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Correlating composition of nutritive solution to electrical conductivity in order to improve a fertigation decision support

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Dedication

I wish to express my appreciation to Ing. João M. Moreira Barradas, Ph.D., my supervisor, who trusted me to do this master thesis, for guidance, supervision, encouragement and his great help in reviewing the manuscript.

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1. Introduction

Stress factors as abiotic and biotic such as salt, low or high temperature, drought, flooding, heat, metal toxicity was showing important role in plant growth and development (Mahajan and Tuteja, 2005; Achuo et al., 2006; Jaleel et al., 2007). Drought and salinity are major abiotic constrains that pose serious threat to crop production (Zhu, 2001; Hu and Schmidhalter, 2005; Soltani et al., 2006; Yang et al., 2007). By estimating it shows that in worldwide 26-20% of all cultivated land are affected by drought and salinity stresses (Flowers and Flowers, 2005;Cicek and Cakırlar, 2008). Every year 2 million hectare of agriculture lands are degraded by salinity stresses (Cicek and Cakırlar, 2008). Water is becoming scarce not only in arid and drought prone areas but also in the regions where rainfall is abundant. In the region with low rainfall, salty irrigation water, high evaporated rate, high water table is occur specially in arid and semiarid regions (Sadat Noori and McNeilly, 2000; Al-Karaki, 2001; Villa-Castorena et al., 2003). Changes in the environment can have a direct response in salinity in soil that is related with plant. All irrigation water contains dissolved mineral salts, but this concentration and composition depend from the source of irrigation water. Example snow melt contain very low amount of salt if we compare with ground water or wastewater typically has higher salt level (Stephen R. Grattan, 2002). The ability of plants to detoxify radicals under conditions of salt stress is probably the most critical requirement (Parida and Das, 2005). If we talk about climate change we can see that part of Middle East, Africa, Australia, the Southwest United State and Southern Europe are predicted to experience increased temperature, lower rainfall and reduction snowmelt (Ragab and Prudhomme, 2002). So the climate change, variability of water supplies, and the consequent impact on food production and environment services has generate significant attention (Rosegrant, 1997; Brown et al., 2002), where salinity may pose an additional risk because nearly one-third of irrigated land worldwide is affected by salinization (Schwable et al., 2006). This threat of salinity may send us to apply water in excess of plant requirements to leach the salts out of the root zone. But this path it started to become very problematic during climate change especially in arid and semiarid

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regions where salinity is the main problem that hold its own response (Connor et al., 2008).

If we talk about alternative strategies to reduce salinity, Silicon (Si) is important element that shows effect by reducing salinity in yield. Silicon is the second most abundant element in earth and is also beneficial for plant growth but not very essential for higher plant (Liang et al., 2006). However, the concentration of Si in plant depends from different species, where 0.1 to 10.0% is the amount of dry weight (Ma et al., 2006). Except salinity regulator, silicon show effect also in improving resistant to pests, pathogens and alleviating heavy metal stress (Gong et al., 2006). The role of silicon in the alleviation of salinity stress in plants has been observed in some species like: wheat (Mecfel et al., 2007), barley (Liang, 1999), tomato (Romero-Aranda et al., 2006), cucumber (Zhu et al., 2004).

There are plenty of researches about role of salinity in plant that bring use to many conclusions that we can use it for different peruses.

Another strategy approached by this present work is to have a correct assessment of water salinity while planning fertigation, where the injection of fertilizers in the water may lead to dangerous levels of salinity both for soil and plant. The development of methods estimating water salinity after fertilizer injection might be one of the strategies to plan irrigation with desired salinity at an accurate level of accuracy and precision.

2. Literature review

2.1. Salinity on soil

Number of causes can affect salinity in soil, which is different in geological and climatic region. Natural causes like drought, low amount of rain and artificial causes like irrigation play important role in salinity of soil. Salts in soils are primarily chlorides and sulfates of sodium, calcium, magnesium, and potassium. Arid region and semiarid region are the most influenced regions where salinity show high level of concentration, where major cations (Na^+, Ca^{2+}, Mg^{2+}, K^+) and anions (Cl^-, SO_4^{-2}, HCO^{-3}, CO_3^{-2}) accumulate in soil in higher level that result in low crop productivity and development (Ndakidemi and Makoi, 2009). The amount of concentration of salts can be expressed on mol/l or in mg/l and can be measure by salinity index that is electrical conductivity (EC), and is expressed in unit of deciSiemen per meter (dS/m) (Rhoades et al., 1992). Important tool for determination it can be also soil water balance models which may include salinity effect (Bernstein, 1964).

2.2. Physiological effects of salinity on plants

The most sensitive indices for screening and knowledge of the genetic variability and they relationship to the yield performance in field are physiological responses of plants. Different plants show different symptoms and behavior during salt stress and other environment stresses, for example salt accumulation on the leaf reduces photosynthesis and growth (Sudhir and Murthy, 2004). In order to maintain homeostasis during saline stress condition, plants exhibit physiological, biochemical and molecular response at both the cellular and whole plant level (Iyengar and Reddy, 1996). Ionic regulation of sodium and chloride, their partitioning, ion absorption and their allocation and increasing osmolytes are important physiological mechanisms that plants apply to resist salinity (Satish et al., 2003). Reduce water uptake is the common response of the plants subjected to water or salt stress (Munns,

2002). Better understanding of physiological and biochemical aspects of salinity stress tolerance mechanisms will not only help breeders in cloning of genes involved in salt stress tolerance, development of transgenic and batter breading programs, but also help scientists to determine accurate screening techniques ultimately aiding to crop improvement in saline soils (Sairam et al., 2002). Remote sensing is very useful tool for rapid measurement of ecosystems, and also can detect vegetation health for early identification of plant stress. The Photochemical Reflectance Index (PRI, also referred to as the Physiological Reflectance Index) has been identified as an accurate estimator of plant physiological status due to reduce photosynthetic efficiency at leaf and canopy scales (Gamon et.al., 1992, 1997; Garbulsky et al., 2011).

2.3. Relation of plant hormones and salinity

It has been determined that the detrimental effects of salinity occur as the result of osmotic stress, the interruption of metabolic activities by ionic excesses and imbalances and the interference of salt ions with the uptake of essential macronutrients and micronutrients (Tester and Davenport, 2003). These effects are manifested in the inhibition of germination, reduction of growth and development (Verslues et al., 2006). The plant hormone Abscisic acid (ABA) is a crucial regulator of plant responses to environmental stress, including drought, low temperature and salt (Finkelstein et al., 2002). Plants that are challenged by drought and salt stress recruit ABA as an endogenous signal that initiates adaptive responses (Zhu, 2002). During late embryogenesis, ABA promotes the acquisition of desiccation tolerance and seed dormancy and inhibits seed germination (Koornneef et al., 2002; Song et al., 2005). ABA signaling appears to involve a complex network of both positively and negatively regulating components, including kinases, phosphatases and transcriptional regulators (Finkelstein et al., 2002; Gonzalez-Garcia et al., 2003; Abe et al., 2003; Fukuda and Tanaka, 2006). Inhibitory effect of NaCl on photosynthesis (Popova et al., 1995), switch from C3 to crassulacean acid metabolism (CAM) (Thomas et al., 1992) and promotes stomata closure under stress condition has done by ABA hormone. However, many of the cellular components and genes involved in ABA reception and downstream transduction have yet to be well characterized.

2.4. Biochemical effects of salinity

The impact of salinity on metabolic processes on plants and several biochemical mechanisms of tolerance have been researched during the time of salinity problems. By synthesizing amino acids such as proline, plants adjust osmotically their cellular content under condition of stress (Ashraf and Harris, 2004). Amino acids, polyamines and sugars appear to be an effective mechanism of stress tolerance (Rosa-Ibarra and Maiti, 1995). Multiple biochemical pathways that facilitate retention or acquisition of water, protect chloroplast function and maintain ion homeostasis are ability of plant to tolerate the salt stress (Parida and Das, 2005).

Biochemical strategies include mainly (i) the synthesis of compatible solutes to mediate osmotic adjustment, (ii) the control of ion movements allowing inorganic ion accumulation and (iii) the up-regulation of a complex antioxidative response system consisting of enzymatic and no enzymatic components to protect plant tissues against oxidative damage (Benlloch- Gonzaleza et al., 2005).
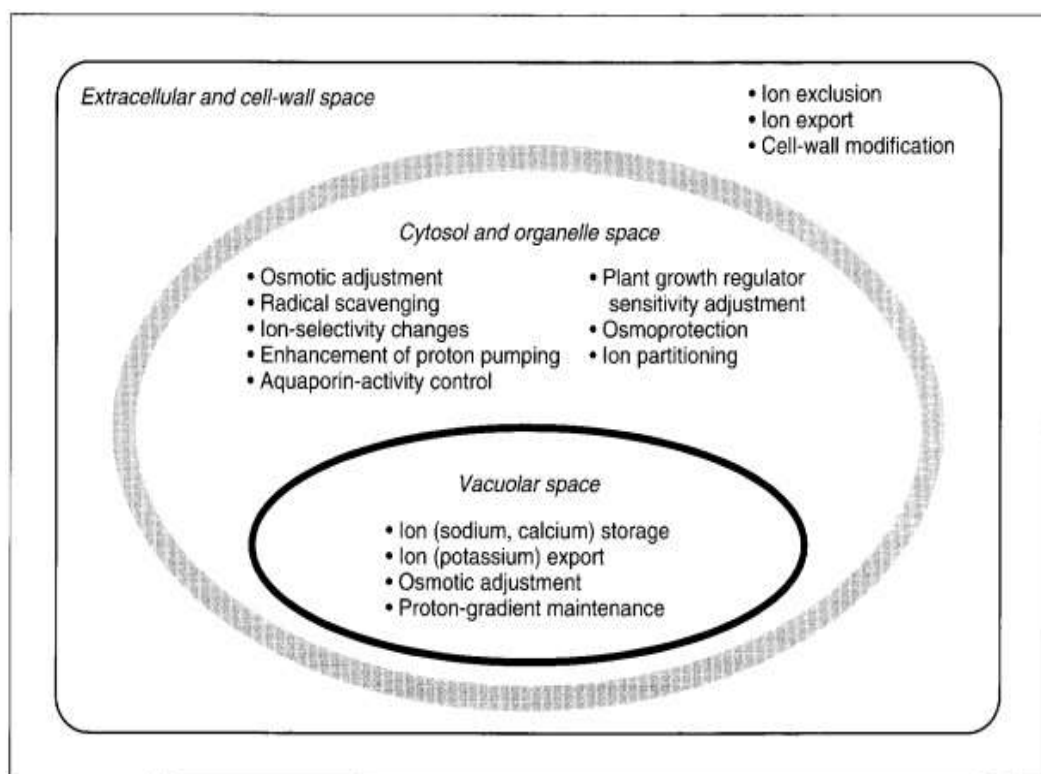

Figure 1. Biochemical functions associated with tolerance to plant salt stress. The schematic presentation of a plant cell includes three compartments that are define by the plasma membrane and tonoplast (reproduced from Bohnert and Jensen, 1996).

Concerning carbohydrates, their major functions are osmotic adjustment, osmoprotection, carbon storage and radical scavenging (Parida et al., 2002). Has been widely reported that accumulation of soluble carbohydrates in plants are response for salinity and drought and decreasing CO_2 assimilation rate (Murakeozy et al., 2003). Carbohydrates such as sugars (glucose, fructose, sucrose, fructans) and starch accumulate under salt stress, playing a leading role in osmoprotection, osmotic adjustment, carbon storage, and radical scavenging (Parida et al., 2002).

Accumulation of protein in plant under saline condition may provide a storage form of nitrogen that is re-utilized later (Singh et al., 1987). In higher plants, osmotic stress induces several proteins in vegetative tissues, which are related to late-embryogenesis-abundant (LEA) proteins. The correlation between LEA protein accumulation in vegetative tissues and stress tolerance indicates its protective role under dehydration stress (Ingram and Bartels, 1996).

Amino acids such as alanine, glycine, proline etc and amides such as glutamine and asparagine's have also been reported to accumulate in plants to salt stress (Mansour, 2000).

Proline occur more in higher plant and play role in accumulation and useable of Nitrogen (Abraham et al., 2003). Also it is osmotically very active and help in membrane stability and mitigate the effect of NaCl on cell membrane (Mansour, 1998). Proline form a hydration sphere around macromolecules and protect them denaturing under stressful condition (Bohnert et al., 1995).

Also the role in plant salt tolerance play polyols that are widely distributed in plant kingdom and can divide in two forms acyclic and cyclic form (Bohnert and Shen, 1999). Polyols make up a considerable percentage of all assimilated CO_2 as scavengers of stress-induced oxygen radicals (Bohnert et al., 1995).

2.5. Salinity tolerance mechanisms

The responses of plant to salt and other environmental stresses have been important for agronomy, ecology and physiology science. Salt stress can result also by nutrient imbalance where can result in plants by various way. Imbalance can be

caused in different way by nutrient availability, competitive uptake, transport of partitioning within the plant or may be caused by physiological inactivation for some element that increase internal requirements (Grattan and Grieve, 1994). The interactive nature affecting nutrient availability, uptake and distribution are topics that are highly complex in the absence of salinity or other stresses (Marschner, 1995). Major mechanisms responsible for reduction in plant growth under salt stress are:

- ✓ Specific ion toxicity
- ✓ Osmotic stress
- ✓ Nutritional imbalance
- ✓ Oxidative stress

2.5.1. Specific ion toxicity

Change of the salt tolerance can also be present by changing the temperature, vapor pressure deficit and radiation. Ion cytotoxicity may adverse effect of salinity on plant growth due to Na^+, Cl^- and SO^{4-} and osmotic stress (Zhu, 2002). Salinity (EC <3.0 dS/m-1) and osmotic potential (< -0.117 MPa) can be susceptible for plant growth. In this salinity level susceptibility appears to be Ion toxicity. Ion cytotoxicity is caused by replacement of K^+ with Na^+ and conformational changes in structure of proteins when Na^+ and Cl^- ions penetrate hydration shells.

2.5.2. Osmotic stress

A decrease in water potential due to the soil salinity cause osmotic stress that lead to turgor loss (Chinnusamy et al., 2005). Osmotic pressure is responding to change compensatory molecular adaptions that allow reestablishing homeostatic of osmotically disturbed aspect of cell structure and function (Kültz and Burg, 1998). Osmotic stress interferes intracellular inorganic ion homeostasis and with cell volume. Because cell volume and ion regulation are not rapid processes, osmotic stress may damage cellular macromolecules and impair cell function until compensatory adaptations counteract the stress. Induction of rapid processes and

protection system, lead to impairment of cell function by damage DNA and proteins (Naegeli, 1997). Osmotic stress and cell volume regulation may be an important aspect of cellular adaption that may serve to compensate for negative osmotic effect on cell. Now is recognized that, if cell is not able to compensate for osmotic stress it lead herself in self-destruction program called cell death (apoptosis) (Schwartz and Osborne, 1993; Katsuhara, 1997)

2.5.3. Nutritional imbalance

Plant growth is related to the concentration of an essential nutrient element that is described by the "generalized dose response curve" (Berry and Wallace, 1981). There is always optimum value for each plant that is response for plant growth and development. Every concentration below the optimum value it result in growth reduction. Also excessive application of nutrient for example NO_3^- in spinach may not effect in yield but may pose a health risk to the consumer (Marschner, 1995). Salinity dominated by Na^+ salts reduce Ca^{2+} transport and growth in regions of the plant, which effect both vegetative and generative organs (Grattan and Grieve, 1999). Interactive effects between Na^+ and NH_4^+ or between Cl^- and NO_3^- decreased nitrogen uptake under saline conditions that ultimately reduced the growth and yield of the crop (Rozeff, 1995). This reduction in NO_3^- uptake is associated with Cl^- antagonism (Feigin et al., 1987; Bar et al., 1997). It is important that phosphate concentration in field decrease by increasing salinity in soil (Sharpley et al., 1992; Qadir and Schubert, 2002). By increasing Na^+ and Ca^{2+} in the root media the presence of potassium will decrease (Asch et al., 2000; Hu and Schmidhalter, 2005), but external Na^+ presence will decrease both K^+ and Ca^{2+} in plant tissues of many species (Hu and Schmidhalter, 1997). This decrease of Ca^{2+} happened because Na^+ displaces Ca^{2+} from its extra cellular binding sites (Cramer et al., 1988). The ability of micronutrient in saline soil depend on the solubility of micronutrients, Ph, natural binding sites on the organic and inorganic particle surface and redox potential of soil solution. Micronutrients deficiency is very common during high Ph (Zhu et al., 2004).

2.5.4. Oxidative stress

When we talk about oxidative stress, salt stress also play very important role by contributing in deleterious effects (Comba et al., 1998; Hernandez and Almansa, 2002; Vronova et al., 2002). During salt stress condition stomata close which result in decrease in CO_2 and O_2 ratio. In this situation the concentration of reactive oxygen species (ROS) start to increase like superoxide (O_2^-), hydrogen peroxide (H_2O_2), hydroxyl radical (OH^-) and singlet oxygen (O_2) (Becana et al., 2000). This attack of ROS occurs in many cellular components such as photosynthesis pigments, proteins, nucleic acid and lipids (Foyer et al., 1994; Lin and Kao, 2000). In recent years, it has become apparent that plants actively produce reactive oxygen intermediates (ROIs) as signaling molecules to control processes such as programmed cell death, abiotic stress responses, pathogen defense and systemic signaling. Under normal growth conditions, the production of ROIs in cells is low (240 µm s−1 O_2^- and a steady-state level of 0.5 µm H_2O_2 in chloroplasts), many stresses that disrupt the cellular homeostasis of cells enhance the production of ROIs (240‑720 µm s^{-1} O_2^- and a steady-state level of 5‑15 µm H2O2) (Pole, 2001). Antioxidants such as ascorbic acid and glutathione, which are found at high concentrations in chloroplasts and other cellular compartments (5‑20 mm ascorbic acid and 1‑5 mm glutathione), are crucial for plant defense against oxidative stress (Noctor and Foyer, 1998). So the steady state level of ROIs can be used for control level of stress that can play important role in cell death (Asada and Takahashi, 1987).

2.6. Foliar salt and saline water

Accumulation of salt in the leaves by sprinkler irrigation, show foliar injury and decrease crop yield. Many different plants like tomato, potato, safflower, sugar beet, cotton was showing different behavior in foliar salt absorption, where some of them has higher occurrence in Na^+ assimilation and the others in Cl^- assimilation. Some of the plants example potato and tomato readily absorb Na^+ and Cl^- and quickly exhibited symptoms of leaf tip and margin necrosis. But in another hand some plant

like safflower that absorb higher rate of salt was injured by sprinklers (Maas et al., 1981). Crop salt tolerance, are generally expressed as a function of soil salinity (Maas and Hoffman, 1977). When the plant are irrigated with surface system of irrigation, salinity problem it occur more in root system. But this is not the case with sprinkler irrigation when foliage is wetted by saline irrigation water. Because of salt absorption through the leaves, some crops will not occur symptoms and yield reduction when they are surface irrigated with the same water. So tolerance will not be the same for saline sprinkler and saline soil salinity (Mass et al., 1981).

Many researches are done and there are many data that shoes crop tolerance to saline sprinkler water. The firs data it was in Orange (Harding et al., 1958). Other conclusion has showed that orange, apricot, almond and plum were sensitive in sprinkler salt application while avocado and numerous vegetables were not (Ehlig and Bernstein, 1959). Studies about grapes (Francois and Clark, 1979) and peppers (Mass et al., 1982) has showed that are readily in salt absorption and are susceptible to foliar injury.

2.7. Relation of salinity and nutrition in fertigation

The availability of good quality water is one of the major limiting factors for plant growth as irrigation water may often contain salts and ions that can have negative impacts on the plant growth and development. Salt water in the root zone induces osmotic changes and directly affect nutrient uptake as Na^+ reducing K^+ uptake or by Cl^- reducing NO_3^- uptake (Cornillon and Palloix, 1997; Halperin et al.,2003). Most of the plants evolved in the condition of low soil salinity, so they create mechanisms to absorb nutrient under non saline condition. This relation between nutrient and salinity is related to the activity of ion in the soil solution (James, 1990), that is related with Ph and composition, the concentration and ratio of elements that play important role in ability of nutrient uptake by root (Lauchli, 1987) and other environment factors. The nutrient induced salinity causes nutritional disorders in most of the plant species. These disorders may result from the effect of salinity on nutrient availability, competitive uptake, transport or partitioning within the plant (Dhindsa et al., 1981). Is reported that salinity have direct effect on nutrient uptake where sodium (Na) reduce potassium (K), than chloride (Cl) reduce nitrate

(NO_3^-) uptake (Grattan and Grieve, 1999). As we know the calcium is very important nutrient that play important role in metabolism but sodium ions may compete with calcium ions for membrane-binding sites (Cramer and Lauchli, 1986). There is numerous literature knowledge about the effect and relations of salinity and nutrient that play key role in plant grow and development.

2.7.1. Nitrogen

Most important element for plant growth and development with 80% of total mineral that is absorbed by plant is Nitrogen (Marschner, 1995). Many studies has shown that reduction of nitrogen in plant accumulation is related with increment of salinity in soil, (Cram, 1973) this is related by increment of Cl^- uptake and decreasing of NO_3^- concentration in cucumber (Martinez and Cerdá, 1989), melon (Feigin et al., 1987) and tomato (Kafkafi et al., 1982; Feigin et al., 1987; Martinez and Cerdá, 1989). But when we talk about relation of Cl^- and NO_3^- we can see that some cultivars are more resistant in salt stress and show different behavior, example more salt-tolerant tomato and melon cultivars had higher NO_3^- influx rates than the more sensitive cultivars (Kafkafi et al., 1992). Even small amount of Cl^- from $CaCl_2$ in amount of 60 mol/m^3 can inhibit NO_3^- in melon and tomato, where that amount of KCl is amount that plant would like to expose in the field, but amount of KCl (100-200 mol/cm^3) can also inhibit NO_3^- uptake (Kafkafi et al., 1992). As nitrogen is uptake in form of NO_3^- , and NH_4^+ the relation of this form to the other elements is different, where addition of Ca^{2+} to the media improve the growth rate of the plants in the NO_3^- treatment but not those treated with NH_4^+ (Lewis et al., 1989). Is shown that Cl^- was reduced in cucumber when only NO_3^- was added to the solution, but when half of NO_3^- was replace with NH_4^+, Cl^- accumulation was enhanced (Martinez and Cerdá, 1989). Nitorgen relations are very complex. There are many studies about this relation of nitrogen and salinity where some of them shown negative effect and the others shown opposite or no effect (Feigin, 1985).

2.7.2. Phosphorous

Phosphorous as important element has shown different behavior in relation with salinity. The effect of salinity in phosphorous is more occur in plant tissues in a presence of salinity (Sharpley et al., 1992). But when we talk about phosphorous uptake, most of the cases result by increasing phosphorous uptake or had no effect in that. This accumulation of phosphorous is related with growth condition, plant type and even cultivars (Grattan and Grieve, 1994). Phosphate availability is reduced in saline soil not only because ionic strength but also because phosphate concentration in soil solution are tightly controlled by sorption process and by los solubility of Ca-P minerals. It is understandable that by increasing NaCl and $CaCl_2$, phosphate concentration in soil will decrease (Sharpley et al., 1992). So presence of Cl^- may have suppressed phosphate uptake and accumulation in tomato (Papadopoulos and Rendig 1983). Phosphate concentration in solution cultures are often orders of magnitude higher than that in soil solutions (e.g. 2 mM vs. 2 mM). Several studies conducted in solution cultures have shown that P concentrations that are optimal in non-saline solutions may adversely affect growth or be toxic to corn (Bernstein et al., 1974; Nieman and Clark, 1976). High concentration of phosphate (2mM) caused lower yield in salt-treated plants than low concentration of phosphate (0.05mM). This lower yield appears to result from excessive uptake of phosphate, with translocation to the leaves, leading to symptoms of phosphorus toxicity (Berstein L., Le Francois., Clark RA. 1974). Some research indicates that salinity stress may increase the P requirement of certain crops. For example, when NaCl increased in the substrate from 10 to 50 to 100 mM, the P concentrations in the youngest mature tomato leaf necessary to obtain 50% yield increased from 58 to 77 to 97 mmol/kg dry weight, respectively. The conclusion was also supported by appearance of P deficiency symptoms that were evident on plants grown at high NaCl but was not evident on others at lower salinity with equal leaf-P concentrations (Awad et al., 1990).

2.7.3. Potassium

The effects of mild cases of salt stress are primarily limited to plant growth, development, and crop productivity, but in extreme cases, salt stress can lead to plant death (Aoki et al., 2005). It was reported that detrimental effects of death of these factors are crucially dependent on a plant's ability to maintain K^+ homeostasis and control K^+ transport across cellular membranes (Shabala and Pottosin, 2010). In many case deficiency of K^+ lead the plants to infection than those with adequate supply of K^+. This we can see by increasing borer infestation where it was more grate when K^+ was in deficiency (Saraw, 2012). K^+ fertilizer play important role by reducing disease incidence of stem rot and aggregate sheath spot, and also the negative correlation ware found between the percentage of K^+ in leaf blades and disease severity (William and Smith 2001). This status enable plants to create stronger cell walls to prevent by pathogens and insect attack and in another hand to obtain more nutrients that can be used to develop stronger defense and damage repair (Mengel, 2001). We can see from many studies that K^+ concentration in plant tissue is reduced as Na^+ salinity or Na^+/Ca^{2+} ratio in the root media is increase (Janzen and Chang, 1987), so event that solution is dominated by Na^+ salts of Cl^- SO_4^{2-} the reduction of K^+ in plant by Na^+ is process that play key role in K^+ deficiency. But increasing extrachloroplastic K^+ concentration in plant cells with and excess K^+ supply could prevent photosynthesis inhibition under drought stress (Egilla et al., 2005). The ability of plants so satisfy their metabolic requirements for K^+ in the presence of salinity by using higher K^+ fluxes and lower Na^+ fluxes that result in higher K^+/Na^+ selectivity ratio is essential for salt tolerance, so there is not define percent of Na^+ that show effect in stress salinity, but is the ratio between K^+ and Na^+ (Shabala, 2010).

2.7.4. Secondary macro nutrients

Secondary macro nutrient refers to nutrients such as calcium (Ca), magnesium (Mg) and sulfur (S). However, the amount needed by some plants for Ca, Mg and S

are similar or sometimes even greater to that of phosphorus. In most basic and acid soil, transport of Ca and Mg occur via mass flow so the amount of Ca and Mg that reach the root by mass flow is bigger than root uptake. As a result Ca and Mg accumulate near to plant root (Barber, 1962). At pre-planting sulfate and Ca are given in quantities greater than nitrogen (N) and phosphorus (P), while uptake by the plant is less than N and P. Therefore the addition of Ca, Mg and S to agricultural crops is secondary in importance. However, the addition of Ca, Mg, and S should be given first priority in acid soil where acute Ca deficiency and high fixation of P can occur (Marschner, 1995).

2.7.5. Micronutrient

All chemical elements that are in plant in small quantities are termed "micronutrient"(Harmsen and Vlek, 1985). The micronutrient that are taken up by plants as cation are iron (Fe^{2+}), manganese (Mn^{2+}), copper (Cu^{2+}) and zinc (Zn^{2+}). The micronutrient taken as anions are molybdenum as molybdate (MoO_4^{2-}) and boron as boric acid [$B(OH_3)$] or as a borate [$B(OH_4^-)$]. The micronutrient, Fe, Mn, Cu, Zn are very reactive with clay particles, so when supply to the soil as simple inorganic salt such as sulfates, the ability to the plant is significantly reduced. However when added in chelated form (Moran, 2004), keeping it available for plant uptake at the root surface, the metal element is released from chelate (Chayney, 1988) and, when absorbed inside the plant, it may combine with internal organic acid such as citric acid to form citrate salts.

2.8. Ferrtigation

Supplying crops in the field with fertilizers via the irrigation water is called fertigation (Bar-Yosef, 1991). This technique provides excellent opportunity to maximize yield and minimize environment pollution (Hagin et al., 2002). Injection of nutrient can be in various frequencies (daily or monthly) depend in system design constrains, soil type and grower performance. The use of drip irrigation may be the best system for increasing the yield, maximizing water and nitrogen use efficiencies and thereby minimizing nitrate leaching (Lamm and Trooien, 2003; Al-Omran et al.,

2005). Important role on nitrogen and water use efficiency play irrigation management. The use of frequent but low water application volumes is superior to the more traditional scheduling of few applications of large irrigation volumes (Locascio, 2005). The benefit of applying water and nutrients at high frequencies is attributed to near constant conditions in the root zone allowing plants to grow in areas with favorable water, oxygen, nutrient, and salt concentrations (Clothier and Green, 1994; Glenn, 1999). Water and nutrients acquisition by plants, and the formation of a depleted zone in the immediate vicinity of the roots are the driving forces for solute movement towards the roots (Silber et al., 2003). Fertigation could reduce ground water pollution (Komosa et al., 1999a) and labor costs (Sharma et al., 2008). Since drip fertigation results in partial wetting of the total soil volume, it creates gradients of soil water content and mineral concentrations across the root systems (Bravdo, 2008). The application of nutrient to a small wetted volume where active root zone is concentrated has showed more precise results than wet total soil volume (Sharma et al., 2008). Due to some similarities to the hydroponic systems that we use in glass house, daily fertigation generally referred as "open hydroponic" when applied under field condition. The word "hydroponic" originates from the Greek "hydro" water and "ponic" work (Mollafilabi et al., 2010). The implies that hydroponically grown plants are actually independent of soil, which is not the case in vineyards. There are many advantage in hydroponics such as higher yields, improvement water and fertilizer economy, lower environment pollution (Mollafilabi et al., 2010). However, the implementation of this concept can be expensive and difficult to manage (Fascella and Zizzo, 2005).

2.8.1. Fertilizer dosing in ferrtigation

To apply the same doses of fertilizer during specific phonological stage of plant, two different models play important role depending in soil type, crop and farm management system (Sne, 2006):

- **Quantitative dosing:** A measure amount of fertilizer is injected into the irrigation system during each water application. Injection may be initiated and controlled automatically and manually

- **Proportional dosing:** In this process, a constant predominated ratio between the volume of irrigation water and the volume of fertilizer solution is maintained, resulting in the constant nutrient concentration in the irrigation water.

Plant nutrient supply must also be regulated, and over the years a large number of nutrient solutions have been formulated for this purpose. Most modern formulations are based on a solution originally developed by D. R. Hoagland, a pioneer in the study of plant mineral nutrition. Individual investigators may introduce minor modifications to the composition of the nutrient solution in order to accommodate specific needs. Such formulations are commonly referred to as modified Hoagland's solutions (Table 1,2) (William and Norman, 2008)

Table 1. The composition of typical one-half strength "modified" Hoagland's nutrient solution, showing the nutrient salt used and their approximate millimolar (mM) concentrations.

		Concentration (mM)
Calcium Nitrate	$Ca(NO)_3$	2.5
Potassium Phosphate	KH_2PO_4	0.5
Potassium Nitrate	KNO_3	2.5
Magnesium Sulfate	$MgSO_4$	1.0
Zinc Sulfate	$ZnSO_4$	0.00039
Manganese Sulfate	$MnSO_4$	0.0046
Copper Sulfate	$CuSO_4$	0.00016
Boric Acid	H_3BO_3	0.0234
Molybdic Acid	MoO_3	0.000051
Iron Sequestrate	Fe	0.179

Table 2. The quantity of each nutrient element in modified Hoagland's nutrient solution.

Element	Mg/L
Calcium	103
Nitrogen	105
Potassium	118
Sulfur	33
Manganese	25
Phosphorous	15
Iron	10
Boron	0,25
Manganese	0,25
Zinc	0,025
Copper	0,01
Molybdenum	0,0052

2.8.2. Suitability of fertilizers for fertigation

Solid and liquid fertilizers are suitable for fertigation depending on the physiochemical properties of the fertilizers solution. For large scare field operation solid fertilizers sources are less expensive. The solubility of these fertilizers does very greatly. When switching to a solid fertilizer source, problems can be avoided in the nurse tanks by ensuring that ample water is added to the stock solution.

Four factors to select fertilizers for fertigation should be considering (Kafkafi, 2005):

- Plant type and stage of growth
- Soil condition
- Water quality
- Fertilizer availability and price

Using fertilizer for fertigation should be with high quality, high solubility and purity, containing low salt and acceptable Ph.

The main properties relating to the suitability of fertilizer to the injection method has done by (Hagin and Lowengard-Aycicegi, 1996):

- Form: Solid and liquid fertilizers are both suitable for fertigation depending on availability, profitability and convenience.
- Solubility: Fertilizer solubility generally increases with temperature, depending on fertilizer.
- Interaction between fertilizers in solution: When one type of fertilizer or more are prepared and mixed by the grower, the compatibility between them must be checked.

Table3. Fertigation fertilizer capability chart

	Urea	Ammo-nium Nitrate	Ammo-nium Sulfate	Calc-ium Nitrate	Pota-ssium Nitrate	Pota-ssium Chloride	Pota-ssium Sulfate	Amm-onium Phosphate	Fe, Zn, Cu, Mn Sulfate	Fe, Zn, Cu, Mn Chelate	Magn-esium Sulfate	Phos-phoric Acid	Sul-phuric Acid	Nitric Acid
Urea	✓													
Ammonium Nitrate	✓	✓												
Ammonium Sulfate	✓	✓	✓											
Calcium Nitrate	✓	✓	X	✓										
Potassium Nitrate	✓	✓	✓	✓	✓									
Potassium Chloride	✓	✓	✓	✓	✓	✓								
Potassium Sulfate	✓	✓	R	X	✓	R	✓							
Ammonium Phosphate	✓	✓	✓	X	✓	✓	✓	✓	□					
Fe, Zn, Cu, Mn, Sulfate	✓	✓	✓	X	✓	✓	R	X	✓					
Fe, Zn, Cu, Mn, Chelate	✓	✓	✓	R	✓	✓	✓	R	✓	✓				
Magnesium Sulfate	✓	✓	✓	X	✓	✓	R	X	✓	✓	✓			
Phosphoric Acid	✓	✓	✓	X	✓	✓	✓	✓	✓	R	✓	✓		
Sulphuric Acid	✓	✓	✓	X	✓	✓	R	✓	✓	✓	✓	✓	✓	
Nitric Acid	✓	✓	✓	✓	✓	✓	✓	✓	✓	X	✓	✓	✓	✓

✓ = compatible   X= incompatible   R= reduced compatibility

Elaine Roddy - Vegetable Crops Specialist/OMAFRA, 2006

There are usually some basic precautions that must be taken:

- Make sure that the fertilizers used are compatible to prevent precipitation. Especially, avoid mixing fertilizer solutions that contain calcium with solutions containing phosphates or sulfates when the pH in the solution is not sufficiently acidic.
- Check the solubility and potential precipitation with the local water chemical composition. Before using a new fertilizer, mix 50 ml of the fertilizer solution with 1 liter of the irrigation water and observe for precipitation within 1-2 hours. If precipitates are formed or the sample becomes cloudy, refrain from using this fertilizer in the irrigation system (Roddy, 2008).
- Check the temperature resulting from mixing various types of fertilizers under field conditions. Some fertilizers alone or in combination may lower the solution temperature to freezing levels.

Table 4. Solubility, pH and other characteristics of some fertilizers

	Maximum amount (kg) dissolved in 100L at 20°C	Time to Dissolve (min)	Ph of the Solution	Insoluble (%)	Comments
Urea	105	20[1]	9.5	Negligible	Solution cools as urea dissolves.
Ammonium Nitrate	195	20[1]	5.62	-	Corrosive to galvanized iron and brass Solution cools as product dissolves.
Ammonium Sulfate	43	15	4.5	0.5	Corrosive to mild steel.
Mono-Ammonium phosphate	40	20	4.5	11	Corrosive to carbon steel.
Di-ammonium phosphate	60	20	7.6	15	Corrosive to carbon steel.
Potassium chloride	34	5	7.0-9.0	0.5	Corrosive to brass and mild steel.
Potassium sulfate	11	5	8.5-9.5	0.4-4[2]	Corrosive to mild steel concrete.
Mono-potassium phosphate	213	-	5.5+/- 0.5	<0.1	Non Corrosive.
Potassium nitrate	31	3	10.8	0.1	Solution cools as product. dissolves. Corrosive to metals.

1 - Solution temperature drops to 0°C, hence it takes longer for all material to dissolve

2 - These figures are the ranges found in shipping analyses and refer to different sources of supply

(Adapted from Primary Industries: Agriculture, 2000).

2.8.3. Fertigation in alkaline and acid soil

Soil pH can be affected by certain fertilizer applications. Generally, soil pH is optimum between pH 6.5 and 7.5. Some fertilizers may change long term soil pH after years of application, whereas others have a more short-term and 'microsite' effect. In this context, microsite refers to the area directly surrounding the fertilizer material and extends approximately 1 inch from the site of placement (NM 8).

2.8.3.1. Alkaline soils

The characteristics of basic or alkaline soils are: The presence of active Ca-carbonate, excess of soluble Ca ions, a rapid nitrification rate and mild fixation of additional P from fertilizers. All type of N fertilizers are suitable to be added with the irrigation water. Even urea, which is completely soluble and causes an initial increase in pH due to the activity of urease in the soil, is safe to use in trickle irrigation as no local increase in urea concentration is expected in the soil. In alkaline soils, the clays are mainly of the 2:1 type and ammonium is adsorbed to the clay, and does not cause ammonium toxicity to roots since it is diluted by the irrigation water. The soil pH has no influence on any priority selection for K, secondary nutrients and all the micronutrients that are supplied in chelated forms, except for Fe^{2+}. Since Fe-EDTA is not stable above pH 6.5 in basic soil, Fe-DTPA is recommended for soils with a pH up to 7.5, while Fe-EDDHA is recommended in extremely high pH soils since it is stable up to pH 9. (A Tool for Efficient Fertilizer and Water Management)

2.8.3.2. Acid Soils

Acid soils are characterized by active aluminum (Al) ions, shortage of Ca, slow nitrification rate, and strong fixation of additional P from fertilizers. The use of nitrate fertilizers as N source increases the pH in the rhizosphere due to nitrate nutrition. Urea is well suited for fertigation because it is relatively cheap per unit of

N and is highly soluble. However, a major problem associated with urea fertigation is soil acidification. This problem is further accentuated in coarse textured soils due to a low soil buffering capacity per unit volume and the narrower, basically cylindrical wetted volume under the emitted (McAuliffe, 1986). Although ammonium based fertilizers have twice the acidifying effect per unit N as urea, urea is considerably more mobile in soil (Haynes, 1989). Acidification resulting from ammonium sulfate fertigation was confined to the top 20 cm of a soil loam while urea, applied under same condition caused acidification to a depth 40 cm (Haynes, 1990). It has been demonstrated that nitrogen (N) fertigation at half the conventionally applied rate did not reduce nitrogen content of temperate fruit trees (Kenworthy 1979). Also, as soli become acidic, base cation Ca, Mg, K, are displaced and become susceptible to leaching (Haynes and Swift, 1986).

Table 5. Recommended fertilizers for fertigation in neutral – alkaline (6.5-8.5) and (4.5-6.5) soils.

Nutrient	Neutral - basic soil Ph 6.5 - 8.5	Soil Ph	Acidic - neutral soils pH 4.5 - 6.5
Nitrogen		Ammonium nitrate (NH4NO3)	
		Potassium nitrate (KNO3)	
		Calcium nitrate (Ca(NO3)2)	
		Urea	
	Ammonium sulfate (NH4)2SO4)		
	Ammonium phosphate (NH4H2PO4)		
Phosphorus		Mono potassium phosphate (KH2PO4)	
		Ammonium polyphosphate	
	Phosphoric acid (H3PO4)		
Potassium		Muriate of potash (KCl)	
		Potassium sulfate (K2SO4)	
		Potassium nitrate (KNO3)	
Secondary nutrients		Calcium nitrate (Ca(NO3)2)	
		Magnesium nitrate (Mg(NO3)2)	
		Potassium sulfate (K2SO4)	
Micronut-rients		B as boric acid	
		Mo as sodium molybdate	
		EDTA complex with Cu, Zn, Mo, Mn	
	Fe-EDDHA		Fe-EDTA
	Fe-DTPA		

2.9. Effect of salinity on water

Good quality irrigation water containing only 200-500 mg/kg of soluble salt. Irrigation water with a salt content of 500 mg/kg contains 0.5 tons of salt per 1,000 m^3. Since crops require 6,000-10,000 m^3 of water per hectare each year, one hectare of land will receive 3-5 tons of salt (Munns et al., 2012).

Current is carried by both cations and anions, but to a different degree. The conductivity due to divalent cations is more than that of mono-valent cations. However, it is not true for anions. The conductivity factors for major ions present in water are listed below.

Table 6. Equivalent Ionic Conductivities at Infinite Dilution (l`) in Aqueous Solutions at 25&C [Modified after MacInnes (1939); Sawyer and McCarty (1978); and Bard and Faulkner(1980)]

Anions		Cations	
Ion (1)	λ^-_∞ (S-cm2/equivalent) (2)	Ion (3)	λ^-_∞ (S-cm2/equivalent) (4)
OH^-	198.0	H^+	349.85
$0.5\ SO_4^{-2}$	79.8	K^+	73.52
Br^-	78.4	$0.5\ Ba^{2+}$	63.64
I^-	76.85	$0.5\ Ca^{2+}$	59.50
Cl^-	76.34	$0.5\ Sr^{2+}$	59.46
NO_3^-	71.44	$0.5\ Mg^{2+}$	53.06
HCO_3^-	44.48	Na^+	50.11
OAc^-	40.9	Li^+	38.69

Figure 2. Shows computed results for water liquids included the pure water, distilled, municipal, industrial, rivers and well waters. The value of the EC is given for the room temperature of 25° C. PW (pure water), DW(Distilled water, ppm5), IW(Industrial water, 100ppm), RW(River water, 100ppm) and MW(Municipal water, 100ppm)
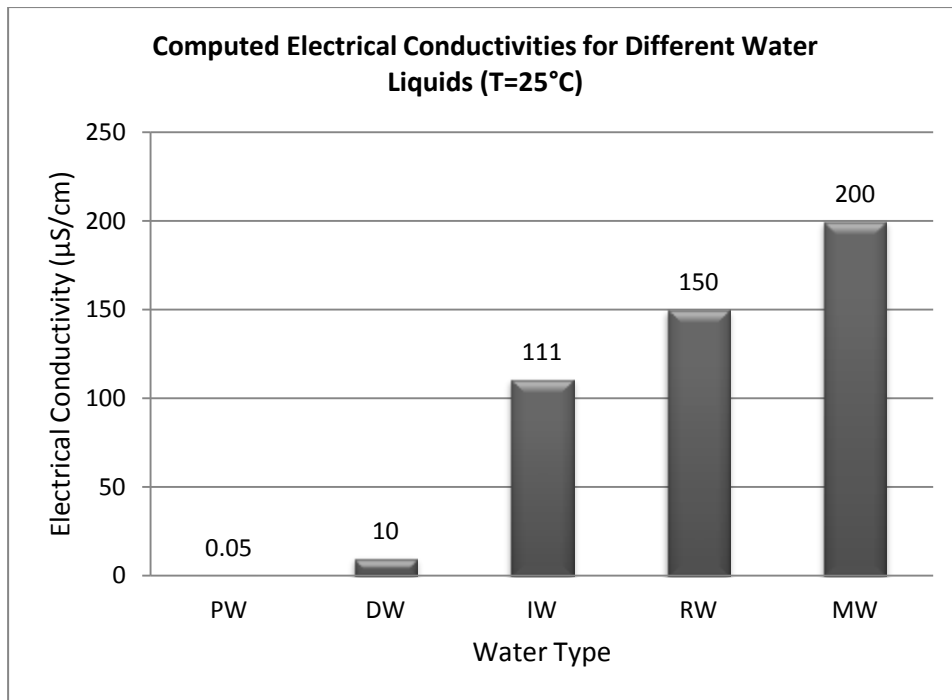
Figure 2. Investigation of electrical conductivity of different water liquids and electrolyte solutions. (Golnabi et al., 2009)

The relationship between the Electrical Conductivity (EC) and Total Dissolved Solids (TDS) has been many times established resorting to linear regressions. The concentration of Total Dissolved Solids TDS $(g.L^{-1})$ can be estimated when multiplying EC $(dS.m^{-1})$ by an empirically determined coefficient (APHA, 1992, standard method 2510) which value has been determined to vary between 0.55 and 0.9. One of the most commonly used values for this coefficient is 0.64 (TDS = 0.64EC), although this adjustment is only valid for EC <5 $dS.m^{-1}$ (Abrol *et al.,* 1988; USSLS, 1954) it suits the purpose when making estimation on water for irrigation which EC must be always lower than that.

2.10. Electrical Conductivity (EC)

Soluble salts are total dissolved salts in the root substrate (root medium) at any given time and are measured by electrical conductivity (EC). Conductivity is the ability of water to conduct an electrical current, and the dissolved ions are the conductors. So salinity is a measure of the amount of salts in the water. Most fertilizer materials, except urea, contribute to the EC content of the medium, and the

most common are nitrates (NO_3), ammonium (NH_4), phosphates (PO_4), potassium (K), Calcium (Ca), magnesium (Mg), sulfates (SO_4), sodium (Na), bicarbonate (HCO_3) and chlorides (Cl). Organic materials (i.e. urea) also contribute to the EC content after they have been changed from an insoluble to soluble form (Brian and Todd, 2000).

Salts and other substances affect the quality of water used for irrigation or drinking. They also have a critical influence on aquatic biota, and every kind of organism has a typical salinity range that it can tolerate. Therefore, conductivity can indicate groundwater seepage or a sewage leak.

The electrical conductivity of a solution containing an electrolyte is commonly known to be directly dependent on its resistance, R, which is proportional to the distance, *l*, between 2 electrodes immerged in it and inversely proportional to their cross-sectional area, *S* (figure 3).
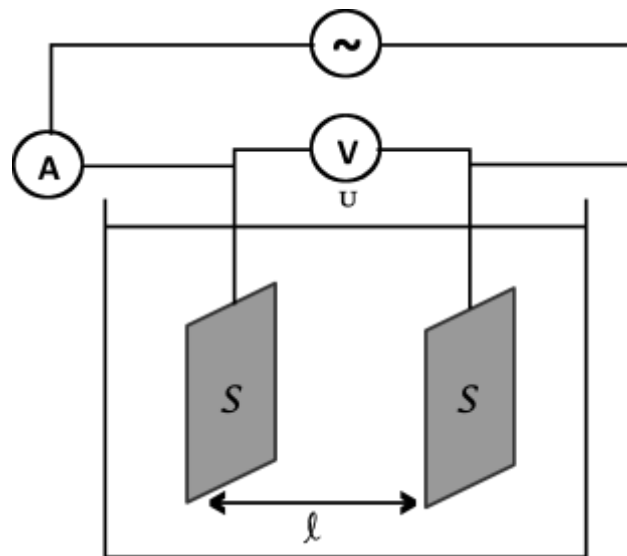

Figure 3 – Electrical conductivity, principle of measurement

With ρ for the specific resistance or resistivity, then R can be expressed as follows (Equation 1).

$$R = \frac{l}{S}\rho \qquad (eq.1)$$

Knowing the measured resistance and the characteristics *l* and S of the cell then the resistivity of the solution ρ can be determined (Equation 2)

$$\rho = \frac{s}{l}R \qquad \text{(eq.2)}$$

The Electrical conductivity EC is defined as the reciprocal of the resistivity ρ. It is expressed in Siemens per meter (S/m) usually at a reference temperature of 25ºC as temperature affects its magnitude (Equation 3).

$$EC = \frac{1}{\rho} \qquad \text{(eq.3)}$$

The EC of a solution varies with the concentration of an electrolyte, however it is not directly proportional and therefore the ions in the solution may have different abilities to transport electric current depending on the concentration in which they are in it.

Therefore the term molar conductivity which is the ratio EC to molar concentration ci (equation 4) appears to be very opportune as it describes the electrolytes behavior on transporting electric current through a wide range of solutions molarity.

$$\Lambda_m = \frac{EC}{ci} \qquad \text{(eq.4)}$$

According to the Debye-Hückel limiting law (equation 5) it is easy to understand why the ions lose their ability to transport electric current with concentration.

$$\ln(\gamma_{\pm}) = \frac{A|z_+ z_-|\sqrt{I}}{1 + B.a.\sqrt{I}} \qquad \text{(eq.5)}$$

Where
    γ - mean activity coefficient of the ions in solution
    A and B – solvent-dependent constant (A_{water} = 0.5085; B_{water} = 0.3281)
    I – ionic strength [mol/kg]
    z_+ – ionic charge of the cations
    z_- – ionic charge of the anions
    a – effective hydrated diameter of the ion in solution [Å]

The Ionic strength I is described by equation 6

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \qquad \text{(eq.6)}$$

with

c_i – molar concentration [mol/kg]

z_i – ionic charge of the ions in solution

The ionic activity a is the product of molar concentration ci by the activity coefficient γ (equation 7)

$$a = \gamma c_i \qquad \text{(eq. 7)}$$

The relationship between γ and ci from equation 7 can be easily visualized in figure 4. By the graph of figure 4, it is clear that the ionic activity decreases with concentration. In the same way the individual ability of the ions to transport electric current will follow the same pattern.
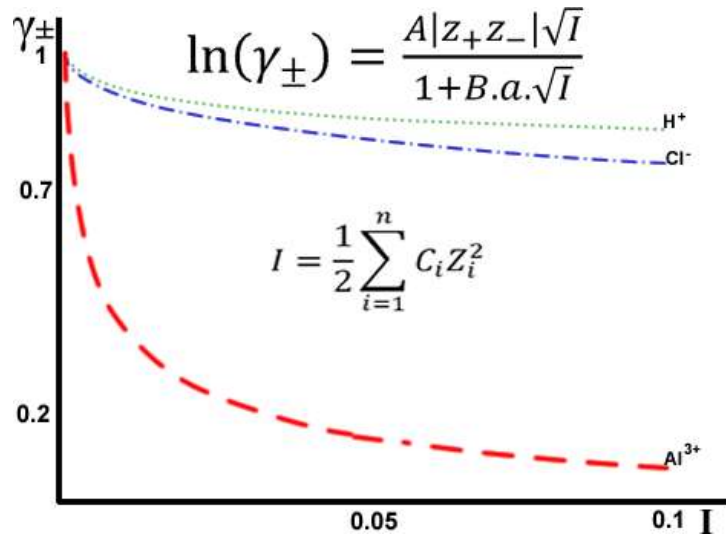

Figure 4 – Relation between the ionic activity coefficient $\gamma_{\pm}$ and Ionic strength I for 3 different ions (H^+, Cl^- and Al^{3+})

The considerations above relating molar conductivity to ionic activity are easily verified according to the nonlinear law for strong electrolytes proposed by Kohlraush, 1875. The molar conductivity Λm is maximum at infinite dilution (Λ_m^o) and decreases with concentration ci according to equation 8.

$$\Lambda_m = \Lambda_m^o - K\sqrt{c} \qquad \text{(eq.8)}$$

Where K is the Kohlrausch coefficient, which depends mainly on the stoichiometry of the specific salt in solution and Λ_m^o the molar conductivity Λm at infinite dilution, also called limiting molar conductivity. This property explains why increments on salt concentration results on gradually smaller increments on EC as shown in figure 5.
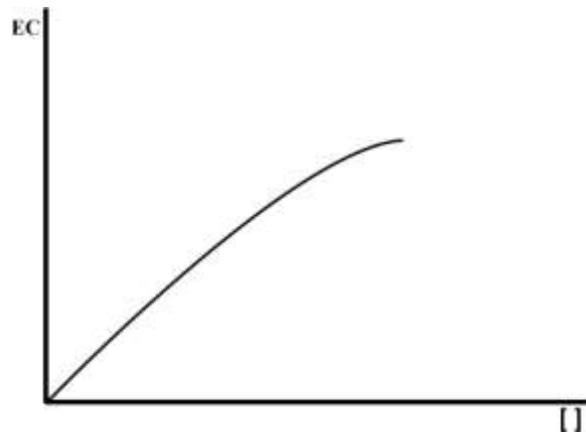

Figure 5 – typical curve EC vs Concentration.

Kohlrausch also found that the conductivity of anions and cations is additive. Therefore the limiting molar conductivity Λ_m^o can be decomposed into contributions from the different ions (Kohlrausch's law of independent migration of ions) as described in equation 9.

$$\Lambda_m^o = v_+\lambda_+^o + v_-\lambda_-^o \quad \text{(eq.9)}$$

Where v_+ and v_- are the number of moles of cations and anions, respectively, which are created from the dissociation of 1 mole of the dissolved electrolyte and λ_+^o and λ_-^o are the limiting molar conductivities of the individual ions.

Figure 6 shows that molar conductivity follows the same pattern as the activity coefficient γ
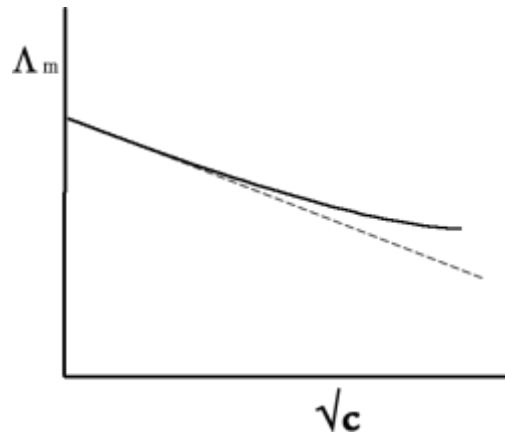
Figure 6 – Variation of molar conductivity with the squared root of molar concentration for strong electrolytes

The electrical conductivity of strong electrolytes increases with concentration but not linearly, as the concentration increases and therefore the activity coefficient decreases, as already described by equation 8 and figure 5. For that reason the rate of EC increment also decreases with concentration.

The useful unit for seawater is milliSiemens per centimeter (mS/cm), ocean waters are around 55 mS. The useful unit for freshwater is microSiemens per centimeter (umhos/cm, or µS); tap water ranges between 50 and 800 µS (depending on the source) (CWT, 2004).

- 1 dS/m = 1 mS/cm
- 1 dS/m = 1 000 µ S/cm
- 1000 µ S/cm = 1 mS/cm

The ideal EC is specific for each crop and dependent on environmental conditions (Sonneveld &Voogt, 2009) (Table 7):

Table 7. Threshold EC for salinity groups and example of crops (Jensen, 1980; Tanji, 1990).

Salinity group	Threshold EC, dS m-1	Example of crops
Sensitive	1.4	lettuce, carrot, strawberry, onion
Moderately sensitive	3.0	broccoli, cabbage, tomato, cucumber, radish, pepper
Moderately tolerant	6.0	soybean, ryegrass
Tolerant	10.0	bermuda-grass, sugar beet, cotton

Some crops can grow with high levels of EC and even a proper management of EC of the nutrient solution can provide and effective tool to improve vegetable quality (Gruda, 2009). In particular, parameters of fruit quality such as soluble solids content, titratable acidity and dry matter augmented by increasing EC level of nutrient solution from 2 to 10 dS m^{-1}. As a consequence, deep sea water (DSW) is being used for nutrient solution due to its high amount of Na^+, Mg^{2+}, K^+ and Ca^{2+} (Chadirin et al., 2007).

Table 8. Capacity of ions in an aqueous solution.

Solution	Conductivity
Absolute pure water	0.055 μS/cm
Power plant boiler water	1.0 μS/cm
Good city water	50 μS/cm
Ocean water	53 mS/cm
Distilled water	0.5 μS/cm
Deionized water	0.1-10 μS/cm
Demineralized water	0-80 μS/cm
Drinking water	0.5-1 mS/cm
Wastewater	0.9-9 mS/cm
Seawater	53 mS/cm
10% NaOH	355 mS/cm
10% H2SO4	432 mS/cm
31% HNO3	865 mS/cm

http://www.eutechinst.com/brochures/annual_catalogue/2011_catalogue_r1_con_tds_salt.pdf

2.11.Influence of temperature on electrical conductivity

Because the conductivity of water increases with temperature, the conductance of different samples cannot be compared unless the measurements are made at the same temperature or adjusted to the conductance at a single temperature. The electrical conductivity of a solution is a summation of contributions from all the ions present. The velocities of the ions depend on the temperature of the solution (Willard et al., 1981). As mentioned above electrical conductivity is strongly temperature dependent. It increases with increasing temperature. It is affected by the nature of the ions and by the viscosity of the water (Foxboro Company, 1987). If it is not possible to make measurements at the reference temperature (25.0 °C) the temperature correction to 25 °C as a reference is needed. The lower the concentration, the higher the correction coefficient (ASTM, 1986). The temperature effect is largely to improve ionic mobility at higher temperature, which is due to the decreasing viscosity of water. For this reason most salts in water have about the same temperature correction coefficient (Gray et al., 1999). The temperature correction coefficient for different solutions is almost always positive and of magnitude from about 0.5-3 %/°C (Willard 1981, Zabarsky 1992). Ultrapure water has by far the largest coefficient 4.55-5.2 %/°C (Foxboro Company, 1987). Ionic salts have temperature correction coefficient of about 2 %/°C, while acids, alkalis and concentrated salt solutions have coefficients typically of 1.5-1.9 %/°C. Acids and alkalis have lower coefficients than ionic salts because of the higher but less temperature sensitive conductivity of hydrogen (hydronium) and hydroxyl ions (Gray at al., 1999).

Table 9. Common temperature correction coefficient for different solution

Sample	Temperature coefficient (%/°C)
10% HCl	1.56 (1.32*)
10% KCl	1.88
5% H2SO4	0.96
50% H2SO4	1.93
98% H2SO4	2.84
10% NaCl	2.14
Ultrapure water	4.55
5% NaOH	1.72

http://www.orionres.com/ionguide/english/ion24eng.html,

http://www .eutechinst.com/techtips/tech-tips25.htm)

Conductometer 350i (device that we use for our measurements) corrects temperature automatically.

A 2-point compensation may be used with an exact match at two temperatures. Some error may exist at the intermediate temperatures (ASTM, 1986; Foxboro Company, 1987). The 2-point temperature coefficient can be calculated by the equation:

$$\theta = \frac{1}{k_{ref}}\left(\frac{k_T - k_{ref}}{T - T_{ref}}\right) * 100 \qquad \text{(eq.10)}$$

Where:

θ - Temperature correction coefficient (%/°C)

T - Measuring temperature (°C)

k_T - Electrical conductivity of the sample at T

T_{ref} - Reference temperature 25°C

k_{ref} - Electrical conductivity of the sample at T_{ref}

3. Hypothesis and Objectives

Hypothesis,

The use of conductmeters requires calibrations and its readings may become inaccurate which rises on opportunity to develop a more simple method of obtaining accurate value of EC through estimation.

Objectives,

To develop a mathematical model to co-relate concentration (g/l) of a given nutritive solution (with known composition) to its resulting EC (mS/cm)

4. Material and methods

4.1. Material

Laboratory work was conducted at the Czech University of Life Science Prague, in the faculty of Agrobiology Food and Natural Resource.

We used eight different salts:

- Ammonium Nitrate (NH_4NO_3), Potassium Sulfate (K_2SO_4), Potassium Nitrate (KNO_3), Calcium Nitrate ($Ca(NO_3)_2$), Magnesium Sulfate ($MgSO_4$), Ammonium Phosphate ($NH_4H_2PO_4$), Potassium Phosphate (KH_2PO_4) and Sodium Bicarbonate ($NaHCO_3$).

4.2. Method

The methodology used was based in correlating concentration of 8 different strong electrolytes to their resulting EC between a range of 0 and 5 g/l (measurements made by 0,2g/l increments). For determination of electrical conductivity (EC) it was used a Conductometer (type 350i). Before use, the device was calibrated by standard solution: 0.01 mol/l of KCl..

By using equation 11 obtained via regression (order3) we can obtain EC for individual salts.

$$k_i = aa_i[]_i^3 + a_i[]_i^2 + b_i[]_i + c_i \qquad \text{(EQ. 11)}$$

k_i (mS/cm) – Resulting electrical conductivity

[] (g/l) – Salt concentration

i - Individual

Regression coefficients in detail for each salt:

Ammonium Nitrate (NH_4NO_3)

$k_1 = 0.009X^3 - 0.029X^2 + 1.6238X + 0.027$

Potassium Sulfate (K_2SO_4)

$k_2 = 0.0051X^3 - 0.0658X^2 + 1.4974X - 0.0049$

Potassium Nitrate (KNO_3)

$k_3 = 0.0042X^3 - 0.0524X^2 + 1.3823X - 0.0049$

Calcium Nitrate ($Ca(NO_3)_2$)

$k_4 = 0.0029X^3 - 0.0496X^2 + 0.9759X + 0.00005$

Magnesium Sulfate (MgSO4)

$k_5 = 0.0039X^3 - 0.0545X^2 + 0.7082X + 0.0406$

Ammonium Phosphate ($NH_4H_2PO_4$)

$k_6 = 0.0036X^3 - 0.0404X^2 + 0.8735X + 0.0125$

Potassium Phosphate ($K_2H_2PO_4$)

$k_7 = 0.0024X^3 - 0.0282X^2 + 0.727X + 0.001$

Sodium Bicarbonate ($NaHCO_3$)

$k_8 = 0.002X^3 - 0.0338X^2 + 1.0279X + 0.0131$

Then the total electro-conductivity k_f might be estimated by linear combination equations above, as follows:

$$k_f = aa_f[]_f^3 + a_f[]_f^2 + b_f[]_f + c_f \qquad \text{(EQ. 12)}$$

f - final

with:

$$[]_f = \sum_{i=1}^{8} []_i$$

$$aa_f = \frac{\sum_{i=1}^{8} aa_i \, []_i}{[]_f}$$

$$a_f = \frac{\sum_{i=1}^{8} a_i \, []_i}{[]_f}$$

$$b_f = \frac{\sum_{i=1}^{8} b_i \, []_i}{[]_f}$$

$$c_f = \frac{\sum_{i=1}^{8} c_i \, []_i}{[]_f}$$

5. Results and Discussion

Table 10. Represent first measurements for each salt [](g/l) vs EC k(mS/cm).

[](g/l)\k(ms/cm)	NH^{4}NO^3	K$_2$SO$_4$	KNO$_3$	Ca(NO$_3$)$_2$	MgSO$_4$	NH$_4$H$_2$PO$_4$	KH$_2$PO$_4$	NaHCO$_3$
0,2	0,35	0,30	0,28	0,19	0,18	0,17	0,15	0,21
0,4	0,67	0,59	0,55	0,38	0,32	0,36	0,29	0,42
0,6	1,00	0,86	0,81	0,56	0,44	0,52	0,43	0,62
0,8	1,31	1,16	1,06	0,75	0,59	0,69	0,57	0,82
1	1,63	1,44	1,32	0,93	0,70	0,86	0,71	1,01
1,2	1,94	1,69	1,58	1,11	0,80	1,02	0,83	1,21
1,4	2,25	1,97	1,83	1,28	0,93	1,18	0,97	1,39
1,6	2,56	2,25	2,09	1,45	1,05	1,32	1,11	1,58
1,8	2,86	2,5	2,34	1,61	1,17	1,46	1,24	1,77
2	3,16	2,8	2,59	1,77	1,27	1,62	1,36	1,95
2,2	3,47	3,03	2,83	1,93	1,38	1,77	1,49	2,13
2,4	3,76	3,26	3,07	2,09	1,49	1,92	1,62	2,31
2,6	4,07	3,53	3,32	2,26	1,58	2,06	1,75	2,49
2,8	4,35	3,77	3,56	2,42	1,67	2,22	1,87	2,67
3	4,66	4,04	3,79	2,57	1,78	2,36	1,99	2,85
3,2	4,96	4,3	4,02	2,71	1,87	2,51	2,12	3,02
3,4	5,25	4,53	4,25	2,86	1,96	2,66	2,24	3,19
3,6	5,55	4,75	4,47	3	2,06	2,8	2,35	3,37
3,8	5,83	5,01	4,71	3,15	2,16	2,95	2,48	3,54
4	6,11	5,26	4,95	3,29	2,26	3,1	2,61	3,71
4,2	6,4	5,5	5,18	3,44	2,35	3,24	2,74	3,89
4,4	6,69	5,75	5,42	3,58	2,43	3,38	2,87	4,06
4,6	6,97	5,98	5,65	3,73	2,52	3,52	2,99	4,22
4,8	7,25	6,22	5,89	3,87	2,61	3,67	3,1	4,39
5	7,53	6,48	6,12	4	2,7	3,81	3,23	4,55

Results that are presented on table 10 shows that different electrolytes behave in different ways related to Electrical Conductivity (EC). It is visible that Ammonium Nitrate has shown higher EC as opposed to other salts. This variability can be observed also on the table 10 (Ammonium Nitrate has produced 7.53 mS/cm in a concentration 5gr/l. Magnesium Sulfate with 2.7 mS/cm in 5gr/l appears to be the one with lower effect on EC). We can see that Magnesium Sulfate expresses 2.7 mS/cm of EC in a concentration of 5g/l, where this range of EC has been reached

only with about 1.6-1.8 gr/l of ammonium nitrate. What we can see is the increase of EC is always going up by increasing salt concentration (however at a decreasing rate).
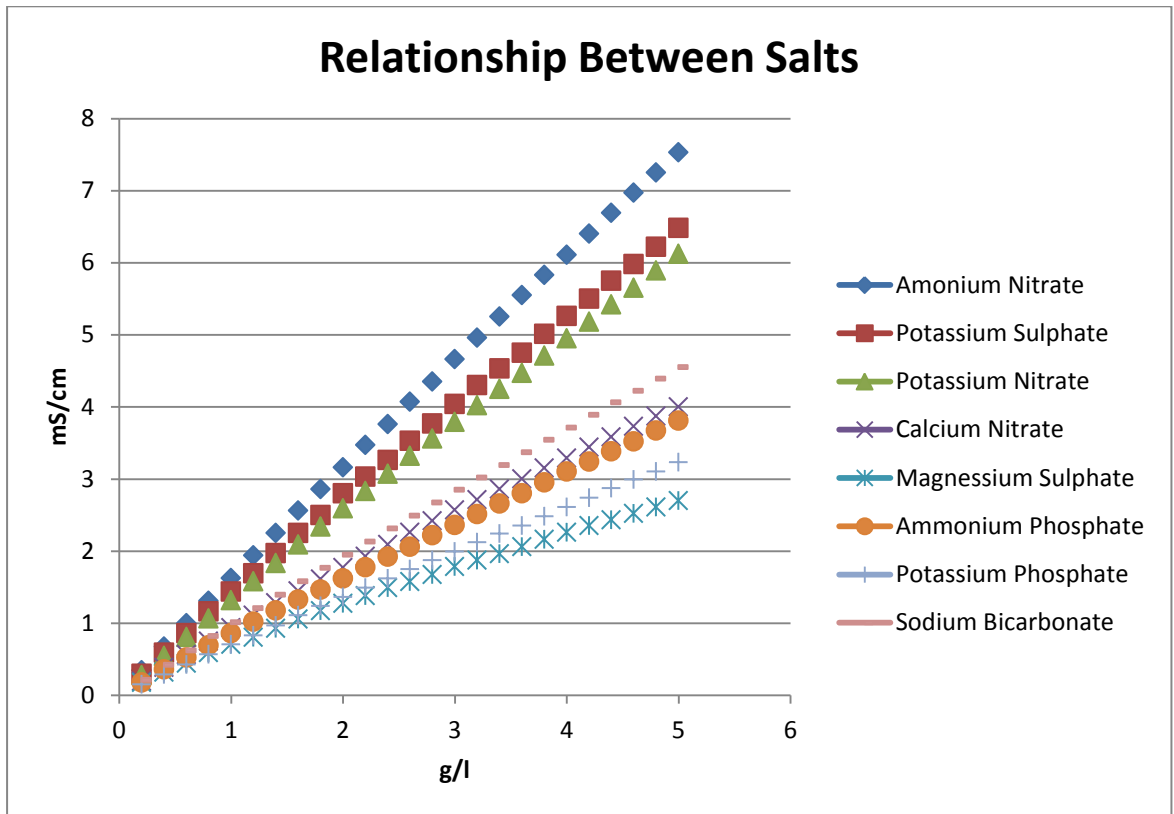

Figure 6. Relationship between salts and electrical conducitivty.

In order to verify the validity of equation 12, we have prepared 78 solutions of the 8 electrolytes from table 10, where the individual participation of each salt in each solution was chosen randomly resorting to EXCEL function "randbetween(0,2)" selecting a random amount of each salt ($[]i$) between 0 and 2 $[]$ (g/l)

The groups of observed EC and estimated EC were finally compared through a t-Test and an Analysis of Variance (ANoVA single factor) for an interval of confidence of 95% (table 11, 12).

The resulting EC was measured through conductometer and estimated through equation 12. Afterwards, a correlation between measured and estimated

results has been created in order to verify the accuracy of the estimation based on the value of correlation R^2.
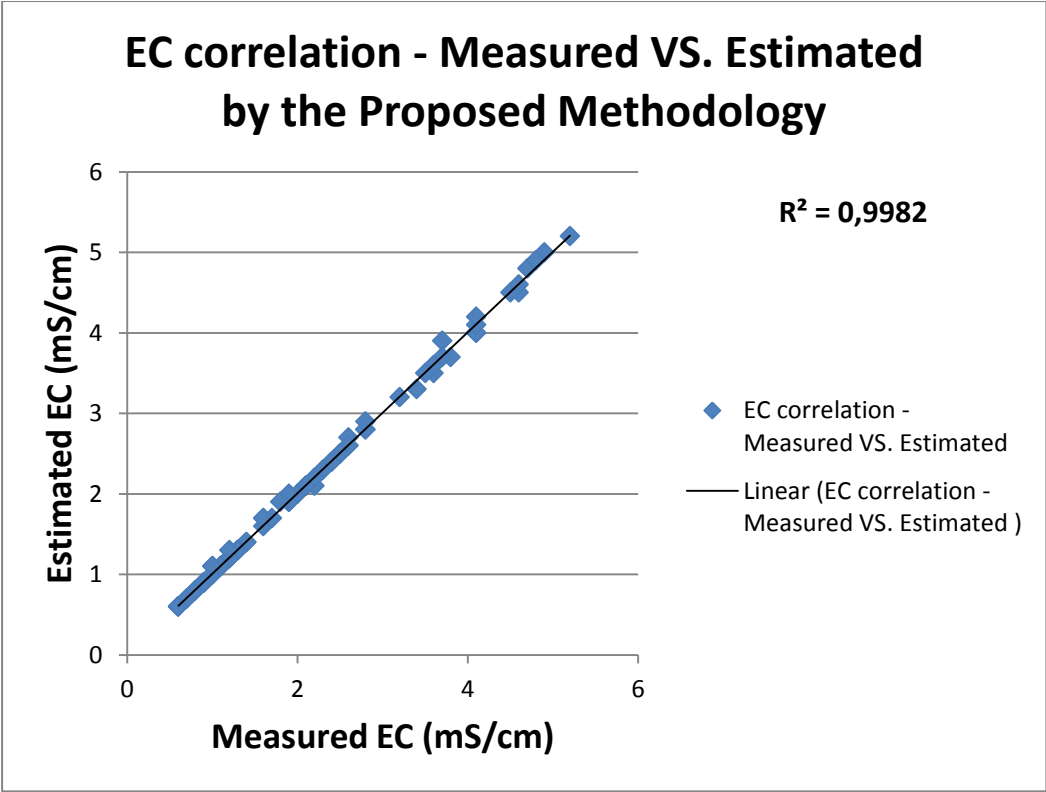

Figure 8. Correlation Estimation vs. Measured according to equation 12.

The R^2 value for this correlation indicates that the accuracy of the estimation using equation 12 is very high.

According to (Abrol et al., 1988) chap. 2.9, using factor 0.64 may not be always precise.

EC correlation - Measured VS. Estimated by Abrol et al. Methodology

$R^2 = 0,9804$
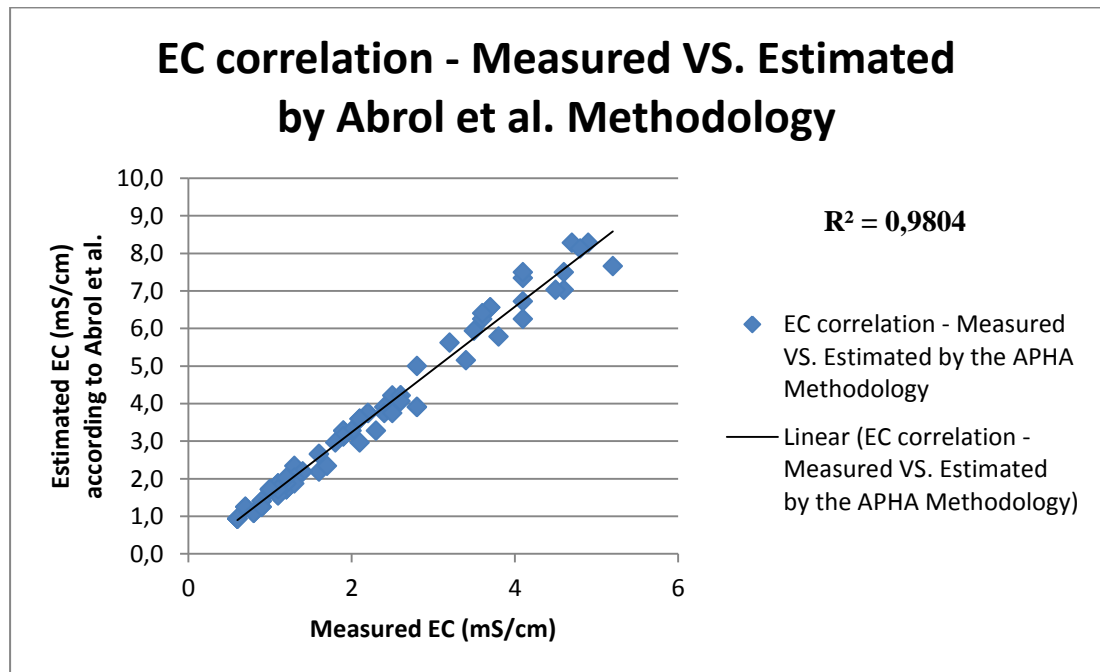
Figure 9. Correlation Estimation vs. Measured according to Abrol et al. methodology.

Comparing R^2 of equation 12 and methodology by Abrol et al. with 0.64 factor, we can occur that correlation of equation 12 is higher.

An analysis of variance (ANOVA single factor for 95% interval of confidence) performed between the estimated values and the observed values shows that we can assume no differences between the estimated values and the observed values.

Table 11 – AnoVA single factor performed between the estimated values and the observed values

SUMMARY

Groups	Count	Sum	Average	Variance
Measured EC	77	166,7840	2,1660	1,6441
Estimated EC	77	168,5515	2,1890	1,6665

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0,0203	1	0,0203	0,0123	0,9120	3,9034
Within Groups	251,6093	152	1,6553			
Total	251,6296	153				

The results of a t-test for an interval of confidence of 95% performed between estimation and observation assumes that no differences between the 2 groups are to be expected.

Table 12 - t-test for an interval of confidence of 95% performed between estimation and observation.

	Variable 1 (measured EC))	Variable 2 (estimated EC)
Mean	2,166025974	2,188980636
Variance	1,644127473	1,66652155
Observations	77	77
Pearson Correlation	0,999289873	
Hypothesized Mean Difference	0	
df	76	
t Stat	-4,088942037	
P(T<=t) one-tail	5,33366E-05	
t Critical one-tail	1,665151353	
P(T<=t) two-tail	0,000106673	
t Critical two-tail	1,99167261	

An analysis of variance (ANOVA single factor for 95% interval of confidence) performed between the estimated values and the observed values according to Abrol et al. methodology shows that there are some differences between the groups.

Table 13 – AnoVA single factor performed between the estimated and observation by the Abrol et al. methodology.

SUMMARY

Groups	Count	Sum	Average	Variance
Column 1	77	167,6	2,176623377	1,659446343
Column 2	77	271,71875	3,528814935	4,724988853

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	70,39425	1	70,39424741	22,05183239	5,89E-06	3,903366
Within Groups	485,2171	152	3,192217598			
Total	555,6113	153				

Table 14 - t-test for an interval of confidence of 95% performed between estimation and observation by Abrol et al. methodology.

	Variable 1	Variable 2
Mean	2,176623	3,528814935
Variance	1,659446	4,724988853
Observations	77	77
Pearson Correlation	0,99013	
Hypothesized Mean Difference	0	
df	76	
t Stat	-12,9509	
P(T<=t) one-tail	3,21E-21	
t Critical one-tail	1,665151	
P(T<=t) two-tail	6,42E-21	
t Critical two-tail	1,991673	

6. Conclusions

According to our results we can conclude that every salts shows different behavior on resulting electrical conductivity. Salts containing major macro elements like ammonium nitrate, potassium sulfate, potassium nitrate have a higher effect on increasing water EC.

According to equation 12, electrical conductivity of a solution can be predicted with high accuracy. The previous methods based on a single correlation coefficient are not as accurate as the one is being proposed, which is a consequence of each salt having a specific effect on water EC.

Final EC largely depends on the combination of salts. That explains the low correlation coefficient of previous methods giving opportunity to a more comprehensive assessment of the effect of salinity on EC.

According to statistical analyses it is clear that the methodology that is proposed above (based on including as many coefficients as salts present in the nutritive solution) shows no difference between groups, which means that measurements resorting to the use of a conductometer and estimation might be considered the same. The great majority of methods (as Abrol et al. methodology) which use a simple correlating factor (0.64 as the average choice) show the null hypothesis rejected after Analysis of Variance (AnoVA) which implies that estimation does not predict reality in that case.

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Link Source:

http://www.eutechinst.com/brochures/annual_catalogue/2011_catalogue_r1_con_tds_salt.pdf

Appendix:

Individual graphs for each element related to g/l vs. electrical conductivity (mS/cm)
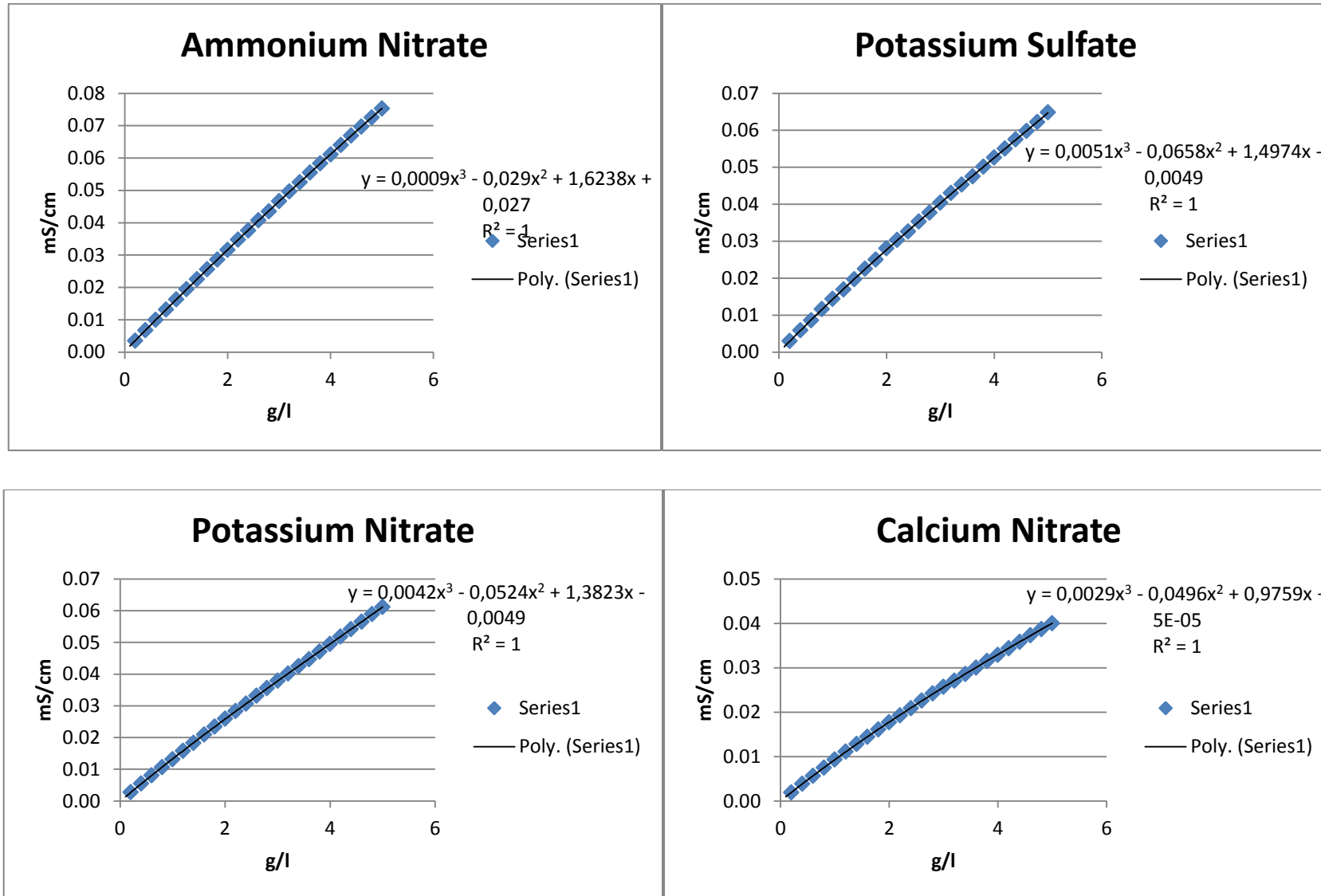
Magnessium Sulfate

$y = 0{,}0039x^3 - 0{,}0545x^2 + 0{,}7082x + 0{,}0406$

$R^2 = 0{,}9999$

Ammonium Phosphate

$y = 0{,}0036x^3 - 0{,}0404x^2 + 0{,}8735x + 0{,}0125$

$R^2 = 1$

Potassium Phosphate

$y = 0{,}0024x^3 - 0{,}0282x^2 + 0{,}727x + 0{,}001$

$R^2 = 1$

Sodium Bicarbonate

$y = 0{,}002x^3 - 0{,}0338x^2 + 1{,}0279x + 0{,}0131$

$R^2 = 1$
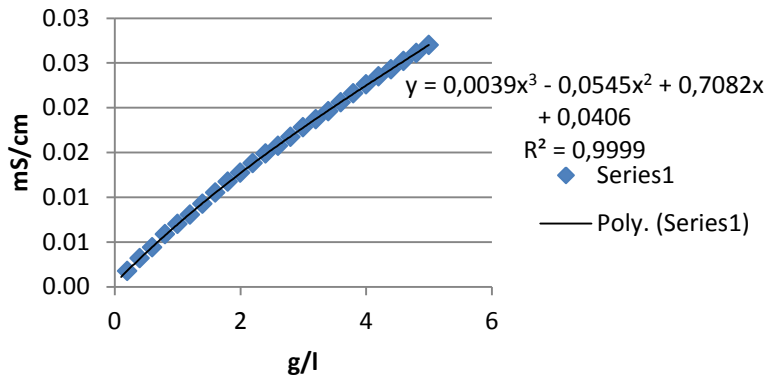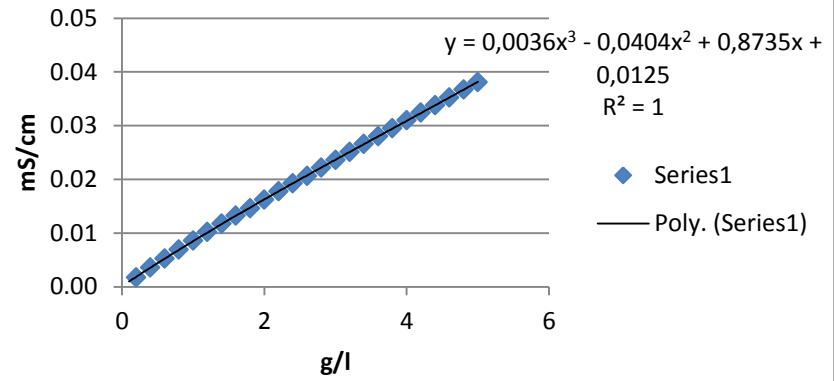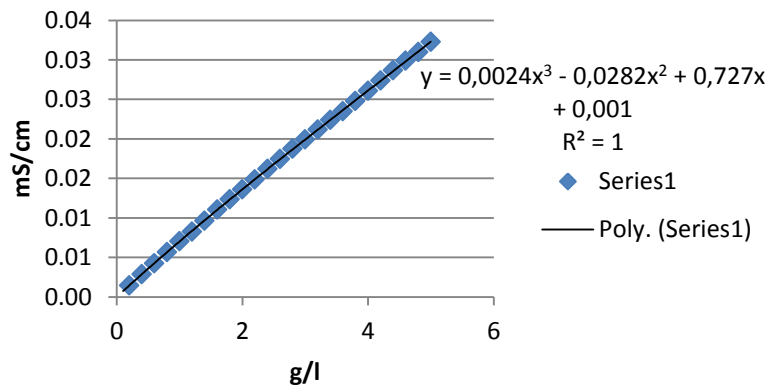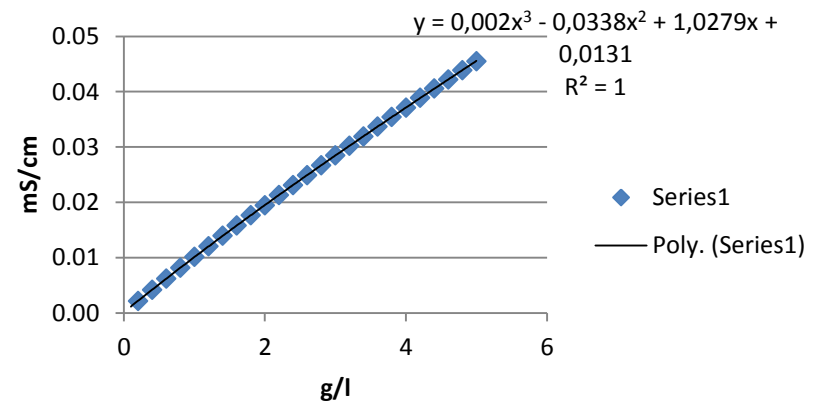
Table 13 – Relation between concentration and EC of random solutions of 8 nutritive salts observed and also estimated by equation 12.

[]1(g/l)	[]2(g/l)	[]3(g/l)	[]4(g/l)	[]5(g/l)	[]6(g/l)	[]7(g/l)	[]8(g/l)	[]f (g/l)	EC k(mS/cm)	EC k(mS/cm)	Abrol et al., 2011. K_i= []/0.64
NH4NO3	K2SO4	KNO3	Ca(NO3)2	MgSo4	NH4H2Po4	KH2Po4	NaHCo3	Total	(Measured)	(Estimated)	(Estimated)
0,9	0,2	0,5	0,6	0,8	0,5	0,2	0,1	3,7	3,8	3,7	5,8
0,1	0,9	0,1	0,6	0,6	0,9	0,7	0,2	4,0	3,6	3,5	6,3
0,5	0,8	0,9	0,9	0,7	0,4	0,1	0,4	4,5	4,6	4,5	7,0
0,5	0,6	0,0	1,0	0,8	0,9	0,0	0,4	4,2	3,7	3,9	6,6
0,4	0,9	0,8	0,5	0,5	0,2	1,0	0,3	4,5	4,5	4,5	7,0
0,5	0,6	1,0	0,5	0,8	0,6	0,7	0,5	5,3	4,9	5,0	8,3
0,6	0,1	0,9	0,3	0,5	0,2	0,6	0,9	4,0	4,1	4,0	6,3
0,6	0,1	0,4	0,4	0,1	0,1	1,0	0,8	3,3	3,4	3,3	5,2
0,1	0,7	0,9	0,4	0,8	0,1	0,7	0,7	4,3	4,1	4,0	6,7
0,4	0,3	0,1	0,4	0,8	0,2	0,7	0,7	3,6	3,2	3,2	5,6
0,1	0,0	0,1	0,1	0,1	0,2	0,3	0,3	1,1	1,0	1,0	1,7
0,1	0,1	0,1	0,1	0,3	0,1	0,1	0,1	0,8	0,7	0,7	1,3
0,1	0,2	0,2	0,2	0,3	0,1	0,2	0,2	1,4	1,4	1,4	2,2
0,1	0,0	0,1	0,2	0,2	0,1	0,0	0,2	0,9	0,9	0,9	1,4
0,1	0,2	0,2	0,2	0,2	0,1	0,3	0,2	1,3	1,3	1,3	2,0
0,0	0,2	0,1	0,1	0,1	0,2	0,1	0,0	0,6	0,6	0,6	0,9
0,2	0,2	0,0	0,1	0,1	0,2	0,1	0,2	1,1	1,2	1,2	1,7
0,3	0,1	0,1	0,3	0,0	0,0	0,2	0,1	1,0	1,1	1,1	1,6
0,1	0,1	0,3	0,1	0,0	0,0	0,1	0,3	0,7	0,8	0,8	1,1
0,1	0,2	0,2	0,1	0,1	0,0	0,1	0,1	0,8	0,9	0,9	1,3
0,2	0,0	0,2	0,2	0,2	0,3	0,5	0,5	2,1	1,9	1,9	3,3
0,1	0,1	0,1	0,2	0,5	0,2	0,2	0,1	1,5	1,3	1,3	2,3

0,2	0,4	0,4	0,4	0,5	0,1	0,4	0,3	2,7	2,6	2,6	4,2
0,2	0,0	0,2	0,4	0,4	0,2	0,0	0,3	1,7	1,6	1,7	2,7
0,2	0,3	0,3	0,4	0,3	0,2	0,5	0,3	2,5	2,4	2,4	3,9
0,0	0,4	0,1	0,1	0,1	0,3	0,1	0,0	1,1	1,2	1,2	1,7
0,4	0,4	0,0	0,2	0,1	0,4	0,2	0,4	2,1	2,3	2,3	3,3
0,5	0,1	0,2	0,5	0,0	0,0	0,4	0,2	1,9	2,1	2,1	3,0
0,1	0,1	0,5	0,1	0,0	0,0	0,1	0,5	1,4	1,6	1,6	2,2
0,1	0,4	0,4	0,2	0,1	0,0	0,2	0,1	1,5	1,7	1,7	2,3
0,1	0,0	0,1	0,1	0,1	0,2	0,3	0,3	1,1	1,0	1,0	1,7
0,1	0,1	0,1	0,1	0,3	0,1	0,1	0,1	0,8	0,7	0,7	1,3
0,1	0,2	0,2	0,2	0,3	0,1	0,2	0,2	1,4	1,4	1,4	2,2
0,1	0,0	0,1	0,2	0,2	0,1	0,0	0,2	0,9	0,9	0,9	1,4
0,1	0,2	0,2	0,2	0,2	0,1	0,3	0,2	1,3	1,3	1,3	2,0
0,0	0,2	0,1	0,1	0,1	0,2	0,1	0,0	0,6	0,6	0,6	0,9
0,2	0,2	0,0	0,1	0,1	0,2	0,1	0,2	1,1	1,2	1,2	1,7
0,3	0,1	0,1	0,3	0,0	0,0	0,2	0,1	1,0	1,1	1,1	1,6
0,1	0,1	0,3	0,1	0,0	0,0	0,1	0,3	0,7	0,8	0,8	1,1
0,1	0,2	0,2	0,1	0,1	0,0	0,1	0,1	0,8	0,9	0,9	1,3
0,1	0,3	0,2	0,3	0,1	0,1	0,0	0,1	1,2	1,3	1,3	1,9
0,4	0,0	0,1	0,5	0,6	0,4	0,2	0,1	2,1	1,9	1,9	3,3
0,2	0,2	0,4	0,6	0,4	0,7	0,2	0,1	2,7	2,5	2,5	4,2
0,2	0,3	0,1	0,3	0,3	0,6	0,5	0,3	2,4	2,2	2,1	3,8
0,0	0,6	0,0	0,8	0,0	0,4	0,6	0,2	2,4	2,2	2,2	3,8
0,4	0,8	0,3	0,8	0,2	0,3	0,0	0,0	2,5	2,8	2,8	3,9
0,2	0,6	0,1	0,5	0,3	0,5	0,1	0,6	2,7	2,6	2,7	4,2
0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	2,4	2,4	2,4	3,8
0,1	0,7	0,4	0,5	0,3	0,2	0,6	0,0	2,6	2,6	2,6	4,1
0,6	0,3	0,4	0,0	0,4	0,0	0,3	0,6	2,5	2,8	2,8	3,9
0,2	0,6	0,4	0,6	0,3	0,2	0,0	0,2	2,4	2,5	2,5	3,8
0,7	0,0	0,2	1,0	1,1	0,8	0,3	0,1	4,2	3,7	3,7	6,6

0,4	0,4	0,8	1,1	0,8	1,3	0,3	0,2	5,3	4,7	4,8	8,3
0,3	0,6	0,1	0,6	0,6	1,1	0,9	0,5	4,7	4,1	4,1	7,3
0,0	1,1	0,0	1,5	0,0	0,8	1,1	0,3	4,8	4,1	4,2	7,5
0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	4,8	4,6	4,6	7,5
0,2	1,3	0,7	0,9	0,6	0,4	1,1	0,0	5,2	4,8	4,9	8,1
1,2	0,5	0,8	0,0	0,7	0,0	0,5	1,2	4,9	5,2	5,2	7,7
0,0	0,1	0,0	0,4	0,1	0,0	0,0	0,1	0,6	0,6	0,6	0,9
0,0	0,2	0,0	0,8	0,1	0,1	0,0	0,1	1,2	1,1	1,1	1,9
0,0	0,0	0,1	0,3	0,1	0,0	0,0	0,1	0,6	0,6	0,6	0,9
0,0	0,0	0,2	0,6	0,1	0,1	0,0	0,1	1,1	1,0	1,1	1,7
0,0	0,0	0,4	1,2	0,2	0,1	0,0	0,1	2,0	1,9	1,9	3,1
0,0	0,2	0,0	0,7	0,1	0,1	0,0	0,2	1,2	1,2	1,2	1,9
0,0	0,3	0,0	1,5	0,2	0,1	0,0	0,2	2,3	2,1	2,1	3,6
0,0	0,0	0,2	0,6	0,1	0,1	0,0	0,2	1,2	1,1	1,1	1,9
0,0	0,0	0,4	1,2	0,2	0,1	0,0	0,2	2,1	2,0	2,0	3,3
0,0	0,0	0,8	2,4	0,4	0,3	0,0	0,2	4,1	3,6	3,6	6,4
0,0	0,0	0,3	0,4	0,2	0,1	0,0	0,2	1,1	1,1	1,1	1,7
0,0	0,0	0,6	0,8	0,3	0,1	0,0	0,2	2,0	1,9	2,0	3,1
0,0	0,0	1,2	1,6	0,6	0,2	0,0	0,2	3,8	3,5	3,5	5,9
0,0	0,2	0,0	0,5	0,1	0,1	0,0	0,2	1,1	1,0	1,1	1,7
0,0	0,4	0,0	1,0	0,2	0,1	0,0	0,2	1,9	1,8	1,9	3,0
0,0	0,4	0,0	0,7	0,4	0,1	0,0	0,2	1,7	1,6	1,7	2,7
0,0	0,8	0,0	1,4	0,7	0,1	0,0	0,2	3,2	2,8	2,9	5,0
0,0	0,3	0,0	0,5	0,3	0,0	0,0	0,2	1,3	1,2	1,3	2,0
0,0	0,5	0,0	1,0	0,5	0,1	0,0	0,2	2,3	2,1	2,1	3,6

Example of final work

	NH$_4$NO$_3$	K$_2$SO$_4$	KNO$_3$	Ca(NO$_3$)$_2$	MgSO$_4$	NH$_4$H$_2$PO$_4$	KH$_2$PO$_4$	NaHCO$_3$				
aai	0.0009	0.0051	0.0042	0.0029	0.0039	0.0036	0.0024	0.0020	**Sum(aai)**	0.0	**aaf**	0.0
ai	-0.0290	-0.0658	-0.0524	-0.0496	-0.0545	-0.0404	-0.0282	-0.0338	**Sum(ai)**	-0.1	**af**	0.0
bi	1.6238	1.4974	1.3823	0.9759	0.7082	0.8735	0.7270	1.0279	**Sum(bi)**	2.8	**bf**	1.0
ci	0.0270	-0.0049	-0.0049	0.0001	0.0406	0.0125	0.0010	0.0131	**Sum(ci)**	0.0	**cf**	0.0
										Total g/l		Estimated (EC)
[]i	0.1	0.2	0.1	1	0.4	0.3	0.6	0.2	**[]$_f$**	2.9	**K$_f$**	2.47