

Specificity?

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Beginning with the basic technology first described under DOE Contract DE-ACO7-84ID-12518 (1984), Aguila Corporation initiated the complete suite of soil sensing technology now embodied in Crop Technology's Soil Doctor system.

Pertinent educational details are available in both the Phase I (NTIS) and II reports ([download](#)) prepared under this contract, and, more particularly, in U.S. Patent #5,033,397. Subsequent extensions of the initial technology are described in the specification and claims of continuing U.S. Patents #5,673,637, #6,138,590, and other patents pending.

Although one can garner the necessary materials by reading these documents, for over ten years many persons, including scientists, have ignored these available materials. By and large, scientists are not prone to discoveries on their own, and when one is presented to them that is not documented in an easily thumbed-to index, many of them simply discount the discovery. In this web page we have attempted to capture all the pertinent logic steps, and not miss a step for those with short attention span. The explanation is generally elementary, but one is advised to pay attention all along the way to develop an in-depth understanding.

Note also that none of the principals of Aguila/CTI or the inventors of any of the patent art owned by these companies have gone out of their way to "explain things" to just anyone at any time. To do so would have precluded our receipt of patents, or resulted in invalidation of a patent if issued. Keeping trade secrets is the only reasonable business practice. Even scientists are not entitled to trade secrets. In a free society the Constitution guarantees protection of those "first to invent". That is why, generally, a monopoly is granted to those "first to invent" and the law provides severe penalties for anyone guilty of patent infringement.

For example, when USDA's pioneer in EC research, Jim Rhoades tried to do

"on-the-go" conductivity measurements with a series of cultivator tines running on adjacent rows, or when USDA also tried to pull four thin electrodes -- one behind the other -- as a four electrode array, we did not jump up and say, WAIT we have already tried that and found that it doesn't work. We simply waited quietly for our better method to issue in a patent. In fact, our work with these failed types of federal configurations preceded the federal work by years. Government, during the Clinton administration, was not interested in what was best for the United States, but in the promotion of the government itself as the solution to problems. Perhaps we would have given Jim a hint, but then again he was hired by two embattled DOE employees in 1990 to defend them in their harassment of the Aguila Corporation. The DOE created an unfortunate limitation to the cooperation between between CTI and USDA then before their attorneys discovered the fraud problems in their own organization. As it turned out, Jim did not engage in any disparagement and the two DOE employees looking for their own non-federal "compensation" were moved out-to-pasture. Aguila/CTI was provided full rights to the technology, with DOE abandoning all patent rights in partial settlement of contract violations. And, Aguila/CTI was NOT required to make any public disclosures of any of its research under federal funds.

So, what have we learned technically and what does a person really need to know as a basic understanding? Briefly, when two electrodes are inserted into the soil and a voltage is impressed across this pair a current flows between the two electrodes. This current generally changes with time and is not steady because the surface of the electrodes changes chemically due to the reaction of the electrode metal with chemicals dissolved in the soil water, or in any liquid applied to the soil that contacts both the insitu soil and an electrode.

When one moves the electrodes, as in an on-the-go variant of the above description, the reaction described does not alter the electrode permanently, because soil-to-electrode abrasion removes any developing compounds. A fresh surface is always presented for the next on-the-go measurement. CTI manuals describe the requirement, for example, to spray coulter blades with a rust preventative (overnight) or to scour the coulters before service that relays on a measurement. Typically, rust is removed and readings are stable within the first ¼ mile of sensor system travel.

In quiescent fluids (such as laboratory beakers) one generally avoids electrode effects through two mechanisms. First, the voltages are held low enough to preclude a troublesome reaction and second, the voltage is usually impressed as an alternating current. This is a classic conductivity measurement

approach, but cannot, in and of itself have specificity for any species or constituent in the soil.

U.S. #5,033,397 describes:

- (1) an electrochemical reaction for ion specificity of dissolved compounds, and**
- (2) correction of the reaction determination for "background" levels of current flow in the earth (due to the electrical conductivity of the soil).**

Work sponsored by the U.S. DOE was confined to limited assistance in development of the electrochemical aspects of the measurement process and not in understanding the nature of electrical conductivity, the "background" process. During that development work, the fundamentals of "voltage overpotential" were clearly described which could initiate the release of NO_x from nitrate in solution, and a porous electrode slurry flow cell incorporating these "NO_x excited" electrodes was reduced to practice. Some "scientists" have misinterpreted and disparaged the work presented in the DOE Phase I report (1986) as emphasizing "resistivity" when the facts of that report are clearly in opposition to such a false review.

One of the interesting and publicly undisclosed research observations arising from CTI research from years prior to 1990 is that:

- (a) under certain voltage/excitation regimes with certain moving electrodes, it matters little whether an additional fluid is introduced to the interface. When this observation was made, during a period at which DOE funding was not available, CTI began extensive development investigation of EC (electrical conductivity) mechanics.**

Moreover, until the publication of U.S. Patent #5,673,637 in October, 1997, we also held as a trade secret the observation:

- (b) that the dominant anion species in the soil solution at sidedress time in mid-west production agriculture is the nitrate anion.**

A properly designed (and not publicly disclosed) sidedressing system even without alternating current can measure soil EC and correlate that with soil nitrates simply because the soil water is composed primarily of nitrate compounds at sidedress time. At sidedress, the soil water is dominated by both Ca and Mg nitrates and either compound has, pragmatically, very similar conductivities at a given ionic concentration. Speculation that other positive or negative ions can confuse the issue are just "purist" pot-shots. Such

speculation simply proves that such speculators have no sense of practical reality and are more concerned about determining the number of angels that can dance on the head of a pin.

In 1991, Dr. Ted Peck of the University of Illinois further investigated the electrochemical aspects of detection and validated the specificity of the technique detailed by CTI (in U.S. #5,033,397) which utilizes particular fluid, excitation, and metallurgical properties of electrodes.

One of the most interesting observations, however, is the insignificance of normally-occurring chemical interferences. That is, scientists speculate that species (such as chlorides) will cause interference in the measurement of nitrate species. While this is an absolute truth in a laboratory environment where you can mix up any combination of chemicals that you can dream of and prove that interferences exist, what combination of species do you actually find in soils?

Our research defining the dominant anion species -- nitrate-- means just that. It is by and large the largest contributor to conductivity of soil liquids. Any other species that exists under normal arable land conditions conducive to crop growth, has only minor effects on conductivity. This observation holds true for arable lands in Mid-West agriculture, although irrigated California agriculture would not follow these data.

When postulating nitrogen management solutions, then, there are several ways that an EC measurement can provide pertinent and valuable information. One can either be "ion-specific" or not, depending on the circumstances.

We leave it for an exercise for those in the scientific community to find out for themselves why conventional EM (electromagnetic) soil conductivity measurements CANNOT discriminate nitrogen rich soils from adjacent deficient soils of the same soil type and moisture, when electrode techniques can already do so. As a further exercise, these researchers are also challenged to figure out why a CTI PulseStar EM Complex Resistivity sensor can also make the necessary discrimination in comparison to conventional EM.

One of the most important aspects of our development has been our deep understanding of the utility of electrical measurements in midwest production soils. Government funded work prior to the accomplishments of Aguila/CTI research concentrated on the use of EC techniques for investigations of soil salinity. From the vast literature on electrical conductivity it can be learned

that the ionic strength of soil pore water has a drastic effect on the apparent soil conductivity.

The work of Rhoades at the salinity laboratory (prior to CTI's discoveries and inventions) was directed to a much higher range of pore water conductivity than is present in most midwest soils. Insofar as soil solution conductivity is concerned, there are two ranges:

- (1) The region below 1000 microS/cm, and
- (2) The region above 1000 microS/cm.

Salinity research generally considers only region (2) and midwest agriculture needs consider only region (1).

Mathematical models for soil conductivity developed by Rhoades, although applicable to the second region become highly inaccurate as pore water conductivity decreases well below 1000 microS/cm. The latest mathematical parameteric models pertinent to this lower pore water conductivity range employed by CTI remain trade secrets. Suffice it to say, these models are not linear as are the Rhoades models, but are non-linear.

The models are non-linear because there is an interaction in the conductivity interactions between the soil CEC structure (surface conductivity) and the pore water that causes the relation between EC_a and EC_w to change as EC_w varies between very low conductivities and 1000 microS/cm. Because of the higher ionic strengths of solutions pertinent to Rhoades investigations, the relationship between EC_a and EC_w is not definitive at low values of EC_w . This earlier work limited knowledge of the definitive contribution of CEC resulting in Rhoades decision not to relate soil matrix conductivity to CEC, but to define, instead, EC_s as simply the contribution of the soil matrix itself to conductivity. In any event, the salinity laboratory's work did not concern itself with the importance of EC_s , other than accounting for it as it influenced the determination of EC_w .

So, in formulating CTI models, the actual ionic strength of the solution in intimate contact with the soil particles becomes extremely important as does the composition of the solution. Since the amount of water contained in the pore space determines the ionic strength of the soil water with a given total salt dissolution, the water content becomes important in any model as well.

CTI models of DC soil conductivity primarily include:

- (a) Soil solution cations (principally Ca and Mg),**
- (b) Soil solution conductivities below 1000 microS/cm. (For nitrate assay in mid-west sidedress situations our experimental data confirms a linear relationship between NO₃-N and pore water conductivity that barely deviates from theoretical values.)**
- (c) Soil matrix CEC and soil porosity, and**
- (d) Soil water content and saturation.**

These models were validated by laboratory and field experiments in agricultural soils, but were derived from CTI founder's experience in the petroleum well-logging field.

CTI patents beyond the first provide much method, system, and process detail for determining both chemical and physical constituents of a soil through on-the-go measurements.

Both the electronic design of instrumentation and the design of the physical measurement apparatus are extremely important. This is why both two electrode and four electrode arrays are described extensively, with the preferred embodiment described in detail incorporating (when required) a four electrode array. This specification anticipates all of the current speculation about either four electrode arrays or, for example, topsoil depth as an important nitrogen prescription parameter.

More importantly (as reiterated in this web page), the specifications show that there are various ways to obtain good measurements (hardware and electronics). As our research has continued, others in the industry have (post patent application filing) also learned more about both the value and limitations of simple soil conductivity.

In the 1986 text: "Methods of Soil Analysis", Jim Rhoades includes a section on TDR (time domain reflectometry) using experimental equipment. Our specification reveals the application of this to on-the-go measurements through the proper design and analysis of transient measurements. These types of measurements (made on-the-go) provide accuracy with only two electrodes, rather than the classical four that many have found applicable in stationary measurements. Such measurements can also be made in four electrode arrays, where required.

Although methods of complex resistivity can be used to assay these

parameters as well, a time-domain TDR method has the distinct advantage of permitting assay with a much simpler electronic design. Advantages of TDR are simultaneous determination of soil conductivity, soil matrix conductivity, soil solution conductivity, and permittivity for a variety of soil depths. Moreover, this methodology has been found to improve soil characterization since electrode contact is of less significance.

Once these soil parameters are determined through pulse transient analysis, one can relate the components to a wide variety of constituents, including but not limited to: nitrate, calcium, potassium, depth of topsoil, water content, organic matter, CEC, clay content, texture, or soil type. Focusing on components rather than the total conductivity improves the functionality and accuracy of correlation relations determined, because extraneous covariant parameters are removed from the basic correlation equations.

It is incumbent on the party proposing a patent application that he reveal the best way of accomplishing the purposes of his invention at the time. But, the inventor must guard against someone proposing an inferior way of doing things that he knows of but deems less important. If, for example, under practical circumstances it really does not matter if a sensor is "ion-specific" for nitrate, then it is foolish to confine one's technology by the limitation desired by scientific purists. However, one must also include the case where such specificity is necessary.

In the search for the best way of solving a problem, the rule is to be vigilant of those who would follow and imitate the scope of your technology base. At the same time, one cannot let a "scientist" tell him what is important in the real world of commerce.

After all, in the world of protective patents, LESS is MORE. If you have an issued patent, and someone else offers another patent application requiring less steps than you think you need to have to be the best, he can have an issued patent that simply leaves out a step the original inventor deemed important. In other words, one must both push the envelope, adding complexity to the problem at hand and also be vigilant that he hasn't over-complicated his invention. In our research, we learned that at least in midwest production you can do just as well with a "correlated nitrate sensor" by using an EC measurement as you can with a perfect nitrate detector. The proof is in determining (by experiment) the typical soil anion species that exists in a soil solution, rather than presuming ion specificity is a prerequisite. These early discoveries lead to our intensive investigation of the potential for EC assays in

midwest soils.

In the case of CTI's patent applications, the full range of technology has been described. Our Issued and pending patents cover and supplant all of the claims of imitators, whether they come from Kansas, France, Illinois, or Missouri. We are the "first to invent" both real-time use and off-line mapping analysis of simple, uncorrected EC (as well as complex) data. Being first is hard on scientists, as well as those imitators trying to follow, but being first is rewarded under the Constitution of the United States of America. Patents give the holder the exclusive right to make, use, or sell technology embracing the underlying patents.

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