>
<td>.005</td>
<td>.005</td>
<td>.005</td>
</tr>
<tr>
<td>D</td>
<td>1.25</td>
<td>.01</td>
<td>.001</td>
<td>.001</td>
<td>.0001</td>
<td>.001</td>
<td>.001</td>
<td>.001</td>
</tr>
<tr>
<td>E</td>
<td>1.25</td>
<td>.01</td>
<td>.0005</td>
<td>.0005</td>
<td>.00005</td>
<td>.0005</td>
<td>.0005</td>
<td>.0005</td>
</tr>
</tbody>
</table>

In addition to the series of standard solutions described above, other series were prepared in which the percent composition of only one of the constituents was varied, the other elements being present in a constant amount. Several series included Mn, Cu, and B in addition to those listed in table 2. However, quantitative determinations of these additional elements were not made.

3. Preparation of electrodes for arcing

Experiment showed that it was important to have the entire end of the electrode covered with the solid material. A drop of the solution was transferred to the end of the electrode by means of a glass rod and the electrode dried quickly in an oven. There was a tendency for the solid material to collect around the edges and leave the center of the electrode bare. Rapid drying of the electrode proved to be the best remedy for this uneven distribution of the residue.
4. Preliminary investigations

The relative merits of various combinations of current, arc gap, and exposure time were investigated. The arc burned very steadily for currents less than 5 amperes and an arc gap of a millimeter or less. In addition to burning erratically, higher current and longer arcs produced considerable band structure and general background even for equivalent short exposure. No real reasons were in evidence for the use of large arc currents, and it seemed advisable to use as small a current as possible in order to utilize the ballast resistance to its fullest extent.

An arc gap of .75 mm. and a current of 2.5 amperes were adopted as standard. This arc burned so steadily that current fluctuations of more than ± .02 amperes were rarely observed on a Weston D.C. Ammeter, Model 45 (range 0 to 3.0 amperes) in the circuit.

The lines used for determining the test elements were of such intensities that all of the analyses could be made from a single exposure and without a condensing lens. The one exception was silicon, which usually occurred in such dilutions that a condensing lens was necessary.

5. The standard procedure

The electrodes were placed in the spring forks of the arc stand and then adjusted to the correct height by means of the
optical system. The correct position for the arc had been previously determined, and, with the electrodes in place, a magnified shadow image of the electrodes was produced on the wall. Lines drawn around the image marked the position of the electrodes and the width of the arc gap. The electrode image was produced by a large glass lens, a frosted incandescent lamp being placed behind the arc and in line with the center of the lens. The entire process of removing the old electrodes, cleaning the holders, inserting and adjusting the positions of a new pair of electrodes required about two minutes.

The upper, negative, electrode was first inserted in its fork. The lower electrode, which carried the sample to be analyzed, was then inserted and adjusted to the correct height after which the upper electrode was lowered into position by the rack and pinion arrangement. With the electrodes in place, the arc was shunted by a switch and the ballast resistance allowed to heat for 60 seconds. At the end of the 60 seconds, the shunt switch was opened and the arc ignited by shorting with an auxiliary carbon rod. After 30 seconds of burning, the shutter over the spectrograph slit was opened and the desired exposure made. The slit used was 5 mm. long and opened to a width of about 0.04 mm. Pre-burning of the electrodes is not used by all investigators, but such treatment was found to add considerably to the reproducibility of results.
After all the desired samples had been photographed, the plate was developed for three minutes at 16°C. For development two parts of water and one part of fresh Eastman D-72 were used.

After the plate had been dried in a dust-proof cabinet, the densities of the spectral lines were measured on the microphotometer. Three readings were made for each line, a reading on the clear plate next to the line, the line reading, and another clear plate reading. The difference between the line reading and the average of two clear plate readings was taken as representing the intensity of the line. Most of the lines measured were in a region where background was a minimum and no other attempt was made to correct for it.

Since this research was partly exploratory, the intensities of most of the available lines of each element were measured. Working curves for each pair of lines of interest were then prepared. By a working curve, the writer means a graph in which the log ratio of intensity of a test element line to the intensity of an internal standard line is plotted against log percent composition of the test element. Such curves are shown in figures 1 to 8, inclusive.

The percent composition of a test element in the unknown solutions is read directly from the working curves after the log ratio of two corresponding lines has been determined.
6. The analysis of dry powders

Several months were spent investigating the technique for analyzing the soil as a dry powder by spectrographic methods.

The organic matter was removed from the soil and analyses made with and without the use of an internal standard. The same apparatus and materials as previously described were used for this work. Standard mixtures were prepared by using pulverized and finely ground quartz for the silica content, adding the other constituents in the form of solutions and evaporating the mixtures to dryness. Each mixture was then carefully homogenized in a mortar and 15 mgm. samples used in the arc. Analyses by this scheme proved too discordant for quantitative use.

It was evident that the variation in the relative amounts of silica and alumina in the samples was markedly affecting the spectra of the minor constituents. This fact was in contradiction to the results of Oertel (14), but, nevertheless, it seemed advisable to determine the relative amounts of silica and alumina in a soil before attempting an analysis for the minor constituents. The most difficult task was to prepare samples in which the silica was uniformly distributed. The silicous materials available at the time were too impure to use as standards. The following plan proved to be satisfactory: A sample of pure crystalline quartz was carefully pulverized and ground until the particles were extremely small. This
powdered quartz was then placed in a beaker of distilled water, and, after one hour, the liquid was decanted. When this liquid was evaporated to dryness, the residue furnished a supply of very finely divided silica which was used in the preparation of the synthetic mixtures. Several decantations and evaporations were necessary to obtain a sufficient quantity of this material but the time seemed well spent.

Synthetic samples were then prepared which contained from 0.1 to 2.0 percent silica and appropriate amounts of the other constituents of the soil. The matrix, which constituted more than 97% of the total weight of each sample, was very pure Sr(NO₃)₂.

A known weight of Sr(NO₃)₂ was added to a sample of soil from which the organic matter had been removed so that the estimated silica content would lie within the range of the prepared working curve. Sn and Zn were used as internal standards when that method was used for the analysis.

Repeated analyses were made of the same soil sample. For these analyses, 15 mgm. samples were placed in a crater in the positive electrode of an arc of 4.8 amperes. The ends of the electrodes were separated 1 mm. and no condensing lens was used.

The data showed that, when Sn was used as the internal standard, the silica and alumina determinations agreed within 15 to 20 percent. In some cases, the agreement was within 10 percent for four determinations. However, even with the utmost
of care, divergent results occurred too frequently to say that the method could insure even 20 percent accuracy for a single determination.

This problem is worthy of further study but it was abandoned in its present state in favor of the analysis of soil solutions, the latter problem being more pertinent to the soil scientist.

C. Results

The working curves used for the quantitative determination of Si, Fe, Al, Mg, K, and Ca are shown in figures 1 to 8, inclusive. The relations shown in figures 1 to 5 were obtained when the exposures were made without a condensing lens. Figures 6, 7, and 8 are the curves obtained when a condensing lens was used. The same Mo lines were not used as reference lines in both cases because the Mo lines at 3132Å and 3170Å were over-exposed in the latter case.

The points obtained when Mo 3193Å was used as a reference line for the determination of Si are shown in figure 1. The deviation of these points from a straight line in the particular case is typical of the curves obtained when Mo 3193 was used.

The lines used and the range of concentrations of the elements quantitatively determined in this investigation are shown in table 3. The range of analysis listed does not, in any sense, indicate the upper or lower limit of the terminations
by the spectroscopic method. They do indicate, however, the range which has been investigated by the writer.

Table 3. Lines used and range of concentrations covered in the analysis of soil solutions

<table>
<thead>
<tr>
<th>Element</th>
<th>Test</th>
<th>Work</th>
<th>Range of analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2831</td>
<td>3112</td>
<td>.00005 - .008</td>
</tr>
<tr>
<td>Si</td>
<td>2881</td>
<td>3132</td>
<td>.0003 - .01</td>
</tr>
<tr>
<td>Si</td>
<td>2881</td>
<td>3170</td>
<td>.0003 - .01</td>
</tr>
<tr>
<td>Al</td>
<td>3092</td>
<td>3112</td>
<td>.0005 - .04</td>
</tr>
<tr>
<td>Al</td>
<td>3092</td>
<td>3170</td>
<td>.001 - .050</td>
</tr>
<tr>
<td>Al</td>
<td>3092</td>
<td>3132</td>
<td>.001 - .050</td>
</tr>
<tr>
<td>Al</td>
<td>3944</td>
<td>3903</td>
<td>.01 - .30</td>
</tr>
<tr>
<td>Al</td>
<td>3961</td>
<td>3903</td>
<td>.01 - .30</td>
</tr>
<tr>
<td>Fe</td>
<td>3020</td>
<td>3112</td>
<td>.0001 - .01</td>
</tr>
<tr>
<td>Fe</td>
<td>3020</td>
<td>3132</td>
<td>.001 - .010</td>
</tr>
<tr>
<td>Fe</td>
<td>3020</td>
<td>3170</td>
<td>.001 - .010</td>
</tr>
<tr>
<td>K</td>
<td>3217</td>
<td>3152</td>
<td>.001 - .10</td>
</tr>
<tr>
<td>K</td>
<td>3217</td>
<td>3170</td>
<td>.001 - .10</td>
</tr>
<tr>
<td>Ca</td>
<td>3933</td>
<td>3903</td>
<td>.0001 - .15</td>
</tr>
<tr>
<td>Mg</td>
<td>2795</td>
<td>3132</td>
<td>.00010 - .10</td>
</tr>
<tr>
<td>Mg</td>
<td>2795</td>
<td>3170</td>
<td>.0001 - .10</td>
</tr>
</tbody>
</table>
FIG. 1 WORKING CURVES FOR Si

LEGEND:
I ~ Si 2881
Mo 3132
II ~ Si 2881
Mo 3170
x ~ Si 2881
Mo 3193
LEGEND:

**FIG. 2 WORKING CURVES FOR Fe**

I ~ Fe 3020  
   Mo 3132

II ~ Fe 3020  
    Mo 3170
**FIG. 3 WORKING CURVES FOR AL**

**LEGEND:**

I \( \sim \) \(\frac{AL 3092}{Mo 3170}\) \hspace{1cm} II \( \sim \) \(\frac{AL 3092}{Mo 3132}\)

III \( \sim \) \(\frac{AL 3944}{Mo 3903}\) \hspace{1cm} IV \( \sim \) \(\frac{AL 3961}{Mo 3903}\)
FIG. 4 WORKING CURVES FOR Mg

LEGEND:

I ~ $\frac{Mg}{Mo}$ 2795
II ~ $\frac{Mg}{Mo}$ 3170
FIG. 5 WORKING CURVES FOR K AND Ca

LEGEND:

I ~ $\frac{K}{Mo} 3217$  
II ~ $\frac{K}{Mo} 3217$  
III ~ $\frac{Ca}{Mo} 3933$
LEGEND:

\[ I \sim \frac{Si \ 2881}{Mo \ 3112} \]

\[ X \sim \frac{Si \ 2881}{Mo \ 3122} \]
LEGEND:

I~ AL 3092
Mo 3112

X~ AL 3092
Mo 3122.
FIG. 8 WORKING CURVE FOR Fe

LEGEND:

I ~ Fe 3020
Mo 3112

X ~ Fe 3020
Mo 3122
IV. DISCUSSION

A. The Method of Analysis

Although the method of analysis described in this thesis has been used successfully for the determination of certain elements in soil solutions, it has several objectional features. The data available indicate that for the determination of Si, Al, Fe, Mg, K, and Ca the accuracy is between 10 and 15%. Greater accuracy than this might be attained if the technique were applied to the routine analysis of soil solutions, but the 10 to 15% accuracy is a tolerable figure for a method using a d-c arc.

Many factors influenced the selection of the spectral lines which were used as reference lines, but the final choice was determined by experiment. It was not always possible to choose the lines which have been generally used for the determination of a particular element. Potassium and calcium are usually determined by comparing the lines K 4044Å, K 4047Å, and Ca 4226Å to a suitable internal standard line. These lines did not give consistent results during the analyses made and the K 3217Å and Ca 3933Å lines were substituted for them. The K 4044Å, K 4047Å, and Ca 4226Å lines were masked by a considerable amount of background for which it was impossible to
correct properly. When the Mo 3158.15Å line was used as a reference line the results were discordant. A possible reason for this may be its proximity to the Ca line at 3158.87Å and the presence of a considerable amount of Ca in all the solutions analyzed.

In its present state of development, the technique used in this research is incomplete in several respects. A more thorough investigation of the effect of the organic matter upon the analyses should be made as well as the effect of the addition of sodium, in large excess, upon the sensitivity of the method. The practice of adding a large excess of some element with a low ionization potential to the sample is recommended by Langstroth and McRae (8). The primary purpose of this spectroscopic buffer, the large excess of sodium in this case, is to stabilize the arc. However, it may have an undesirable effect upon the limits of detection of the various elements. The magnitude of this effect could be determined by analyzing the solutions without using a spectroscopic buffer.

B. Problems in Soil Analysis

Several of the problems confronting a worker in this field have been mentioned in part A of this section. From the standpoint of spectroscopic technique, the analysis of soil solutions should not be more involved than the analysis of any complex solution. However, many of the important spectral lines of the
soil elements lie in a region which is not available in a method using a low voltage, d-c, carbon arc because the cyanogen bands obliterate a large portion of the region between 3800A and 4200A. This difficulty might be overcome by concentrating the solutions so that short exposures could be made. A more logical cure would be the use of a different spectroscopic source. High voltage sources suppress the cyanogen, or air bands, to a great extent and for this reason, among others, should be investigated as possible spectroscopic sources for soil analysis. The recent successful application of the high voltage a-c arc to the analysis of a wide variety of materials (2) makes it a worthwhile object of study. The writer thinks that, although a satisfactory method has been developed using the low voltage d-c arc, its continued use in this field is probably not to be recommended. Certainly a more convenient method can be found.
V. SUMMARY AND CONCLUSIONS

A technique for the spectrochemical analysis of soils using a d-c carbon arc as a spectroscopic source has been developed. The arc was excited by a 500 volt storage battery; a 1 mm. arc gap and 2.5 amperes were used. The soil solutions were analyzed by comparing their spectra to the spectra of synthetic solutions which contained the elements in known amounts. Molybdenum was used as an internal standard in all solutions. Si, Al, Ca, K, Fe, and Mg were determined with an accuracy of 10 to 15%.

Several problems in technique have been suggested for future work in the analysis of soil solutions by spectroscopic methods. Although the possibilities of this method of analysis have not been entirely exhausted, the success of the high voltage a-c arc as a spectroscopic source for the analysis of other complex solutions indicates that it might be a more suitable means of exciting the arc than the method described in this thesis.
VI. LITERATURE CITED


4. Fitch, A. A. Spectrum Analysis in Mineralogy. Adam Hilger, Lt'd., London. 1930 (?).


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