Thesis
on
Value of solvents in Soil Analysis
for
Degree of B. S.
in
School of Chemistry
By
L. P. Kenoyer
May 1883
The value of Solvents in Soil Analysis.

When science first began to give attention to the chemical analysis of soil, they seemed not to have realized the intricacies of the problem.

Davy, at the beginning of this century, delivered a course of lectures upon the science of chemistry, among which is one on the analysis of soil to determine its agricultural value. He says: "The instruments required for analysis of soil are few and little expensive; they are, a balance capable of weighing with a grain, a cien, Argand lamp, glass bottles, hessian crucibles, a porcelain evaporating dish, pestle and mortar, filter-paper and tom knife." Such were the apparatus with which he proceeded to analyse soil and this is the way he proceeded.
The soil was washed well in water, and after thoroughly mixing it, was allowed to stand, thus separating the coarser particles which he called "silicious." The finer portion that remained suspended in the water was collected and treated with twice its weight of HCl and diluted to double its volume. It was then allowed to stand for a time, filtered, dried, and weighed. The difference in weight representing the amount dissolved. The solution is treated with "Pruss of Potash" to throw down the Fe. The Ca is taken with Na₂CO₃, and the Mg by boiling the solution from the Ca. Such was the crude and elementary mode of analysis recommended by Davy in 1812.

After this, no little advances seem to have been made for the next forty years. In Johnston's "Elements of Agricultural Chemistry," edition of 1853, he says:—"Chemical analysis is a difficult art, one that demands much skill in manipulation as well as chemical knowledge, and it is only by aiming at minutely correct results that chemical analysis can hope to throw light on the
frequent importance of these evils which though similar in composition differ greatly in their agricultural values.

About this time "Practical Chemical Manipulation & Analysis" appears, in which he recommends digesting the soil with HCl and filtering and washing and preceding it analysis the manner very much as we do now.

Living in his "Complete Works on Chemistry" explains the action of HCl and CO2 and how they are beneficial to the soil.

In the 1855 edition of "Boussingault's Rural Economy" he says it had long the practice to burn off the fumes in order to determine it. Priestly and Arthur Young recommended fungus in closed vessels and collecting the gas. These trials as unsatisfactory on account of other chemical changes that take place when burning. "Boussingault" recommends an ultimate analysis of the soil by burning it in CO2 in a current of oxygen.

Later, we find Sprengel & De Cosa taking another step and asserting that, as means not only known the elements of the soil,
but their combination. They treat the soil successively with KO
2H SO3 andLastly by fusion with alkaline carbonate.
Their theory was that the constituents soluble in KO were
immediately available as plant food. Those soluble in the acids
available after suction of CO2 and humic acid of the soil.
The remainder only after suction for some time to cultivation
and the action of the atmosphere. They supposed that substances
must be in solution in order to be available as plant food.

In 1873 Bajard devised an ingenious apparatus by which
he imprints to improve on the celito analysis. It was by keeping
a curule during in motion and thus stirring the suspended soil
constantly, by which he claimed to have secured better and more
accurate results than by the old method.

Brandew in this time suggests the use of
H2CO3 as a solute, and employs it in his analyses and
evaluation of the black coals of Russia.

The solute then, that will most nearly repre-
the materials available to future food has been the object of
search for the chemist and upon this line his find a
great diversity of opinions.

Among the extracts that have been recommended
are Agna regia, Cinh Hel, the Hel of different strengths, NH4Cl
and HCl. These dissolved in water and tare of all Hell.
The apparent difference of opinion concerning the color
of their extracts which gives some 22% to 27% of solubly
material (or even greater in the case of Agna regia) led me to
the premises study of the subject.

In any experiment I have taken Hel, NH4Cl, HCl, C6H5
2% C6H5 saturated solution and lastly H2O, and determined
the percent of the different substances dissolved by them, for the
purposes of comparison.

Hel seems as favorable a extract as is worthy of
consideration. For its uses to appear at any one that
brings the soil to depression with Cinh Hel or even digesting for
on a water-bath is unreasonable. I have therefore taken the
four other named chemicals for the purpose of containing their
relative values.

The sample shown for analysis was, I think, a
virgin soil never having been plowed. It was taken
from the edge of the v.C.R.R. about a mile south of the
farm. After taking off two or three inches of the surface
soil, from which it was seen the various soil from the pass,
a hole was dug to the depth of a foot and the soil
taken from it reserved as a sample. The soil was air-
dried. It was then ground tightly in a large porcelain
mortar and sifted through a number of sails, to take out
roots and small pebbles. The latter was carefully washed
dried and weighed, and was found to be 2% of the whole.
This portion was discarded and that which passed through
the sieve taken as the specimen for analysis.

From the soil thus prepared there was taken
for the different analyses amount as follows:

- HCl and H₂CO₃ 200 c.c. 200 c.c. HCl
- CO₂ 200 c.c. 200 c.c. H₂O + CO₂

These were allowed to stand from 4 to 5 days to a week when they were filtered off with a fine dry filter. The solution was then brought to an excess of a weak solution of a silver nitrate in a platinum dish and weighed to estimate amount of soluble matter. The residue was then gently heated to dry and then added and again treated and weighed showing amount of insoluble matter soluble.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>HCl</th>
<th>H₂CO₃</th>
<th>CO₂</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic</td>
<td>4.055</td>
<td>.3086</td>
<td>.0241</td>
<td>.018</td>
</tr>
<tr>
<td>Mineral</td>
<td>2.1321</td>
<td>.1186</td>
<td>.0894</td>
<td>.253</td>
</tr>
<tr>
<td>Total</td>
<td>6.1871</td>
<td>.4262</td>
<td>.0538</td>
<td>.0359</td>
</tr>
</tbody>
</table>
The table given on the preceding page shows the
presence of organic, mineral, and total matter found in the
residues from the different solutions. It will explain
itself.

The residue remaining after the organic matter
is burned off, is treated with HCl and washed into a porcelain
dish, a few drops of HClO₃ added to oxidize the Fe present. It
is then brought to complete dryness. HCl again added and
digested for sometime on a water-bath, then diluted and
filtered, and thoroughly washed. The residue from the filter
is estimated as soluble silicious matter.

The filtrate from the silicious matter was tested with
AgS for any thing in that group, but in no case was any
thing found. The P, Fe and Al were then taken with HClO₃
and filtered; the residue dissolved in HClO₃ and divided into
two portions, which we shall distinguish as solutions A and B.
The Fe and Al were taken from solution A with HClO₃ and H₃O₇ as before.
filtered, ignited and weighed. It is then dissolved in aqua regia and the Fe estimated volumetrically and the Al estimated by difference. The P in solution is first driven off with HCl, evaporation of NH₄OH, filtered, dissolved in NH₄OH and precipitated with magnesium nitrate. Filtered, dried, and weighed.

The solution that remained from the first step of P, Al, and Fe was tested for the estimation of Mg, MgCa, and Fe. It was first treated with Br⁻ and titrated, which threw down the Mg. This was filtered off and estimated in the usual manner.

The Magnesium is then thrown down with Na₂HPO₄, allowed to stand 24 hours and re-estimated in the usual way.

I thought at first that by the use of NH₃ salt instead of Na or K for magnesium in the work described above, I could estimate the Na or K from the solution remaining. I found however in practice that it was almost impossible to keep the solution free from Na or K, and also
of \( \text{KSO}_4 \) as my perchlorate, especially in the last case over 100\% large. I therefore prepared solutions with the different
extracts in the same proportions as before, for the estimation
of \( \text{KSO}_4 \) and the alkalies. The \( \text{KSO}_4 \) was first with BaCl
The excess of BaCl was from the concentrated solution with \( \text{HCl} \).
Then an excess of HCl added and brought to dryness in a Pt
dish, and gently heated to drive off the HCl gases; it was then
dissolved in water and (if necessary) filtered to secure a clear
solution; then a few drops of HCl is added and brought to dryness
and weighed as \( \text{KCl} \) or \( \text{HCl} \). The \( \text{KCl} \) is then fused in the
ordinary manner with PtCl and estimated. The \( \text{KCl} \)
may then be estimated by difference.

Having thus obtained the amount of the different
substances dissolved by its respective solvent, it was now
necessary to make a complete analysis of the oil as a whole.
For this there was taken for general analysis
2 grams, and for \( \text{H_2O} \), \( \text{alkaline} \) and \( \text{organic} \) matter 2 grams.
General Estimation: The two grams were fused with an equal mixture of K$_2$CO$_3$ and Na$_2$CO$_3$. The fused mass was digested for some time with water in a porcelain dish. Then an excess of KOH added and brought completely to a depression. Again it was treated with acid and water—digested for a time and filtered. The residue is estimated as SiO$_2$. The solution from the Si was treated almost exactly according to the process given above for the extract of soil.

The remaining two grams were then heated in an air oven for several days at a temperature of 110°C until the weight became constant. It was then heated gently to drive off the organic matter—then moistened with 1 M KOH to convert the Ca to CaCO$_3$, gently heated and weighted. It was then taken for estimation of alkalis. It was first mixed with two grams of NaOH and 2 parts of pure BaCO$_3$ and then heated in a long fire crucible for an hour or more. The mass is then treated with water in a porcelain dish.
digested for a time and the lime filter with 0.4% CCl₂ and filtered off, after which the 7% salt may be drawn off and the 
Na₂CO₃ estimated as above.

Litharge. — The total nitrogen of the soil
was estimated by burning 6 grams of the soil in a tube in the
ordinary way. For the titration I prepared a very dilute
solution of K₂CO₃ of which 38.8 cc. = 0 cc. Normal H₂SO₄

Ammonia. — The amount of N₂H₃ present
in the soil was determined as follows: — Thirty grams
of soil was filled in the
flask of and about 10 cc.

of MgO and H₂O Enough to
cover well. YB is a flask
containing warm water and
is intended principally to favour stirring the solution by the
flowing back and forth of the liquid in G which I found to be very
hard to foresee. In $G$ is 0.75 c.c. of Standard $\text{H}_2\text{SO}_4$ and diluted.

Add $B$ and keep boiling. Thus the ammonia of the acid is driven off by the $\text{H}_2\text{SO}_4$ and is carried over to neutralize part of the acid of the flask $G$. The amount of acid neutralized by the ammonia is thus determined by titration with the dilute standard $\text{KOH}$ used in the titrations above.

Amount of Nitrogen found | 0.18 | 0.192
Amount of Ammonia found | 0.035 | 0.04
Tabulated results of analyses.

<table>
<thead>
<tr>
<th></th>
<th>Total analysis of 8 soil.</th>
<th>1% HCl Solution</th>
<th>1% H2 CO3 Solution</th>
<th>CO2 Solution</th>
<th>H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic</td>
<td>4.71</td>
<td>4.83</td>
<td>3.08</td>
<td>0.24</td>
<td>0.13</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>1.42</td>
<td>1.00</td>
<td>0.01</td>
<td>0.001</td>
<td>0.0006</td>
</tr>
<tr>
<td>Al2O3</td>
<td>12.53</td>
<td>1.09</td>
<td>0.39</td>
<td>0.23</td>
<td>0.032</td>
</tr>
<tr>
<td>MgO</td>
<td>3.602</td>
<td>0.03</td>
<td>0.17</td>
<td>0.13</td>
<td>0.018</td>
</tr>
<tr>
<td>CaCO3</td>
<td>4.92</td>
<td>2.35</td>
<td>0.03</td>
<td>0.09</td>
<td>0.039</td>
</tr>
<tr>
<td>H2SO4</td>
<td>1.324</td>
<td>1.13</td>
<td>0.14</td>
<td>0.065</td>
<td>0.025</td>
</tr>
<tr>
<td>H2O</td>
<td>1.5269</td>
<td>0.412</td>
<td>0.092</td>
<td>0.079</td>
<td>0.077</td>
</tr>
<tr>
<td>Na2O</td>
<td>1.2766</td>
<td>0.125</td>
<td>0.046</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2O5</td>
<td>0.14</td>
<td>0.08</td>
<td>0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO2</td>
<td>70.3876</td>
<td>2.00</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na2CO3</td>
<td>4.00</td>
<td>1.357</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td>2.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

97.9724
In order to determine the amount soluble in solutions of different jermacite solutions, I made the following determinations.

<table>
<thead>
<tr>
<th>Strength of Soln.</th>
<th>Saturated Soln.</th>
<th>10% Soln.</th>
<th>5% Soln.</th>
<th>2.5% Soln.</th>
<th>1.5% Soln.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Org. Ash</td>
<td>1.48</td>
<td>1.14</td>
<td>1.04</td>
<td>0.75</td>
<td>0.69</td>
</tr>
<tr>
<td>Pel. 25.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H Cl</td>
<td>1.39</td>
<td>3.72</td>
<td>1.73</td>
<td>1.02</td>
<td>3.01</td>
</tr>
</tbody>
</table>

From the above analyses we see that the amount of mineral matter dissolved by different solutions of $NH_2CO_3$ increases regularly while the organic reaches its maximum at about 10%. The HCl solutions are seen to increase regularly in amounts dissolved of both organic and inorganic.

Taking then the amount soluble in a 10% solution of $NH_2CO_3$ as available matter for plant food, we have in an acre of ground one foot deep, 10.810 Kilograms, or about 21.6 cwt. And in all HCl 4337.698 Kilo., or about 8075.3 cwt.
Continuing these calculations I have estimated the weight of the different substances collected in various portions from an acre of ground. Thus, by comparing the amounts taken off by an average crop, it will not be difficult to make an approximate estimation of the time the soil will (chronically) furnish the crop within any thing they return.

<table>
<thead>
<tr>
<th></th>
<th>Grain</th>
<th>Staw</th>
<th>Total</th>
<th>Grain</th>
<th>Stawk</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>48.00</td>
<td>104.</td>
<td>152</td>
<td>42</td>
<td>126</td>
<td>168</td>
</tr>
<tr>
<td>AlK.s</td>
<td>17.12</td>
<td>12.</td>
<td>29.12</td>
<td>17.6</td>
<td>46.9</td>
<td>64.5</td>
</tr>
<tr>
<td>Mgo</td>
<td>5.10</td>
<td>2.7</td>
<td>7.7</td>
<td>5.8</td>
<td>7.1</td>
<td>12.9</td>
</tr>
<tr>
<td>CaO</td>
<td>1.60</td>
<td>0.7</td>
<td>2.3</td>
<td>5</td>
<td>13.8</td>
<td>15.3</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>1.24</td>
<td>9.3</td>
<td>11.7</td>
<td>-</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>P2O5</td>
<td>21.36</td>
<td>4.4</td>
<td>25.76</td>
<td>14.58</td>
<td>10.4</td>
<td>24.9</td>
</tr>
<tr>
<td>SiO2</td>
<td>36</td>
<td>71.22</td>
<td>107.2</td>
<td>1.8</td>
<td>36.2</td>
<td>38.0</td>
</tr>
</tbody>
</table>
The table below shows the amounts in lbs. of materials in one acre of ground by the different chemicals.

<table>
<thead>
<tr>
<th></th>
<th>Alk.</th>
<th>MgO</th>
<th>CaO</th>
<th>FeO</th>
<th>P2O5</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH42CO3</td>
<td>33000</td>
<td>9000</td>
<td>2000</td>
<td>1600</td>
<td>540</td>
</tr>
<tr>
<td>CO2</td>
<td>4740</td>
<td>2100</td>
<td>5400</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td>4620</td>
<td>1100</td>
<td>2400</td>
<td>400</td>
<td>-</td>
</tr>
</tbody>
</table>

From the above table and the one on the preceding page, it will be seen that for most substances, the amounts soluble from the soil by alkali CO2 or MgO are far in comparison to the amounts taken out by the crops. As, for instance, it will take 1000 years for wheat to exhaust the alkaline soluble in \((NH4)2CO3\). On the other hand, however, the P2O5 will be exhausted in 20 years. Of course this is not entirely reliable, nor do we pretend to say that the soil remains...
will produce where so many years as the table indicates.

But it shows the relation of the amount in the soil to
that taken off by the average crop.
Estimation of Nitro Acid.

As a sort of appendix to this work, I thought it proper to give special attention to the estimation of HNO₃ in soil, it being found in such small quantities and at the same time is of such great importance in the agricultural value of soils, the subject upon which much work and thought is given.

Many methods are given for the estimation of HNO₃ in soil, but none seem to be accurate enough and as the same time simple enough in its operation for practical work. The method described in the English edition of Forsinins, by Schütze, is used perhaps as much as any and seems to be as convenient as any I have seen described. It is operated upon the principle of generating H₂ gas with HNO₃ and Al., ascertaining by exhausting the amount of H₂ given off by a certain weight of Al.
also the amount taken up when a nitrate as KN3 is present in known quantity, it may then be found the amount of nitrate present in small quantities as in

end. It was my intention to test the accuracy of this process, and if found sufficiently accurate for the delicate work required, to devise a piece of apparatus by which the gas from off could be measured much more closely than by any method I have ever seen.

For this purpose I invented a buret with a glass tap, in a mercury trough. The buret consisting as a kind of syphon, which could be filled by allowing the Hg up and then turning the tap.

A small (10-20) bottle furnished with a delivery tube for transferring the gas to the inverted buret, contain a small quantity of a solution of KHO (about 30% sol). The bottle is so arranged that a weighed quantity of

Ah. of KN3 may be immersed in the KHO at pleased.
The gas thus given off passes out of the delivery tube into the
innertube buret, replaces the B.g. and may be read off by the
scale marked on the buret.

By inserting the buret inside a calomelometer, the
readings of the air may be very accurately compared.
and thus may be found the number of mm. in each c.c.
of the scale. It may thus be ordered to the formula for
gas analysis by reducing all measurements to mm. The
"volume" used is the c.c. and any accurate measurement
may be made. Then by reducing the reading from c.c. to
mm. and using Bunsen's formula for reducing to
normal pressure for temperature, any accurate measurement
of the gas may be made.

With this apparatus we made a great number
of experiments, and found that the amount of gas given
off by the same weight of H. in different experiments was
not constant. The weight of H. used in each experiment
was 12 grams. The amount of 1 gram of carbon dioxide
in a c.c. was generally from 0.05 to 0.06. This variation
in its density is not important for practical work. I tried to find when the
mass was, I made my connections and by immersing
the tube with stopper and connections wholly under water,
air by forcing a few cubic inches of water in the delivery tube
above the ends of the immersed buret, it was shown to be perfectly
light. I then filled my Al and found it to be very
uniform, having a large quantity of Fe in it. I next filled
the Al and mixed the filezgo thoroughly, thinking that if the
mass was not uniformly mixed Fe in it is afraid it would
so in this way, this again made no difference. I also
tried using water instead of SJ but found it no difference.
Again I thought to remove the last trace of a doubt.
I made sure make the pressure of the gas removed the
pressure of the SJ on the orifice of the delivery tube, but
would make the delivery tube extend to the very tip of the buret.
Thus having the tension of the gas in the tube and the £. of the breath the same, and when the Al was immersed in the KHO the py. began at once to fall. This again was of no avail. The tests from experiments thus were made with the Al in fine water mixed filings, long delivered to a 9c. max. £. 0.5 - 0.0 - 0. - 0. 6, such results made it certain for practice.

And much as I dislike negative results in a series of experiments I must conclude that the estimation of £. by the measurement of $t$ taken off when generated by Al and KHO is not trustworthy in any sense with the Al that I used, which seems a very inmaterial qualification as the Al was made fine and thoroughly mixed. I see no other conclusion than can be drawn. I have noted every plausible objection that preceeded itself, either in the apparatus itself or in the substances. The apparatus is undoubtedly capable of very accurate work which reveals a faculty process.
The apparatus shown on the next pages is the principal part of that used in the experiments on the \( \text{Al} \) process. At the left is shown the tunnel bucket made from a platinum cone, encased from the end of a glass and then slides through the bolt in the outer cloths, thus enabling the bucket and contents to be immersed as will as in the \( \text{KNO}_3 \).

In using the apparatus the clothes and bucket are removed from the bottle, as shown in the left of the pages. The original \( \text{Al} \) (and \( \text{KNO}_3 \) when desired) is placed in the bucket and the rod drawn up so that the bottom of the cone comes in touch with \( \text{KNO}_3 \) solution in the bottle. They are again refitted, the end of the bucket immersed in a \( \text{HF} \) users, and the \( \frac{1}{2} \) ounce of \( \text{HF} \) users until the bucket is free, and the tap turned. The rod may now be pushed down, and the bucket and contents.
immersed in the XHCl. The H₂ gas on the wire begins to come off causing the HCl to form in the beaker.

The XHCl should be about 30% or more, and should be changed in the beaker at the end of each operation. The solutions may be reserved, however, as long as an XHCl is used, and may be used several times. The object in changing is to keep the same strength solution throughout the same series of experiments.

The H₂ should be in fine filigree. The operation, if the H₂ is fine, will be complete in an hour.