

# Investigating the reliability of aquarium test kits and ion-selective electrodes for nutrition management of hydroponic systems

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## Abstract

Regular nutrient level monitoring is crucial for plant production hydroponic systems. The nutrient solution's imbalance can result in diminished yields, nutrient losses, environmental emissions, and financial costs. While traditional laboratory analyses of individual ions are accurate, they are often time-consuming and costly. This study investigates two alternative measurement methods: ion-selective electrodes (ISEs) and aquarium test kits. These methods were evaluated for their measurement repeatability and accuracy for  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cu}^+$ ,  $\text{Fe}^{2+}$  ions, and pH measurements in two types of hydroponic solution: Hoagland's solution and commercially available Vegbloom solution.

Results show varying performance based on solution type and ion concentration. For nitrate ( $\text{NO}_3^-$ ) measurements, the Red Sea test kit was the most reliable for both solutions, though its narrow range necessitated serial dilution. For nitrite ( $\text{NO}_2^-$ ), Sera Aqua test kit excelled in measurement accuracy. Ammonium ( $\text{NH}_4^+$ ) measurements showed that the Fluval kit performed best with the Hoagland solution, while the API kit excelled with the Vegbloom solution.  $\text{NH}_4^+$  ISE had a large margin of errors while measuring Hoagland solution but improved noticeably with Vegbloom solution measurements. For phosphate ( $\text{PO}_4^{3-}$ ) measurements, API and Sera Aqua test kits demonstrated the best overall accuracy across both solutions. Potassium ( $\text{K}^+$ ) measurements were most effectively handled by the K ISE, which showed minimal offset and high precision across a broad range. For calcium ( $\text{Ca}^{2+}$ ), the Red Sea test kit emerged as the most reliable for both solutions. While the calcium ISE proved reliable, its accuracy was inferior to most test kits. For magnesium ( $\text{Mg}^{2+}$ ), the Seachem test kit demonstrated the highest overall accuracy. For copper ( $\text{Cu}^+$  and  $\text{Cu}^{2+}$ ) measurements, JBL test kit stands out with the best overall performance across both solutions. For iron ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ), Fluval and Sera Aqua test kits were most accurate, though all kits tended to overestimate actual ion concentration. NT Sensors pH electrodes outperformed aquarium kits for pH measurements, offering superior accuracy and precision over a wide measurement range.

Factors like cost, frequency, and environmental conditions must be considered when selecting measurement methods. While ISEs offer wide ranges and potential for automation, they face issues like signal drift and interference with other ions, whereas aquarium test kits have limited ranges and subjective color interpretation. A color chart corresponding to the color changes with hydroponic solutions needs to be developed to use aquarium test kits for

hydroponic systems. This study can be used as a guide to growers to compare and choose the most reliable, and cost-effective measurement method based on their measurement requirements and specifications of the system.

## Résumé

Une surveillance régulière du niveau d'éléments nutritifs est cruciale pour les systèmes hydroponiques de production végétale. Les déséquilibres dans la solution nutritive peuvent entraîner une diminution des rendements, des pertes d'éléments nutritifs, des émissions environnementales et des coûts financiers. Bien que les analyses de laboratoire traditionnelles des ions individuels soient précises, elles prennent souvent beaucoup de temps et sont coûteuses. Cette étude étudie deux méthodes de mesure alternatives : les électrodes sélectives d'ions (ESIs) et les kits de test d'aquarium. Ces méthodes ont été évaluées pour leur précision et leur répétabilité de mesure pour les ions  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cu}^+$ ,  $\text{Fe}^{2+}$ , et les mesures de pH dans deux types de solution hydroponique : les solutions de Hoagland et de Vegbloom, disponibles commercialement.

Les résultats montrent des performances variables en fonction du type de solution et de la concentration d'ions. Pour les mesures de nitrate ( $\text{NO}_3^-$ ), le kit d'essai Red Sea était le plus fiable pour les deux solutions, bien que sa plage de mesure limitée ait nécessité une dilution en série. Pour le nitrite ( $\text{NO}_2^-$ ), le kit de test Sera Aqua a excellé dans la précision de mesure. Les mesures d'ammonium ( $\text{NH}_4^+$ ) ont montré que le kit Fluval était le plus performant avec la solution Hoagland, tandis que le kit API excellait avec la solution Vegbloom.  $\text{NH}_4^+$  ISE avait une grande marge d'erreur lors de la mesure de la solution Hoagland, mais s'est sensiblement améliorée avec les mesures de solution de Vegbloom. Pour les mesures de phosphate ( $\text{PO}_4$ ), les kits de test API et Sera Aqua ont démontré la meilleure précision globale sur les deux solutions. Les concentrations de potassium ( $\text{K}^+$ ) ont été le plus efficacement mesurées par le  $\text{K}^+$  ISE, qui a démontré la meilleure précision à travers un large éventail de concentrations. Pour le calcium ( $\text{Ca}^{2+}$ ), le kit d'essai Red Sea est apparu comme étant le plus fiable pour les deux solutions. Tandis que le degré de fiabilité de l'ISE de calcium s'est également avéré élevé, sa précision de mesure des concentrations était inférieure à celles de la plupart des autres kits d'essai. Pour le magnésium ( $\text{Mg}^{2+}$ ), le kit Seachem a démontré la plus grande précision globale. Pour les mesures de cuivre ( $\text{Cu}^+$  and  $\text{Cu}^{2+}$ ), le kit de test JBL se distingue par les meilleures performances globales sur les deux solutions. Pour

le fer ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ), les troussees de test Fluval et Sera Aqua étaient les plus précises, bien que toutes les troussees aient eu tendance à surestimer la concentration réelle d'ions. Finalement, pour les mesures du pH, les électrodes de pH NT Sensors ont surpassé les kits d'aquarium, offrant une précision et exactitude supérieures sur une large gamme de mesures.

Lors du choix des méthodes de mesure, des facteurs tels que le coût, la fréquence et les conditions environnementales doivent être pris en compte. Bien que les ESIs offrent de larges éventail de mesure et un potentiel d'automatisation, ils sont confrontés à des problèmes tels que la dérive du signal et l'interférence avec d'autres ions, tandis que les kits de test d'aquarium ont des plages de mesure de concentration limitées et une interprétation subjective des couleurs. Afin d'utiliser des kits de test d'aquarium pour les systèmes hydroponiques, une charte de couleur correspondant aux changements de couleur avec des solutions hydroponiques doit être développé. Cette étude peut servir de guide aux producteurs pour comparer et choisir la méthode de mesure la plus fiable et la plus rentable en fonction de leurs exigences et des spécifications du système.

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## Contribution of authors

According to the guidelines for the traditional thesis, this section states the contributions of authors are as follows:

Nastaran Alizadeh is the main writer of this thesis, supervised by Dr Mark Lefsrud from the Department of Bioresource Engineering, McGill University, Montreal, Quebec, Canada.

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Dr. Sarah MacPherson revised and proofread the manuscript.

Dr. Philip Wiredu Addo assisted with data analysis and interpretation of results and made valuable comments to improve the manuscript.

## Declaration of AI and AI-assisted technologies in the writing process

During the preparation of this thesis, ChatGPT (GPT-4) [Large language model] and QuillBot [AI writing tool] were used for paraphrasing, revision, and grammar check. After using this tool/service, the text was extensively reviewed and edited with all modifications and changes accepted by the author.

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# 1. Literature review

In 1600, Belgian Jan van Helmont discovered that plants obtain substances necessary for growth from water through his study of a willow tree in a controlled mass of soil (Krikorian & Steward, 1968). Nearly three centuries later, in 1930s, William Gericke introduced the word “hydroponic”, derived from the Greek words hydro (water) and ponos (work), signifying "water work". Gericke used hydroponic systems on a commercial scale for the first time (Resh, 2022). Today, hydroponics are a widely used technique for cultivating plants without the use of soil (Sharma et al., 2018).

With increasing concerns about population growth, food shortage crises and insufficient arable land in the future, hydroponic systems offer a sustainable alternative to soil cultivation (Pilbeam & Morley, 2016). There have been numerous studies comparing conventional soil cultivation with hydroponics systems. These studies conclude that hydroponics systems have higher yield, faster growth and increase survival rate of the plants with the same nutritional value or higher (Buchanan & Omaye, 2013; G., 2014; Gashgari et al., 2018; Goldstein et al., 2016; Nicola et al., 2004; Sgherri et al., 2010; Treftz & Omaye, 2016). With proper adjustments, this technique conserves water, optimizes utilization of light, water and fertilizer resources, while reducing the need for pesticides and fungicides (Sardare & Admane, 2013). Regardless of its numerous strengths, hydroponic systems have high initial and maintenance costs, requiring technical expertise for proper adjustments (Khan, 2018; Sardare & Admane, 2013). Compared to soil-based systems, hydroponic systems are less forgiving due to low nutrient buffering capacity (Sanchez et al., 2021; Sardare & Admane, 2013). Nutrient fluctuations can rapidly lead to deficiencies and toxicities in hydroponically grown plants, which makes it necessary to maintain and monitor nutrient solutions at all times (Sathyanarayan et al., 2023). Proper nutrient management can lower economic and environmental costs, improve water and nutrient efficiency, and reassure maximum yield (Bugbee, 2003).

## Essential elements

The main goal of a hydroponics system is to efficiently and consistently supply sufficient amounts of essential nutrient elements to plants throughout the growing season (Niu & Masabni, 2022). According to Hoagland and Arnon (1950), for an element to be classified as essential, it should have three conditions. First, its absence prevents the plant from

completing either its vegetative or reproductive life cycle stages. Second, the deficiency is specific to that particular element and the only effective remedy should be by supplying it. Last, the element directly contributes to the plant's nutrition, beyond any potential role it might play in improving the growth mediums. Essential elements are divided into macronutrients and micronutrients (Marschner, 2011). Primary and secondary macronutrients are needed in significant amounts and include carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg). Micronutrients are needed in far less amounts yet are equally important and include iron (Fe), manganese (Mn), boron (B), zinc (Zn), copper (Cu), molybdenum (Mo), nickel (Ni), and chlorine (Cl) (Marschner, 2011; Raven et al., 2004; Trejo-Téllez & Gómez-Merino, 2012). These are listed in Table 1. There is a third group of nutrients known as beneficial elements that can enhance crop quality and plant growth while boosting the plants' tolerance to abiotic stressors, illnesses, and pests. This group consists of sodium (Na), silicon (Si), cobalt (Co), iodine (I), cobalt (Co), vanadium (V), selenium (Se), platinum (Pt) and aluminum (Al) (Marschner, 2011; Resh, 2022). Except for carbon (C) and oxygen (O) and hydrogen (H), which are sourced from the atmosphere, all other necessary elements are acquired from the growth medium (Trejo-Téllez & Gómez-Merino, 2012).

Table 1. Summary of nutrients for hydroponic crop growth (Khan, 2018).

Type of Nutrients	Name of Nutrients	Function in plants
Macro	Nitrogen	Chlorophyll, amino acids and proteins synthesis
	Phosphorus	Photo synthesis and growth
	Potassium	Enzyme activity
	Hydrogen	Water formation
	Oxygen	Release of energy from sugar
	Carbon	Formation of organic compounds
	Calcium	Cell growth
	Magnesium	Enzyme activation
	Sulfur	Formation of amino acids and proteins
	Iron	Used in photosynthesis
Micro	Boron	Vital for reproduction
	Chlorine	Help roots growth
	Copper	Enzyme activation
	Manganese	Compound of chlorophyll
	Zinc	Compound of enzymes
	Molybdenum	Nitrogen fixation
	Cobalt	Nitrogen fixation

## Nitrogen

The importance of nitrogen for plant growth and development was first pointed out by Saussure (Barker & Bryson, 2016). Nitrogen plays vital physiological and metabolic processes roles within plants. It is essential for plant structure, function, and reproduction (Marschner, 2011; Tripathi et al., 2014). Nitrogen is a constituent of nucleic acids, including DNA and RNA which carry genetic materials. It is a major component of amino acids, proteins, enzymes, chlorophyll, membrane lipids, and energy production within plants (Ohyama, 2010; Richa et al., 2021; Tripathi et al., 2014). Nitrogen is easily mobilized in the plant; normally, nitrogen and proteins move to fruits and seeds from older leaves (Pilbeam & Morley, 2016). In case of nitrogen deficiency, older leaves turn pale green color or yellow and in case of severe deficiency brown. Nitrogen deficient plants look stunted or spindly with narrow or distorted leaves (Marschner, 2011; Pilbeam & Morley, 2016; Wen et al., 2019). Nitrogen deficiency will result in loss of chlorophyll, a decrease in photosynthetic capacity, degradation of chloroplast structure, loss of membranes and proteins, accelerated senescence and maturation and lower yield (Marschner, 2011; Ohyama, 2010; Pilbeam & Morley, 2016; Wen et al., 2020). High nitrogen might show itself as vigorous growth, dark green color, elongation, delayed maturity, reduction of number and quality of seeds and fruits, proneness to insect and fungus infestations (Goyal & Huffaker, 1984; Ohyama, 2010). Excess nitrogen might result in S deficiency or a reduction of sugar content in some plants (Goyal & Huffaker, 1984). Nitrogen may take place in many different forms and compounds but it is mostly consumed by plants as nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) (Pilbeam & Morley, 2016). Approximately 80% of all the ions uptake is allocated to ammonium and nitrate (Marschner, 2011).

## Nitrate ( $\text{NO}_3^-$ )

Nitrate is the preferred form of nitrogen by most higher plants and usually is available to plants at higher concentrations (Li et al., 2013; Owen & Jones, 2001). Nitrate easily translocate in plants and unlike ammonium, can be stored in vacuoles without causing any toxicity (Pilbeam & Morley, 2016). High levels of nitrate are tolerated by most plants. Some research shows that increasing nitrate concentration in a hydroponic solution leads to higher yield, visual quality and root development for lettuce (*Lactuca sativa*), but not toxicity



(Wenceslau et al., 2021). However, excessive nitrate can be toxic, particularly to calcifuge plants (Goyal & Huffaker, 1984). Nitrate toxicity might show itself as chlorosis or iron deficiency. When nitrate uptake exceeds metabolic needs, most plants accumulate nitrate (Blom-Zandstra, 1989). Nitrate availability is the main reason of nitrate accumulation (Wenceslau et al., 2021), which pose health hazards at high concentrations (Anjana & Iqbal, 2007). Nitrate accumulation is more common in hydroponic cultivation since  $\text{NO}_3^-$  is readily available to plants (Guadagnin et al., 2005; Santamaria, 2006). Elevated nitrate levels in agricultural runoff have detrimental effects on both human health and the environment (Yang et al., 2008). Nitrate deficiency in plants impacts their growth and development (Jiang et al., 2017). Low nitrate levels result in inhibited growth, which can manifest as a reduced number of leaves and lower biomass (Becker et al., 2015). Prolonged nitrate deficiency further exacerbates these issues, leading to decreased photosynthesis and promoting premature aging of the plants (Wen et al., 2020). As a result, insufficient nitrate availability can severely compromise plant health and productivity.

## **Nitrite ( $\text{NO}_2^-$ )**

Nitrite is an intermediate product in the nitrification process (Goyal & Huffaker, 1984). Nitrite is usually the product of high concentration of ammonia and high pH (Barbouch et al., 2012). There are published papers that show nitrite can be absorbed by the plants (Barbouch et al., 2012; Goyal & Huffaker, 1984; Oke, 1966; Yoneyama et al., 1980). However, plants that accumulate nitrite can result in serious damage to human health (Anjana & Iqbal, 2007). Such plants undergo morphological and metabolic changes (Hoque et al., 2007; Pécsváradi & Zsoldos, 1996). Nitrite toxicity hinders enzymes involved with assimilation of nitrogen compounds, including the synthesis of amino acids and proteins (Pécsváradi & Zsoldos, 1996; Wingsle et al., 1987). It inhibits photosynthesis by acidification of the chloroplast stroma (Hoque et al., 2007; Shingles et al., 1996). Qiao and Murray (1998) examined the effect of nitrite on soybean plant. They concluded that nitrite can reduce nitrate uptake, assimilation of ammonium and plant growth, and increase the acidity of the plant and its medium. Hoque et al. (2007) studied two types of hydroponically grown lettuce with different levels of  $\text{NO}_2^-$  and reported  $\text{NO}_2^-$  toxicity mostly caused damage to roots. Other symptoms reported were reduced biomass, root and leaf discoloration, lower height, lower number of leaves, and wilting at night in two-week old plants. They further reported that increasing  $\text{NO}_2^-$ -N in the solution will hinder

$\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N uptake. In a similar study on tomato (*Solanum esculentum*), Barbouch et al. (2012) reported dramatically lower dry mass, lower lipids and fatty acids in the nitrite plants compared to the plants grown in nitrate. Nitrite concentration in the plant tissue corresponded with the nitrite concentration in the solution but had a higher concentration in the plant roots.

## Ammonium ( $\text{NH}_4^+$ )

Ammonium ( $\text{NH}_4^+$ ) is one form of nitrogen present in hydroponic nutrient solutions, and is particularly preferred by calcifuge plants adapted to acidic root environments (Lee, 1998). Plants such as lisianthus (*Eustoma grandiflorum*) (Mendoza-Villarreal et al., 2015), arabidopsis (*Arabidopsis thaliana*) (Gazzarrini et al., 1999), sweet potato (*Ipomoea batatas*), potato (*Solanum tuberosum*), tea tree (*Camellia sinensis*), and soybean (*Glycine max*) prefer higher concentrations of  $\text{NH}_4^+$  (Li et al., 2013). The assimilation of ammonium requires less energy, and a proper proportion of  $\text{NO}_3^-$ :  $\text{NH}_4^+$  can optimize plant growth by balancing intracellular pH (Liu et al., 2017; Marschner, 2011). Different plant species may have varying tolerance levels and preferences for ammonia concentrations (Cao & Tibbitts, 1993; Gentry & Below, 1993). Researchers have investigated adding ammonia to nutrient solutions to reduce nitrate accumulation and achieve better yield. The optimal  $\text{NO}_3^-$ :  $\text{NH}_4^+$  ratio for various crops, including tomato (Liu et al., 2017), lettuce (Wenceslau et al., 2021), strawberry (*Fragaria ananasa*) (Roosta, 2014), and Chinese broccoli (*Brassica oleracea* var. *Alboglabra*) (Farid Bdr et al., 2020), was found to be 75:25, 50:50, 77:23, 50:50, and 12:1. However, higher concentrations of ammonium can be toxic and deplete plant carbon reserves (Pilbeam & Morley, 2016; Wenceslau et al., 2021). Ammonium accumulation in plants will result in the accumulation of inorganic anions in the plant and hinder uptake of some essential cations like potassium or calcium (Britto & Kronzucker, 2002; Coskun et al., 2013). Excessive levels can lead to decreased plant growth, crop yield, leaf area reduction, root growth reduction, stem lesions, leaf discoloration, and tissue death, ultimately resulting in plant mortality (Barker et al., 1966a, 1966b; Gerendás et al., 1997; Maynard et al., 1966, 1968; Maynarp & Barker, 1969; Raab & Terry, 1995). It is crucial to closely monitor ammonia levels, especially in applications of organic hydroponic fertilizers or in aquaponic systems (Park & Williams, 2024).

## Phosphorus (P)

Phosphorus (P) is an essential nutrient for plants, playing a key role in energy metabolism, cell membrane function, and nucleic acids, phospholipids, and certain coenzyme (Geilfus, 2019; Resh, 2022). Inorganic and organic phosphates in plants function as buffers to maintain cellular pH levels (Pilbeam & Morley, 2016). The most bioavailable form of phosphorus is orthophosphate, which depending on pH, can be in the form of  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  (Maher & Woo, 1998). To cope with phosphorus deficiency, plants have developed mechanisms like the phosphorus starvation response (PSR) (Plaxton & Tran, 2011). When phosphorus is scarce, plants adjust their root systems by promoting root growth while limiting leaf expansion to access phosphorus from other sources (Sachay et al., 1991; Shen et al., 2011). This adaptation results in a higher root-to-shoot ratio and increased chlorophyll levels, which can cause plants to appear darker green or bluish, with occasional chlorosis and necrosis on older leaves (Roberto, 2005; Valentinuzzi et al., 2015). Prolonged phosphorus deficiency is likely to result in smaller fruit sizes and reduced yields of harvestable vegetables (Pilbeam & Morley, 2016). Phosphorus deficiency boosts the production of oxygen radicals, which can damage cellular structures and molecules. In response, plants generate anthocyanins to protect against harmful UV radiation (Liu et al., 2015). These anthocyanins can give a red to purple shade to leaves, stems, and petioles (Hernández & Munné-Bosch, 2015). A controlled P deficiency can enhance the production of anthocyanins and other secondary metabolites (Knobloch & Berlin, 1983) which can be beneficial if included in the human diet (Hoensch & Oertel, 2015; Khoo et al., 2017; Li et al., 2017). Moreover, anthocyanins can cause an attractive color change and improve the storage of fruits, reducing damage during postharvest and extending their shelf life (Jezek et al., 2018; Zhang et al., 2013). Controlling phosphate levels in hydroponic solutions is crucial because excess phosphate can lead to nutrient imbalances and algal blooms, which can harm plant health. One of the most frequent symptoms of excess phosphorus is of phosphate-induced micronutrient deficiencies, especially deficiencies in zinc, copper (Rowley et al., 2012; Sathyanarayan et al., 2023). Maintaining the right concentration of phosphate ensures a stable and healthy growing environment.

## Potassium (K)

Potassium (K) is crucial for plant health as it is the most prevalent cation in plant tissues. It plays a vital role in numerous physiological processes, including cell metabolism, growth,

and development. Potassium aids in protein synthesis, photosynthesis, and maintaining cell function, and it enhances stress resistance, drought tolerance, and overall plant strength (Pandey & Mahiwal, 2020). Potassium is regarded as crucial for the operation of over 50 different enzymes (Marschner, 2011). Sufficient potassium fertilization is essential for increasing agricultural crops' production and quality. Controlling potassium levels at different crop growth stages can improve the yield of specialist horticulture crops that are beneficial to human health. For instance, low-potassium fruits and vegetables such as lettuce, tomato, melon, and strawberry might enhance the quality of life (QOL) of those with chronic kidney disease (Asaduzzaman & Asao, 2018).

As a key cation, potassium contributes to the balance between anions and cations, regulates turgor pressure and osmotic pressure, and facilitates water movement within the plant. It improves various quality aspects of plant products, such as fruit size, color, taste, and shelf life, by affecting processes like photosynthesis, protein synthesis, and enzyme function. Potassium boosts plant resilience to environmental stress and enhances both productivity and fruit quality. Furthermore, it influences pH, osmotic pressure, and electrical conductivity in nutrient solutions, which affects overall plant productivity and nutrient absorption (Betül & Ali Cengiz, 2017).

Potassium deficiency initially reduces root growth and, as it progresses, increases soluble carbohydrates in the leaves. This imbalance decreases the synthesis of higher-molecular-weight compounds, making leaves more vulnerable to pests and diseases. Potassium is highly mobile in plants, so deficiency symptoms first appear in older leaves, starting with marginal chlorosis and progressing to necrosis and leaf breakage (Flávio José Rodrigues et al., 2017). K deficiency lowers protein synthesis and leads to the accumulation of harmful soluble nitrogen compounds (Flávio José Rodrigues et al., 2017). Leaves may show dark green areas, similar to phosphorus deficiency, and thickened veins (Flávio José Rodrigues et al., 2017). In fruits, K deficiency reduces levels of glucose, fructose, and sucrose, diminishing color intensity due to reduced pigment synthesis (Jiang et al., 2023). Overall, a lack of potassium can severely impact plant dry mass production, disrupt nutrient balance, and cause various morphological changes (Flávio José Rodrigues et al., 2017; Levine & Mattson, 2021). More so than vegetative biomass in pepper plants (*Capsicum annuum*), fruit yield characteristics are impacted by the appropriate quantity of K in fruits (Botella et al., 2017). By boosting fruit hardness, TSS content, soluble sugars, and ascorbic acid concentration, the increased  $K^+$  in the nutrition solution enhanced the quality of pepper fruit. Potassium increase can lead to increased nitrate

absorption and can cause decreased absorption of magnesium and calcium (Flávio José Rodrigues et al., 2017).

## **Calcium (Ca)**

Calcium was identified as a macronutrient by Sprengel in 1828 (van der Ploeg et al., 1999). Even though it is identified as a macronutrient, it is generally not required in large amounts by plants (Burstrom, 1968) and it is actively excluded by plants' cytoplasm (Pilbeam & Morley, 2016). Bangerth (1979) lists the effect of calcium in plants as: (a) interactions between calcium and phytohormones; (b) effects on membranes; (c) impacts on cell walls; and (d) effects on enzymes. The amount of calcium required varies greatly among higher plants (Wallace & Soufi, 1975). It provides stability to the structure of cell tissues and enhances product quality in certain crops, while in others, it leads to undesirable rigidity (Carolus, 1975). The availability of calcium directly effects the calcium concentration in the plant tissue (Loneragan & Snowball, 1969a). Accumulated calcium in plants is not easily transported to young tissues and plants show signs of calcium deficiency as soon as the rate of calcium absorption drops below the required amount (Loneragan & Snowball, 1969b). Calcium deficiency in plants shows itself as yellow-green color in upper part of the shoot and a dark green color in the lower parts (Nightingale et al., 1931). Calcium deficiency can cause blossom end rot (BER) in fruits such as tomatoes, peppers, squash, cucumbers, melons, etc., tip burn of leafy crops like lettuce and cabbage, bitter pit of apple, black heart of celery, internal rust spot in potato tubers and carrot roots, internal browning of pineapple (*Ananas comosus*) (Birlanga et al., 2022; Pilbeam & Morley, 2016; Storey et al., 2002). Calcium toxicity can hinder seed germination and diminish rates of plant growth (White, 2003).

Calcium is largely available in most soils and it is rare to see calcium deficiency in nature (White, 2003). However, calcium levels need to be closely monitored in hydroponic systems in order to avoid Ca-related disorders (Birlanga et al., 2022). Birlanga et al. (2022) suggested smart nutrient management systems and using sensors as a way to solve calcium related disorders in hydroponic systems.

## Magnesium (Mg)

Magnesium is one of the most adaptable and multifunctional essential nutrients in biological systems, playing a key role in processes involving ATP, cellular pH regulation, and maintaining the balance of cations and anions. It serves as the central atom in chlorophyll molecules, supports the activity of over 350 enzymes in plants, is necessary for RNA biosynthesis and biological functions, and can significantly impact nitrogen accumulation in plants (Marschner, 2011; Weston, 2008).

Magnesium plays a crucial role in the size, composition, and functionality of chloroplasts and is essential for photosynthesis in plants (Mcswain & Tsujimoto 1976). A deficiency in magnesium impairs CO<sub>2</sub> absorption and reduces the efficiency of light energy use for CO<sub>2</sub> fixation, disrupting photosynthesis. This leads to chloroplast damage and the production of reactive oxygen species (ROS) (Cakmak & Kirkby, 2008; Peng et al., 2019; Tränkner et al., 2018). Additionally, magnesium deficiency affects protein synthesis and degradation, resulting in reduced carbohydrate export from leaves. Consequently, nonstructural carbohydrates like sugars and starch accumulate, increasing the dry matter content of the leaves (Cakmak et al., 1994; Fischer & Bussler, 1988; Hermans et al., 2004; Hermans & Verbruggen, 2005; Kobayashi & Tanoi, 2015). This buildup means fewer carbohydrates are available for the pods and roots, leading to reduced seed carbohydrate content while seed count was not affected, impairing seed germination and seedling growth (Ceylan et al., 2016; Peng et al., 2018; Zhang et al., 2020). Young plants suffering from magnesium deficiency produce fewer roots, which increases the shoot-to-root ratio and negatively impacts drought tolerance and adaptability to nutrient-poor conditions (Hermans et al., 2004; Hermans & Verbruggen, 2005; Koch et al., 2020; Mengutay et al., 2013). Moreover, magnesium-deficient plants exhibit heightened light sensitivity resulting in chlorosis and necrosis, making them less resilient to acidic soils, aluminum toxicity, heat stress, salt tolerance and other physiological challenges, particularly under high light stress and elevated atmospheric CO<sub>2</sub> levels (Bose et al., 2011; Cakmak & Kirkby, 2008; Chen et al., 2017; Kong et al., 2020; Mengutay et al., 2013; Rao et al., 1987; Yilmaz et al., 2017). Excess magnesium results in low biomass and interfere with calcium and potassium assimilation (Vojnich et al., 2015). Both deficiency and excess magnesium can affect various physiological functions, so it is essential to keep its levels within an appropriate range (Huber & Jones, 2013).

## Copper (Cu)

Copper is essential for humans, animals, and plants, but excessive concentrations can be harmful (Kumar et al., 2021). It has been reported for its antimicrobial properties (Bugbee, 2003). Before copper was recognized as a vital element, copper fungicides likely helped alleviate deficiencies (Pilbeam & Morley, 2016). Copper's oxidizing ability is critical for photosynthesis, respiration, enzyme production, and the functioning of over 260 different proteins within the plant electron transport chain (Marschner, 2011). However, copper is absorbed and transported slowly within plants (Marschner, 2011). Its uptake is influenced by several factors, including the concentration of copper in the growth medium, the pH of the solution, and the presence of competing elements (Pilbeam & Morley, 2016).

Symptoms of copper deficiency vary by plant species and the severity of the deficiency (Pilbeam & Morley, 2016). Chapman (1966) provided detailed descriptions for 36 crops, noting that due to copper's immobility, symptoms typically emerge in the later growth stages. Common indicators include curled and wilting leaves, rosetting, necrotic spots, chlorosis, stunted growth, and diminished enzymatic activity, particularly in lentils (*Lens culinaris*), faba beans (*Vicia faba*), chickpeas (*Cicer arietinum*), and wheat (*Triticum aestivum*) (Marschner, 2011; Pilbeam & Morley, 2016; Yruela, 2005). Copper deficiencies negatively impact respiration, carbon fixation, enzyme activity, and other critical functions, with different plant species exhibiting varying levels of sensitivity to these effects (Pilbeam & Morley, 2016). Plants lacking adequate copper, experience weakened lignification, leading to reduced physical defenses and lower disease resistance (Dey et al., 2023; Marschner, 2011; Pilbeam & Morley, 2016; Roberto, 2005). Copper contamination in water bodies and soil can result from mining and smelting activities, as well as the extensive use of copper-containing fertilizers, pesticides, and fungicides in agriculture (Chrysargyris et al., 2021; Mir et al., 2021). This accumulation can lead to toxic levels of copper in plant tissues, adversely affecting their growth and development. Research indicates that roots are the primary sites of metal accumulation (Chrysargyris et al., 2021). Plants exhibit varying responses to excess copper ions depending on the concentration levels.

Excess copper ions can lead to stunted root development and leaf chlorosis. Stunted roots are characterized by poor growth and dark coloration, while chlorosis, caused by copper interference in photosynthesis, can mimic symptoms of iron deficiency (Pilbeam & Morley, 2016). Additionally, elevated copper levels can compromise membrane permeability, reduce

chlorophyll content, and diminish the capacity of plants to absorb UV radiation, significantly hindering the growth of species such as mung beans and radishes (Pilbeam & Morley, 2016). Excess copper may induce oxidative stress, resulting in damage to DNA, lipids, and proteins (Dey et al., 2023; Marschner, 2011; Mir et al., 2021). Both low and high concentrations of copper can negatively impact plant health, which in turn affects human health. It is essential to maintain optimal copper levels and monitor its bioavailability (Marschner, 2011).

## **Iron (Fe)**

Iron is a crucial micronutrient that plays a vital role in biological redox reactions, due to its ability to switch between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  oxidation states (Marschner, 2011; Pilbeam & Morley, 2016; Rout & Sahoo, 2015). It is essential for the synthesis of various enzymes as well as two major categories of proteins: heme proteins and iron-sulfur (Fe-S) proteins. These proteins are integral to the light-dependent stages of photosynthesis (Marschner, 2011; Pilbeam & Morley, 2016). Iron's low solubility and tendency to oxidize make it the third most common nutrient-related growth inhibitor in plants (Rout & Sahoo, 2015).

Fe deficiency is a common disorder that adversely impacts chloroplast size, photosynthesis, and  $\text{CO}_2$  fixation rates (Rout & Sahoo, 2015). Insufficient iron typically causes the leaves to turn yellow, or in severe cases, white, while the veins remain dark green. This deficiency tends to affect younger leaves more significantly than older ones. Iron deficiency is a widespread issue affecting plants, animals, and humans alike. In 2019, iron deficiency anemia impacted 29.9% of women and 39.8% of children globally (WHO, 2021). Ensuring optimal iron uptake in plants is crucial not only for enhancing plant growth but also for improving human health (Kasozi et al., 2019). In aquaponic systems, which are often deficient in iron, careful management of iron levels is essential for maintaining plant health (Kasozi et al., 2019).

Excess iron can be toxic, leading to damage and eventual death of cellular structures (Rout & Sahoo, 2015). Symptoms of iron toxicity include the appearance of small reddish-brown spots on leaves (bronzing) and darkening of the roots. In severe cases, all leaves may turn brown and die. Additionally, excessive iron can interfere with the uptake of other essential nutrients such as phosphorus, potassium, calcium, magnesium, and manganese (Rout & Sahoo, 2015). Zhang et al. (2016) reported that elevated iron concentrations can induce both morphological and physiological changes in hydroponically grown *Panax ginseng* plants. Their



study observed reddish-brown deposits on the plant roots and a notable increase in pH with higher Fe<sup>2+</sup> levels. Similarly, high iron concentrations negatively impacted the root and stem growth of the hyperaccumulator plant, perumpung (*Phragmites karka*), ultimately leading to plant death at a concentration of 150 mg/L (Rusmanta et al., 2019)

Iron exists in various compounds, many of which are insoluble in water. Consequently, only soluble forms of iron, typically chelated iron, are used in nutrient solutions for hydroponic systems. The type and concentration of iron in these solutions significantly influence plant yield, quality, and the content of iron, vitamin C, and chlorophyll (Metwally & Eissa, 2023; Su et al., 2015). Moradi et al. (2020) investigated the effects of various iron sources, Fe-EDTA, Fe-DTPA, Fe-EDDHA, and FeSO<sub>4</sub>, on hydroponically grown tomatoes. They found that Fe-EDTA yielded the best results for plant height, fresh and dry mass, stem diameter, flower number, and iron concentrations in stems and roots. Similarly, Su et al. (2015) reported that Fe-EDTA was the most effective source of iron for Chinese kale (*Brassica oleracea* var. alboglabra). In a study, Gülser et al. (2019) identified nanoFe as the superior iron source for soybean plants compared to FeSO<sub>4</sub>, Fe-EDDHA, and nanoFe.

## **pH and electrical conductivity**

To effectively optimize nutrient and water use efficiency in a hydroponic system, various monitoring and management methods are conventionally set in place (Fathidarehnijeh et al., 2023). One of the most common methods is controlling pH and electrical conductivity (EC) which is low cost, fast, and simple monitoring method (De Rijck & Schrevens, 1994; Wada, 2019). pH is one of the most crucial factors for which an adequate management is required (Rouphael et al., 2016) and should be maintained at a low acidic level between 5.5 and 6.5 to ensure proper nutrient uptake, solubility and availability for plants (Gillespie et al., 2021). Keeping this stability is crucial, as many researchers noted that systems containing high acidic root environments can drastically decrease the plant's ability to absorb essential macronutrients such as phosphorus, nitrogen, magnesium, potassium, and calcium (Gillespie et al., 2020; Niu & Masabni, 2022; Trejo-Téllez & Gómez-Merino, 2012). Higher pH values in the nutrient solution cause a precipitation reaction of many nutrients such as calcium, magnesium, phosphate, and iron which makes them unabsorbable by the plant roots (Velazquez-Gonzalez et al., 2022). Uptake of iron, manganese, zinc, and copper are hindered by overly basic solutions, stunting the plant's growth (Velazquez-Gonzalez et al., 2022).

EC provides an estimate of the concentration of dissolved nutrients in the hydroponic solution (Wortman, 2015). EC can affect osmotic potential and consequently plant nutrient uptake (Sonneveld et al., 2009). The optimal range of EC is between 1.5 to 2.5 dS/m depending on the crop and environmental conditions (Patil et al., 2020). The plant's absorption of water and minerals, and water evaporation can impact EC levels in a hydroponic solution (Majid et al., 2021). Many researchers note that, the electrical conductivity of the solution tends to increase over time (Fayezizadeh et al., 2021; Lee et al., 2017; Son et al., 2020; Wortman, 2015). A major drawback of this method for nutrient monitoring was noted by Massa et al. (2008) and subsequently by Neto et al (2014). While EC can give a solid estimate of the total concentration of dissolved ions in a solution, the concentration of individual ions from macro- and micronutrients cannot be determined (Massa et al., 2008; Steidle Neto et al., 2014). Different plants need different rates of macronutrients. For example, nitrogen uptake at a high frequency is necessary for leafy vegetables to develop a large quantity of leaves, while calcium and potassium are vital for high-quality fruit production (Lee et al., 2017). The uptake of each ion is performed at different rates depending on the plant type and can cause a more localized imbalance if not properly identified, which the use of electrical conductivity cannot detect (Pardossi et al., 2002). According to Lee et al. (2017) changes in  $\text{PO}_4^{3-}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ , Mn,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and dissolved Fe ion concentrations did not show a consistent relationship with EC levels, suggest monitoring these specific ions separately and adjusting their supply to ensure optimal growth conditions (Lee et al., 2017).

Massa et al. (2010) conducted a series of three experiments in a semi-closed hydroponic system using tomatoe, to optimize nitrogen use efficiency (NUE) and water use efficiency (WUE). Serving as a baseline, the first experiment used EC to determine at which point a solution should be replaced, in this case at 4.5 dS/m The second experiment replaced the solution once the concentration of  $\text{NO}_3^-$ -N dropped below 0.07 g/L. Measurements were taken every 2 to 4 days interval using a reflectometer. The third experiment used both measurements of EC and nitrate-nitrogen to determine the best NUE and WUE by diluting the solution with water to bring the  $\text{NO}_3^-$ -N concentration to 0.07 g/L once the EC reached a level of 4.5 dS/m. A comparison of all three management methods demonstrated that the second experiment using a nitrogen-based monitoring achieved the best NUE, while the third experiment combining both EC and nitrate-nitrogen showed the highest WUE, especially against the baseline (Experiment 1 using only EC as a monitoring tool) (Massa et al., 2010). In a similar study, an EC-based monitoring strategy and a nitrogen-nitrate monitoring strategy using a reflectometer

were compared for amaryllis (*Hippeastrum hybridum*) production. The nitrate-based management system showed 56 % higher WUE compared to the alternative while maintaining the same plant development and nutritional content in plant tissue (Rouphael et al., 2016). Using EC to monitor the nutrient solution in closed hydroponic systems not only results in waste of water and nutrients but it can unbalance the ratios of nutrients, which can lower agricultural productivity and damage crop quality (Cho et al., 2017). It is vital to carefully monitor individual nutrient concentrations in hydroponic solutions before reusing them, this helps to optimize the nutrient mix in the regenerated solution and enhance plant growth (Jung et al., 2015).

## **Laboratory analytical measures**

To obtain an off-line comprehensive analysis of a given nutrient solution, water samples must be sent to a testing laboratory in specific intervals to determine whenever there is a change in the water source (Jones Jr, 2016). There are a variety of nutrient measurement methods for space and terrestrial applications that are thoroughly discussed by Bamsey et al. (2012), including high-performance liquid chromatography (HPLC), colorimetric solid phase extraction (CSPE) and ion chromatography (IC). IC is regarded as the standard method for chemical analysis of nutrient solutions in laboratories (Michalski, 2006), and it is a refined form of HPLC that allows for accurate and highly sensitive detection of inorganic ions within a complex mixture (Lau, 2001; Tabatabai et al., 2003). IC offers several advantages, including excellent accuracy and precision, a wide variety of applications and detection methods, high selectivity and separation efficiency and well-established hardware with low consumable costs (Michalski, 2018). While this information remains highly valuable and, in some cases, essential for growers, it restricts farmers to conducting infrequent off-line analyses (typically every 1 to 3 weeks), during which nutrient solution samples must be physically sent to the laboratories for testing (Bamsey et al., 2012; Voogt & Sonneveld, 1997). During the shipping, processing, and reporting delays, the condition of the on-farm nutrient solution is likely to change significantly. This shift can limit the usefulness of the data, which is often expensive to obtain (Hartz & Hochmuth, 1996).

## **Ion selective electrodes (ISEs)**

The necessity for effective nutrient management has prompted the use of ion-selective electrodes (ISEs) as advanced sensing tools to automatically track hydroponic nutrient levels (Jung et al., 2019; Xu et al., 2019; Xu et al., 2020). ISEs are potentiometric electrochemical sensors, used to measure the concentration of specific ions in a solution, with their signals varying based on the ion activities (Lau, 2005; Štulík, 2005). ISEs respond selectively to particular ionic species by measuring the electrical potential between a reference electrode and a membrane that is sensitive to the specific ion of interest (Orellana et al., 2011; Štulík, 2005). ISEs are classified into three groups: glass, solid state and liquid electrodes (Horváth & Horvai, 2005). ISEs are used in a variety of applications in water analysis and environmental analysis (Scott, 1995), medicine (Yan et al., 2016), food science (Mello & Kubota, 2002), research, etc., and are utilized for measuring a broad range of anions and cations. ISEs provide rapid, continuous, and on-site measurements that are unaffected by color, turbidity, or other water characteristics (Orellana et al., 2011).

ISE enable computerization and connectivity, and their integration with the Internet of Things (IoT) to enhance and streamline the monitoring of hydroponic nutrient solutions in the farming sector (Richa et al., 2021). Automation of nutrient management systems allows for AI-based decision making, and workforce reduction (Rajaseger et al., 2023). However, these sensors may have issues with reduced accuracy over time and can be impacted by interfering substances and signal drift (Ikrang et al., 2022; Kim et al., 2013; Orellana et al., 2011). Frequent exposure to organic substances in the hydroponic nutrient solution may cause biofilm accumulation on the sensor (Geoffrey et al., 1997). Table 2 lists studies that examine the ISE performance when employed in hydroponic systems.

Table 2: Summary of studies examining use of ions selective electrodes in hydroponics.

<b>Ion selective electrode</b>	<b>Calibration points</b>	<b>Measured solution</b>	<b>Results</b>	<b>Reference</b>
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$	2	Single ion solution, spiked and diluted hydroponic solution	Satisfactory results for nitrate and potassium. Not adequate sensitivity and selectivity for $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ ISEs	(Kim et al., 2013)
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{Ca}^{2+}$	2	Hydroponic solution	20 mg/L RSME error in comparison to the ion chromatography. Overestimation of potassium and underestimation of calcium	(Cho et al., 2018)
$\text{NO}_3^-$	2	Soil solution, nutrient solution and sap water	14% and 22% relative error for nutrient and soil solution. Does not recommend using ISEs for measuring sap water due to low accuracy.	(Peña-Fleitas et al., 2021)
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{Ca}^{2+}$	1	Hydroponic solution	Measurement with all sensors were satisfactory.	(Vardar et al., 2015)
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{Cl}^-$	3	Hydroponic solution	$\text{K}^+$ and $\text{Ca}^{2+}$ excellent slope stability, can function with one point calibration $\text{NO}_3^-$ and $\text{Cl}^-$ , potential drift, minimum 2-point calibration needed	(Rius-Ruiz et al., 2014)
$\text{NO}_3^-$ , $\text{NH}_4^+$	1	Manure, manure with molasses	Results were 15 to 28% below the readings of Lachat flow injection autoanalyzer.	(Tikász, 2019)
$\text{K}^+$ , $\text{Na}^+$ , $\text{Cl}^-$	3	Hydroponic solution	Results statistically varied from ICP-OES readings. No positive correlation between ISEs ICP-OES for $\text{K}^+$ and $\text{Na}^+$	(Lee et al., 2017)
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{Ca}^{2+}$	2	Hydroponic solution,	ISEs were successfully used in an automated nutrient management system. $\text{K}^+$ concentrations were 40% more than target value due to change in the sensitivity of $\text{K}^+$ ISE.	(Hyun Jung et al., 2015)
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{Ca}^{2+}$	2	Hydroponic solution,	33% higher calcium concentration than the target value, probably caused by change in the sensitivity of $\text{Ca}^{2+}$ ISE or interfering ions	(Cho et al., 2017)
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{Ca}^{2+}$	2	Hydroponic solution	Using ISEs for IoT-based multi-ion monitoring system. Reported mean absolute value error between standard ion analyzer and ISE readings of 65.8, 96.6, and 7.6 mg/L for $\text{K}^+$ , $\text{NO}_3^-$ and $\text{NH}_4^+$ respectively. Probable interference of $\text{K}^+$ ions for $\text{NH}_4^+$ electrode.	(Wu et al., 2023)
$\text{NO}_3^-$ , $\text{NH}_4^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$	2	Hydroponic solution	IoT nutrient sensor system constructed using SCISEs for real time assessment. $\text{NH}_4^+$ results were higher than IC measurements due to interference with $\text{K}^+$ . The concentration error was under 20 ppm, which makes it suitable for real-world hydroponic use.	(Wu et al., 2024)
$\text{K}^+$ , $\text{Na}^+$ , $\text{NH}_4^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$	2	Vegetable sap	$\text{K}^+$ , $\text{Na}^+$ , and $\text{Ca}^{2+}$ levels were consistent with ion chromatography reading across seven different vegetable sap samples. ISE readings of $\text{NH}_4^+$ and $\text{Mg}^{2+}$	(Huang et al., 2021)

<b>Ion selective electrode</b>	<b>Calibration points</b>	<b>Measured solution</b>	<b>Results</b>	<b>Reference</b>
			In tomato, basil, and amaranth contradicted with the results of ion chromatography.	
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{PO}_4^{3-}$	2	Hydroponic solution	Phosphate ISE resulted in RMSE of $10.9 \pm 7.1\%$ in comparison to standard analysis in the sample range of 40 to 120 mg/L $\text{PO}_4^{3-}$ .	(Jung et al., 2019)
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{PO}_4^{3-}$	ND	Hydroponic solution	programmable logic controller (PLC) and ISEs used simultaneously and were able to keep the nutrient within the proper threshold	(Xu et al., 2020)
$\text{NO}_3^-$ , $\text{NH}_4^+$ , $\text{K}^+$ , Na, Cl	Total calibration solutions: 34 Training solutions: 27	Hydroponic nutrient solution, drainage solution and tap water	Electronic tongue made of an array of eight non-specific all-solid-state ISEs sensors. Multivariate calibration tool by cross-response processing was based on a multilayer artificial neural network (ANN) model. Promising results for all ions except for Cl with 10% mean relative error. This system was able to recompense the temperature effect of $\text{NH}_4^+$ , $\text{K}^+$ , Na and Cl ions.	(Gutiérrez et al., 2007)
$\text{NO}_3^-$ , $\text{NH}_4^+$ , $\text{K}^+$ , Na, Cl, $\text{PO}_4^{3-}$	Training solutions: 54 Testing solutions: 20	Hydroponic nutrient solution and drainage solution	Electronic tongue made of an array of 11 non-specific all-solid-state ISEs sensors. Multivariate calibration tool by cross-response processing was based on a multilayer artificial neural network (ANN) model. The measurement method demonstrated strong performance. Low accuracy with Cl sensor was addressed. $\text{PO}_4^{3-}$ exhibited significant limitations with a mean error of 31.9%.	Gutiérrez et al., 2008)
$\text{NO}_3^-$	ND	Hydroponic solution	A combination of inductively coupled plasma (ICP) spectroscopy and ISEs was suggested. The ISEs demonstrated measurement accuracy within 1–5% and reproducibility at $\pm 2\%$ .	(Hartz & Hochmuth, 1996)
$\text{NO}_3^-$ , $\text{K}^+$ , $\text{Ca}^{2+}$	2	Closed hydroponic solution	The RMSE values for the $\text{NO}_3^-$ , $\text{K}^+$ , and $\text{Ca}^{2+}$ between ISEs and ICP were 43.6, 11.5, and 11.1 mg·L <sup>-1</sup> , respectively. All ISEs demonstrated a slope near 1, and the coefficient of determination of 0.92 or greater, indicating strong linearity.	(Kim et al., 2023)

## Quick test kits

Quick water test kits (QTK) are faster, more affordable, easier and portable alternative to laboratory analyses, which, while providing data of high quality, can be quite expensive to run and time-consuming. These commercial QTK for measuring water quality variables are designed for use in the field with variable complexity and methods for a wide range of water quality variables and industries (Naigaga et al., 2017). Despite their widespread use, there has been very limited published research on the reliability of data gathered from test strips in water quality monitoring (Naigaga et al., 2017).

Previous studies report measuring nitrogen with QTKs in soil extracts. Roth et al. (1991) reported that various extracting solutions showed variations in the development of strip colors. The comparison of QTK results with laboratory analyses for aluminum sulfate ( $0.025\text{M Al}_2(\text{SO}_4)_3$ ) and calcium chloride ( $0.02\text{M CaCl}_2$ ) extractants resulted in the slope and intercept of 0.58 and 8.08 for 0.02M calcium chloride extract and slope and intercept of 0.78 and 5.46 for 0.025 M aluminum sulfate extract. This was followed by comparative analyses of the results of 610 filed soil samples with QTKs and laboratory methods, whereby it was concluded that the QTK method was less accurate than the laboratory method, yet still reliable enough for practical use (Roth et al., 1992). In a similar study, Hartz (1994) compared colorimetric test strips, QTK, nitrate-selective electrodes and laboratory analysis for soil nitrate measurements. The quick test procedure underestimated soil  $\text{NO}_3\text{-N}$  concentrations but it was suggested as a useful on-farm monitoring tool to enhance nitrogen management practices. Bischoff et al. (1996) evaluated the performance of nitrate test strips for nitrate measurement of well water by comparing the reading to HPLC data; the test strips overestimated nitrate concentration by 5%.

Schmidhalter (2005) reported a strong agreement between the results of reflectometric nitrate test strips of soil measurements with laboratory outcomes. Allison and Jones (2006) compared three different types of QTKs (test strips, color disc and colorimeter tests) with laboratory methods for measuring nitrate content in soil. The color disc demonstrated the highest correlation with the lab's average nitrate, and soil water content significantly affected on soil nitrate readings. When calibrated properly, these kits could offer end users reasonably accurate data on soil nitrate-N levels; however, they should not be considered a substitute for laboratory analyses.

Findings indicated a 35 to 45% likelihood of underestimating or overestimating laboratory  $\text{NO}_3^-$ -N levels.

A nitrate evaluation of hydroponic, nutritive and soil solutions was reported with three different methods that employed Handion Priva electrodes, Nanocolor photometric equipment, and test equipment for ELE hydroponic solutions (Jiménez et al., 2006); of these, the electrode method was most effective nitrate measurement method. In contrast, the Nanocolor and ELE equipment underestimated nitrate concentrations when values exceeded  $3 \text{ mmol L}^{-1}$ . Five commercial test kits were used on soil extracts for nitrate, pH, phosphorus ( $\text{P}_2\text{O}_5$ ), and potassium ( $\text{K}_2\text{O}$ ) (Faber et al., 2007). The results indicated that commercially available Rapitest and La Motte Soil Test Kits demonstrated accuracy rates of 92% and 94%, respectively. Overall, findings indicate that QTKs are useful for nutrient management on farms, though they have the limitation of providing only approximate or categorical results. For precise nutrient measurements or detailed interpretations, analytical laboratories should be utilized.

Maggini et al. (2010) conducted pioneering research on test kits designed to evaluate the efficacy of measuring key nutrients—nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), and inorganic phosphate (Pi)—in soil water extracts and hydroponic nutrient solutions. They employed color-reactive strips and a handheld reflectometer, comparing results to ion chromatography, the laboratory standard. A linear regression analysis assessed the relationship between these measurement sets, focusing on linearity, accuracy, precision, and specificity. The nitrate test kit exhibited robust performance, showing strong linearity (high  $R^2$ ), low variability (6.6%), and minimal interference from high chloride or sulfate concentrations. The phosphate kit demonstrated high precision but was less accurate, particularly in the presence of sulfate, while showing a strong correlation with ion chromatography for hydroponic solutions above  $30 \text{ mg/L}$ . The ammonium kit, however, struggled with precision (10.5% variation) and accuracy, especially at higher concentrations, leading to significant underestimations due to interference from nitrate. Overall, the nitrate kit proved most reliable, while the ammonium kit was less dependable.

Lee et al. (2017) compared the results of the nitrate and phosphate test kits with standard laboratory methods (ICP-OES) while monitoring nutrient fluctuations in a closed hydroponic system. His study proves the necessity of measuring individual ions in the hydroponic solution due



to a lack of correlation between EC fluctuations phosphate concentrations and few other ions. There were consistent results between ICP and QTK for nitrate measurements, but they did not align closely for specific time intervals. Overall, results acquired with both methods showed no significant difference ( $p\text{-value} > 0.05$ ) and demonstrated a positive correlation ( $R^2 \geq 0.65$ ).

Parks and Milham (2017) measured nitrate in a hydroponic solution and sap (xylem or shoot extract) from several leafy vegetables: pak choy (*Brassica rapa* ssp. *chinensis* cv. Sumo), Swiss chard (*Beta vulgaris* var. *cicla* cv. Silverstar) and cos lettuce (*Lactuca sativa* var. *longifolia* cv. Vivian). A comparison between ISE, QTK and laboratory analysis showed that QTKs can be a better choice for onsite measurements of sap nitrate. The presence of plant organic compounds in sap, such as oils and fats, as well as samples with high conductivity or salt concentration, significantly interfered with ISE measurements. This made ISEs unsuitable for measuring sap and affected the accuracy of nutrient solution readings due to the strong interference from chloride ions. Chloride ion and temperature can both affect the sensitivity of the test strips as well; sample dilutions are required due to the limited measurement range of QTKs which had a positive effect on readings by lowering the interference effect of chloride.

Tikász (2019) investigated the performance of QTKs and ISEs with flow injection analysis for ammonium and nitrate measurements in chicken, cow, and turkey hydroponic extract solutions. The results of both measurement methods were statistically different from those recorded by the Lachat flow instrument ( $p < 0.05$ ). These findings indicate that the QTK results were influenced by the presence of high concentrations of unknown ions, as well as the coloration and turbidity of the samples. Although a pretreatment and dilution step were implemented to enhance accuracy, the API readings varied by over 300% compared to the Lachat values. Adjusting ISE  $\text{NH}_4^+$  readings using a second-order polynomial equation significantly improved measurement precision. Additionally, the  $\text{NO}_3^-$  content in the manure extracts approached the ISE's detection limit (below 20 ppm), and no dilution step was necessary when using ISEs. Enhancements in ISE results could be achieved through improved calibration with manure solutions and increased sampling size.

Research on the use of quantitative test kits for measuring nitrogen and phosphorus in hydroponic systems has been scarce and there has been little investigation into the measurement of other macro and micronutrients using QTKs in hydroponic systems. Lab-based analytical

services are costly, not always accessible and can take weeks to provide results, highlighting the need for reliable on-site measurement tools. This is crucial, as certain nutrient ions need to be supplied within a narrow timeframe to promote optimal plant growth (Bamsey et al., 2012; Lee et al., 2017).

This study seeks to identify cost-effective alternatives to laboratory testing that facilitate on-site measurements without requiring extensive training. Our specific objective is to assess the repeatability and accuracy of QTKs and ISEs for nutrient measurement in hydroponic systems.

## 2. Methodology

### 2.1. Preparing solutions

This study was conducted in the Biomass Production Laboratory at McGill University's Macdonald Campus (Sainte-Anne-de-Bellevue, Quebec, Canada). Hoagland's hydroponic nutrient solution (Hoagland & Arnon, 1950) and VEG+BLOOM One-Part Powder Nutrient - RO/SOFT (Hydroponic Research, San Diego, USA) were prepared at double concentrations using dH<sub>2</sub>O water for nutrient analysis. The nutrient solutions were stored in a refrigerator (4 °C) between tests and were replaced every month during the study period. A 300 ml sample of each solution was sent for laboratory analysis (A&L Canada Laboratories, London, Ontario, Canada) to confirm the nutrient profile. Nutrient composition of both solutions is listed in Table 3, among which sulfur, boron, chloride, manganese, zinc, molybdenum and sodium were not of interest in this study. Before each test, solutions were diluted with dH<sub>2</sub>O water according to the measurement range of each test. Tests were conducted at room temperature.

Table 3. Nutrient profile of Hoagland solution and average of five laboratory analysis of commercially available VEG+BLOOM RO/Soft (Hoagland & Arnon, 1950).

Parameter			VEG+BLOOM RO/Soft average (ppm)	Hoagland & Arnon (1950) (ppm)
Macronutrients - Primary	N-NH <sub>4</sub> <sup>+</sup>	Ammonia	9.0 ± 1.44	-
	N-NO <sub>3</sub> <sup>-</sup>	Nitrate	71.6 ± 13.45	210
	P	Phosphorous	40.9 ± 3.25	31
	K	Potassium	129.8 ± 14.85	234
Macronutrients -Secondary	Ca	Calcium	89.8 ± 6.23	160
	Mg	Magnesium	28.8 ± 2.73	34
	S	Sulfur	187.6 ± 12.37	64
Micronutrients	B	Boron	0.1 ± 0.02	0.5
	Cl	Chloride	1.9 ± 0.07	-
	Cu	Copper	0.1 ± 0.01	0.02
	Fe	Iron	1.2 ± 0.09	2.5
	Mn	Manganese	0.5 ± 0.03	0.5
	Zn	Zinc	0.1 ± 0.01	0.05
	Mo	Molybdenum	0.0 ± 0.03	0.01
Additional nutrients	Na	Sodium	2.5 ± 0.61	-

For pH measurements, the pH of both plant foods at normal dosage was adjusted to four levels with pH 6, 6.5, 7, 7.5 using a Fisherbrand™ Accumet™ AB150 pH Benchtop Meters (Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA). Sodium hydroxide (Fisher Chemical, Pittsburgh, Pennsylvania, USA) and sulfuric acid (Fisher Chemical, Pittsburgh, Pennsylvania, USA) were used to adjust pH.

## **2.2. Aquarium tests**

All aquarium tests performed in this study are commercially available products from API® (Aquarium Pharmaceuticals Inc. Chalfont, Pennsylvania, USA), Fluval (Hagen Group Inc., Baie-D'Urfé, Quebec, Canada), JBL GmbH & Co. KG. (Neuhofen, Germany), Salifert (Duiven, Netherlands), Seachem Laboratories, Inc (Madison, Georgia, USA), Red Sea (Eilat, Israel), and Sera Aqua (Heinsburg, Germany). Measurements were carried out according to the manufacturers' instructions. Aquarium tests employed different methods depending on the measured parameter. Titration and turbidity methods were used for calcium, magnesium, and potassium tests. Nitrate, nitrite, phosphate, ammonia, copper, iron, and pH were measured with colorimetric tests.

## **2.3. Titration and turbidity tests**

Titration tests were performed according to the manufacturer's instructions. For all tests, reagents (indicators) were added to the test samples (analyte) to establish the starting color for titration. Next, the titrant was slowly added to the kit's sample vial or vial check using a 1 ml syringe or an eye dropper, counting drops or measuring the volume from the syringe. The process of adding and mixing continued until the end color showing in the test kit directions were achieved. Concentrations were calculated based on the titration volume in accordance with the instructions provided in each test kit.

The only turbidity test used in this study was the JBL Potassium PROAQUATEST. According to the manufacturer's instructions, the two reagents enclosed in the test kit were added to each 15 ml diluted sample and a scaled reading tube was placed over a cross on the color card.

The turbid sample was then poured into the tube until the cross in the bottom was no longer visible. The corresponding concentration was determined by the volume of the sample in the marked reading tube.

A list of test kits used to determine calcium, magnesium and potassium concentrations in this study is provided in Table 4. The smallest measurable step, shown in the accuracy column of Table 4, is based on the minimum volume of titrant that can be added to samples as determined by the design of each test kit.

Table 4. Titration and turbidity test kits were used in this study.

<b>Description</b>	<b>Brand</b>	<b>Test kit name</b>	<b>Method</b>	<b>Accuracy</b>
Calcium	Sera Aqua	Sera calcium-test ( $\text{Ca}^{2+}$ )	Titration	20
Calcium	Red Sea	Calcium pro reef test kit	Titration	5
Calcium	Salifert	$\text{Ca}^{2+}$ profi test	Titration	5
Calcium	JBL	PROAQUATEST Mg-Ca	Titration	20
Calcium	Seachem	Reef status <sup>TM</sup> calcium	Titration	5
Calcium	API	Calcium test kit	Titration	20
Calcium	Fluval	Calcium test kit	Titration	20
Magnesium	Seachem	Reef status <sup>TM</sup> magnesium	Titration	12.5
Magnesium	Sera Aqua	Sera magnesium-test ( $\text{Mg}^{2+}$ )	Titration	60
Magnesium	Red Sea	Magnesium pro reef test kit	Titration	20
Magnesium	Salifert	$\text{Mg}^{2+}$ profi test	Titration	30
Magnesium	JBL	PROAQUATEST Mg-Ca	Titration	20
Potassium	JBL	PROAQUATEST $\text{K}^+$ Potassium	Turbidity	depends on dilution factor
Potassium	Salifert	Potassium reef test	Titration	10
Potassium	Red Sea	Trace-colors pro multi test kit	Titration	3

### 3.2.1 Colorimetric test

#### 3.2.1.1 Calibration of the colorimetric test kits

Standard solutions with a known concentration (Table 5) were used for each ion and diluted to match the measurement range of each of the tests in the sets. QTKs were used to measure ionic concentration of at least 4 concentrations of 0 ppm, low, mid and high-range depending on the measurement range of each test. In the case of a wider range of measurements, 5 concentrations were tested. The test kits covered a wide range of concentrations, nutrients were tested within the range of hydroponic solutions. Calibration measurements were repeated three times to ensure accuracy of results. Since the

method used by each test kit was not disclosed, a full-spectrum analysis was performed within the range from 300 nm to 800 nm using the Biochrom Ultrospec 2100 Pro UV/visible spectrophotometer (Harvard Bioscience Inc, Holliston, MA, USA). The wavelength that displayed the greatest sensitivity to different concentrations was identified as the optimal indicator. The light absorption at the identified wavelength was used to develop a linear calibration equation.

Cu and Fe standard solutions were made by solid  $\text{CuSO}_4$  and  $\text{FeSO}_4$  in the laboratory and the concentrations were confirmed by analytical lab testing by A&L Canada Laboratories (London, Canada). Copper standard solution was diluted to reach 0.2, 0.02, 0.01 and 0 ppm for calibration. Iron standard solution was tested at 0.5, 0.25, 0.1 and 0 ppm.

Table 5. List of standard solutions used for calibration in this study.

Chemical	Type	Description	Calibration concentration
1000 mg/l $\text{NO}_3^-$	Nitrate standard solution	$\text{NaNO}_3$ in $\text{H}_2\text{O}$ (EMD Millipore Corporation, Darmstadt, Germany)	0, 10, 25, 40, 50, 80, 100 and 160 ppm
50.0 mg/L $\text{NH}_4^+$ -N	Ammonium Standard Solution	$\text{NH}_4^+$ -N in $\text{H}_2\text{O}$ (EMD Millipore Corporation, Darmstadt, Germany)	0, 0.5, 1, 1.5 and 3 ppm
1000 ppm $\text{NO}_2^-$	Nitrite Standard	(Ricca Chemical Company, Arlington, USA)	0, 0.1, 0.5 and 1 ppm
25 ppm P (76.7 ppm $\text{PO}_4^{3-}$ )	Phosphate phosphorus standard	(Ricca Chemical Company, Arlington, USA)	0, 0.2, 0.6, 1.8, 3.5 and 7 ppm
pH 7.5	Buffer solution	Phosphate, 0.5 M buffer soln., (Thermo Scientific Inc, Waltham, MA, USA)	
pH 7.5	Buffer solution	Phosphate buffer (Thermo Scientific Inc, Waltham, MA, USA)	
pH 6.5	Buffer solution	Phosphate, 0.5 M buffer soln., (Thermo Scientific Inc, Waltham, MA, USA)	
pH 6.5	Buffer solution	MES, 1.0 M buffer soln., (Thermo Scientific Inc, Waltham, MA, USA)	
pH 6	Buffer solution	(certified) Fisher chemical, Waltham, MA, USA	
pH 5.5	Buffer solution	MES, 1.0M buffer soln., (Thermo Scientific Inc, Waltham, MA, USA)	

### 3.2.1.2 Nutrient solution testing with colorimetric test kits

After calibration, test kits were used to measure the ions and pH in the hydroponic plant solutions. Colorimetric aquarium tests for marine and freshwater were conducted according to the manufacturer's instructions and timing except for the final step. At the end of the tests, water samples developed a color and were analyzed using Biochrom Ultrospec 2100 pro UV/visible spectrophotometer (Harvard Bioscience Inc, Holliston, MA, USA) at the identified wavelength as the earlier step. Using the calibration equation, the concentration of each sample was calculated and compared to the laboratory findings and ion-selective electrode measurements.

Table 6. List of colorimetric tests used in this study.

Description	Brand	Test kit name	Measurement range	Number of tests per kit	Identified wavelength
Ammonia	API	Ammonia test kit	0 -8 ppm	130	680
Ammonia	Fluval	Ammonia test kit	0 - 6.7 ppm	50	656
Ammonia	JBL	PROAQUATEST NH <sub>4</sub> <sup>+</sup> Ammonium	0.05 - 5 ppm	50	396
Ammonia	Red Sea	Marine care multi test kit	0- 2 ppm	50	694
Ammonia	Salifert	NH <sub>4</sub> <sup>+</sup> Profi test	0- 2 ppm	50	376
Ammonia	Sera Aqua	Sera ammonium/ammonia-test (NH <sub>4</sub> <sup>+</sup> /NH <sub>3</sub> )	0- 10 ppm (freshwater)	60	696
Copper	API	Copper test kit	0 - 4 ppm	90	450
Copper	JBL	PROAQUATEST Cu Copper	0.05- 1.6 ppm	50	602
Copper	Salifert	Cu Profi test	0- 2 ppm	50	622
Copper	Seachem	MultiTest™ Copper	0- 0.8 ppm	75	602
Copper	Sera Aqua	Sera copper-test (Cu)	0- 2 ppm	50	596
Iron	Fluval	Iron test kit	0- 1 ppm	50	596
Iron	JBL	PROAQUATEST Fe Iron	0.02- 1.5 ppm	50	560
Iron	Red Sea	Trace-Colors pro multi test kit	0- 0.5 ppm	50	524
Iron	Seachem	MultiTest™ Iron	0- 2 ppm	75	560
Iron	Sera Aqua	Sera iron-test (Fe)	0- 1 ppm	75	564
Nitrate	API	Nitrate test kit	0-160 ppm	90	544
Nitrate	Fluval	Nitrate test kit	0- 110 ppm	80	544
Nitrate	JBL	PROAQUATEST NO <sub>3</sub> <sup>-</sup> Nitrate	0- 200 ppm	40	450
Nitrate	Red Sea	Marine care multi test kit	0- 50 ppm	50	534
Nitrate	Salifert	NO <sub>3</sub> <sup>-</sup> Profi test	0- 100 ppm	60	534
Nitrate	Seachem	MultiTest™ Nitrite/Nitrate	0- 50 ppm	70	552

Description	Brand	Test kit name	Measurement range	Number of tests per kit	Identified wavelength
Nitrate	Sera Aqua	Sera nitrate-test ( $\text{NO}_3^-$ )	0- 100 ppm	60	548
Nitrite	API	Nitrite test kit	0- 5 ppm	180	544
Nitrite	Fluval	Nitrite test kit	0 -3.3 ppm	75	540
Nitrite	Red Sea	Marine care multi test kit	0- 1 ppm	50	540
Nitrite	Seachem	MultiTest™ Nitrite/Nitrate	0- 25 ppm	70	536
Nitrite	Sera Aqua	Sera nitrite-Test ( $\text{NO}_2^-$ )	0- 5 ppm	75	548
pH	API	PH test kit	6 - 7.6	250	616
pH	Fluval	pH low range test	6 - 7.6	225	616
pH	JBL	PROAQUATEST pH 3.10-10.0	3- 10	50	616
pH	Sera Aqua	Sera pH-Test	6.5- 9	100	616
Phosphate	API	Phosphate test kit	0-10 ppm	150	694
Phosphate	Fluval	Phosphate test kit	0 - 5 ppm	70	700
Phosphate	JBL	PROAQUATEST $\text{PO}_4$ Phosphate Sensitive	0.02- 1.8 ppm	50	710
Phosphate	Red Sea	Phosphate marine test kit	0- 1 ppm	100	700
Phosphate	Salifert	$\text{PO}_4$ Profi test	0- 3 ppm	60	700
Phosphate	Seachem	MultiTest™ Phosphate	0- 3 ppm	75	640
Phosphate	Sera Aqua	Sera phosphate test ( $\text{PO}_4^{3-}$ )	0- 2 ppm	60	710

## 2.4. Ion-selective electrodes

A set of carbon nano tube solid-contact electrodes were used for nitrate, ammonium, potassium and calcium measurements (Imacimus 5, NT sensors, S.L. Tarragona, Spain). The set of four ISEs was conditioned in a single probe for 30 min before each sampling. A three-point calibration was performed according to the NT sensors instructions, using mid-range or low-range calibration solutions based on the ion concentrations of the samples. The ISEs were recalibrated after every five measurements. A glass/PVC double cell electrode was employed for pH measurements alongside the multi-ion probe (Reference/ pH electrode, Imacimus 5, NT sensors, S.L. Tarragona, Spain). The pH meter was calibrated before each set of measurements using a pH 4.01 and pH 7 calibration solutions. The process of calibration and batch measurements was executed using the recommended computer-operated platform for the NT sensors.



The results obtained from the multi-ion probe were later compared to the laboratory results and the outcomes of the aquarium test kits. Measurements of the pH probe were compared with readings from Fisherbrand™ Accumet™ AB150 pH Benchtop Meters (Thermo Fisher Scientific Inc., Waltham, MA, USA) and the results of aquarium test kits.

Table 7. Ion range of calibration solutions (Calibration Standards Multi ION Low Range, NT sensors, S.L. Tarragona, Spain)

Ion	<b>Medium-range calibration solution</b> (Calibration Standards Multi ION, #HP08, NT Sensors, S.L. Tarragona, Spain)			<b>Low-range calibration solution</b> (Calibration Standards Multi ION Low Range, # LR03, NT Sensors, S.L. Tarragona, Spain)		
	Solution 1	Solution 2	Solution 3	Solution 1	Solution 2	Solution 3
<b>Calcium</b>	36 mg/L	180 mg/L	360 mg/L	9 mg/L	45 mg/L	90 mg/L
<b>Potassium</b>	39 mg/L	195 mg/L	390 mg/L	5 mg/L	25 mg/L	50 mg/L
<b>Ammonium</b>	4 mg/L	20 mg/L	40 mg/L	1 mg/L	5 mg/L	10 mg/L
<b>Nitrate</b>	132 mg/L	660 mg/L	1320 mg/L	27 mg/L	135 mg/L	270 mg/L

## 2.5.Laboratory analysis

After preparing each plant hydroponic solution or standard solution, a 300 ml sample was sent to A&L Laboratories Inc. (London, Ontario, Canada) for analysis, where an automated flow injection analysis (FIA) with cadmium reduction was used for nitrate concentration detection. The salicylate colorimetric method with a spectrophotometer was employed for ammonia detection. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to measure the concentrations of phosphorus, calcium, magnesium, potassium, copper, and iron.

## 2.6.Statistical analysis

Percentage prediction error was calculated for all individual measurements. A simple linear regression analysis compared results from each test kit and ISEs to those obtained from A&L Canada Laboratories (London, Ontario, Canada). The parameters derived from the regression were utilized to evaluate zero offset and sensitivity offset of the test kits and ISEs. Coefficient of determination ( $R^2$ ) was employed to assess the linearity of test kits. For further comparison, Accuracy of the measurement or total measurement error was calculated by Equation 1. To

evaluate precision or measurement repeatability equation 2 was applied and standard error of regression (SER) was calculated by equation 3. Microsoft Excel (Microsoft 365 MSO 2024, Microsoft Corporation) were used to conduct statistical analysis.

(Equation 2)

$$Accuracy = \sqrt{\frac{\sum_{i=1}^N \sum_{j=1}^3 (y_{ij} - y_{ij}^{lab})^2}{3 * N}}$$

(Equation 3)

$$Precision = \sqrt{\frac{\sum_{i=1}^N \sum_{j=1}^3 (y_{ij} - \bar{y}_i)^2}{2 * N}}$$

(Equation 3)

$$SER = \sqrt{\frac{\sum_{i=1}^N \sum_{j=1}^3 (y_{ij} - y_{ij}^{reg})^2}{3 * N - 2}}$$

Where N is the number of tested concentrations,  $y_{ij}$  is each individual data point measured by ISE or aquarium test kits, and  $y_{ij}^{lab}$  is the laboratory measurement by ICP-OES,  $\bar{y}_i$  is the sample mean for each concentration,  $y_{ij}^{reg}$  is estimated values from the regression model.

### 3. Research findings and results

This section presents the findings from the comparative analysis of ISEs and test kits.

#### 3.1. Nitrate measurements

The findings from the full spectrum light absorption analysis of standard solutions and calibration curves, are shown in Figure A 1 through Figure A 7. The linear regression summary for colorimetric test kit calibration demonstrated high correlation coefficient of 0.902 to 0.998 (Table A 1).

Table A 2 and Table A 3 presents all the measurements along with their corresponding percentage errors. The ISE readings show a spiked percentage error on nitrate concentrations below 20 ppm for both Hoagland and Vegbloom solutions (50.6 % to 614.9 %). The percent error of ISE for Vegbloom solution reading was nearly seven times higher than Hoagland reading.

Regression fit between laboratory analysis and the results of the nitrate test kits are shown on Table 8. Test kits tend to underestimate nitrate readings except for JBL, Salifert and ISE. The summary of regression fit (Table 8) indicates that Red Sea and Sera Aqua QTKs had high correlation to the laboratory results for Hoagland solution with slopes of 0.88 and 0.88 and low intercept of 0.97 and -3.13 and R-squares of 0.99 and 0.99 respectively. JBL test kit had the closest slope to one (0.94) but a high intercept of 24.67 resulted in overestimation of nitrate concentration in all Hoagland samples.

The linear regression of laboratory results and measurements of QTKs and ISE for Vegbloom solution is presented on Figure A 8 and Figure A 9, which shows over estimated measurements on lower ranges (below 50 ppm) and under estimation at higher concentrations. Red Sea had the closest results to laboratory measurement for Vegbloom solution with slope and intercept of 1.17 and -2.27. The  $\text{NO}_3^-$  ISE had a high sensitivity offset for Vegbloom (slope of 2.5) and high zero offset for Hoagland solution (intercept of -20.15), resulting in overestimating nitrate concentration in all samples.

Table 8. Performance comparison of different brands of aquarium test kits and ISE for Hoagland, Vegbloom, and in total for nitrate.

	Accuracy (ppm)	Precision (ppm)	R <sup>2</sup>	Slope <sup>*†</sup>	Intercept <sup>‡</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
API	45.79	7.03	0.89	0.45 <sup>*</sup>	15.73 <sup>‡</sup>	10.39
Fluval	373.89	4.90	0.54	0.02 <sup>*</sup>	18.56 <sup>‡</sup>	7.11
JBL	27.92	18.07	0.89	0.94	24.80 <sup>‡</sup>	20.95
Red Sea	2.46	1.04	0.99	0.88 <sup>*</sup>	0.97	0.96
Salifert	29.74	27.46	0.76	0.72	20.12	26.72
Seachem	4.09	1.09	0.98	0.75 <sup>*</sup>	3.59 <sup>‡</sup>	1.51
Sera Aqua	17.38	16.13	0.86	0.88	-3.13	15.55
NT sensors	116.50	25.89	0.996	1.29 <sup>*</sup>	-3.31	28.21
<b>Vegbloom</b>						
API	24.07	1.10	0.99	0.45 <sup>*</sup>	9.27 <sup>‡</sup>	1.09
Fluval	22.64	4.05	0.93	0.65 <sup>*</sup>	28.69 <sup>‡</sup>	11.26
JBL	28.48	11.54	0.94	0.69 <sup>*</sup>	4.69	11.39
Red Sea	3.78	0.57	0.99	1.17 <sup>*</sup>	-2.27 <sup>‡</sup>	0.93
Salifert	60.16	30.07	0.42	0.66	62.81 <sup>‡</sup>	48.73
Seachem	16.45	1.17	0.42	0.58	19.33 <sup>‡</sup>	12.35
Sera Aqua	24.46	6.39	0.82	0.46 <sup>*</sup>	8.84	6.76
NT sensors	146.50	32.45	0.92	2.50 <sup>*</sup>	9.89	45.18
<b>Total</b>						
API	38.04	5.36	0.91	0.47 <sup>*</sup>	11.48 <sup>‡</sup>	8.26
Fluval	279.09	4.50	< 0.01	0.00 <sup>*†</sup>	49.25 <sup>‡</sup>	40.31
JBL	28.20	15.16	0.77	0.83	13.59	27.52
Red Sea	3.19	0.84	0.97	1.07	-1.49	3.21
Salifert	47.45	28.79	0.50	0.68 <sup>*</sup>	42.21 <sup>‡</sup>	42.33
Seachem	11.98	1.13	0.51	0.67 <sup>*</sup>	11.07 <sup>‡</sup>	10.72
Sera Aqua	21.21	12.27	0.77	0.74 <sup>*</sup>	-0.56	14.27
NT sensors	132.35	29.35	0.94	1.26 <sup>*</sup>	48.21 <sup>‡</sup>	79.23

### 3.2. Nitrite measurements

Table A 4 and Figure A 10 to Figure A 14 display the results of the full spectrum light absorption analysis of standard solutions, along with the calibration curves and the linear regression summary for colorimetric test kit calibration with correlation coefficients ranging from 0.993 to 1.

\* Marks the slopes significantly different than 1 at alpha = 0.05.

† Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

‡ Marks the intercepts significantly different than 0 at alpha = 0.05.

The measurements and their associated percentage errors are provided in Table A 5, ranging from 0.5% to 162.2% percent error. Correlation of test kits with the laboratory results shows that Seachem and Sera Aqua with a slope of 0.975 and 0.96 had the closest slope to one, and Sera Aqua and Fluval had the closest intercept to zero (0.014 and 0.018 ppm respectively) for the combined results of both solutions (Figure A 15). Fluval with the least measurement repeatability error ( $\pm 0.023$  ppm  $\text{NO}_2^-$ ) was the most precise test kit for both solutions. Sera Aqua with  $\pm 0.08$  ppm  $\text{NO}_2^-$  and API with  $\pm 0.128$  ppm  $\text{NO}_2^-$  had the least total measurement error and highest accuracy for both solutions respectively (Table 9).

Table 9. Performance comparison of different brands of aquarium test kits for Hoagland, Vegbloom, and in total for nitrite.

	Accuracy (ppm)	Precision (ppm)	R <sup>2</sup>	Slope <sup>++</sup>	Intercept <sup>†</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
API	0.146	0.085	0.976	1.207 <sup>*</sup>	-0.008	0.08
Fluval	0.041	0.029	0.993	0.944	0.010	0.03
Red Sea	0.169	0.101	0.930	1.134	0.042	0.13
Seachem	0.113	0.081	0.975	1.142	-0.002	0.08
Sera Aqua	0.105	0.101	0.940	0.891	0.008	0.09
<b>Vegbloom</b>						
API	0.107	0.024	0.998	1.218 <sup>*</sup>	-0.048 <sup>‡</sup>	0.02
Fluval	0.303	0.016	0.998	1.431 <sup>*</sup>	0.027	0.02
Red Sea	0.183	0.119	0.958	1.329 <sup>*</sup>	-0.084	0.12
Seachem	0.278	0.209	0.661	0.807	0.267	0.24
Sera Aqua	0.042	0.023	0.997	1.029	0.021	0.02
<b>Total</b>						
API	0.128	0.062	0.986	1.213 <sup>*</sup>	-0.028	0.06
Fluval	0.216	0.023	0.873	1.187	0.018	0.18
Red Sea	0.176	0.110	0.939	1.232 <sup>*</sup>	-0.021	0.12
Seachem	0.212	0.159	0.807	0.975	0.133	0.19
Sera Aqua	0.080	0.073	0.953	0.960	0.014	0.08

\* Marks the slopes significantly different than 1 at alpha = 0.05.

† Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

‡ Marks the intercepts significantly different than 0 at alpha = 0.05.

### 3.3. Ammonium and Ammonia measurements

Table A 6 and Figure A 16 to Figure A 21 present the full spectrum light absorption analysis of standard solutions, the calibration curves, and the summary of linear regression for the calibration of colorimetric test kits. During calibrations and nutrient solution testing, the JBL test kit showed no visual color change and was the only test kit with negative calibration slope indicating the possible corruption of the test kit. Test kits had the R-square value of 0.797 to 1 for calibration.

Table A 7 and Table A 8 contain the full list of measurements and the corresponding percentage errors. The measured values ranged from 0.3 ppm to 5.91 ppm  $\text{NH}_4^+$ , with percentage errors of test kits varying from 0.22% to 208.67%. Comparison of regression lines between laboratory analysis and results of ISE and QTKs, indicates that the API test kit and ammonium ISE had the best correlation by the slope of 0.816 and 1.107 and intercept of 0.009 and 0.378 for the Vegbloom solution. However, both ISE and API test kit performed poorly with the Hoagland solution (Table 10, Figure A 22 and Figure A 23). Fluval test kit achieved slope and intercept of 1.021 and 0.09 and a low total measurement error of  $\pm 0.2$  ppm  $\text{NH}_4^+$  in Hoagland measurements. The  $\text{NH}_4^+$  ISE overestimated the ammonium concentration in all samples and had high zero and sensitivity offsets for Hoagland solution (slope and intercept of 0.23 and 10.65 respectively).

Table 10. Performance comparison of different brands of aquarium test kits and ISE for Hoagland, Vegbloom, and in total for ammonium.

	Accuracy (ppm)	Precision (ppm)	R <sup>2</sup>	Slope <sup>*†</sup>	Intercept <sup>‡</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
API	0.407	0.056	0.593	0.497*	0.308	0.25
Fluval	0.195	0.051	0.995	1.021	0.093	0.15
JBL	2.301	0.050	0.722	-0.059*	0.946 <sup>‡</sup>	0.07
Red Sea	0.820	0.093	0.996	1.988*	-0.395 <sup>‡</sup>	0.08
Salifert	0.540	0.066	0.919	0.381*	0.215 <sup>‡</sup>	0.07
Sera Aqua	0.792	0.122	0.986	1.876*	-0.275 <sup>‡</sup>	0.14
NT sensors	9.310	1.213	0.075	0.235 <sup>*†</sup>	10.650 <sup>‡</sup>	1.66
<b>Vegbloom</b>						
API	0.717	0.188	0.949	0.816*	0.009	0.10
Fluval	0.857	0.115	0.961	0.738*	0.110	0.12
JBL	2.841	0.044	0.845	-0.064*	1.038 <sup>‡</sup>	0.04
Red Sea	0.817	0.167	0.813	1.440	0.020	0.19
Salifert	0.749	0.120	0.644	0.443*	0.205	0.13
Sera Aqua	0.563	0.199	0.888	0.788	0.060	0.12
NT sensors	0.751	0.094	0.975	1.107	0.378 <sup>‡</sup>	0.29
<b>Total</b>						
API	0.583	0.138	0.946	0.805*	0.017	0.22
Fluval	0.580	0.085	0.922	0.858*	0.143	0.46
JBL	2.546	0.048	0.689	-0.057*	0.974 <sup>‡</sup>	0.07
Red Sea	0.818	0.135	0.904	1.614*	-0.133	0.24
Salifert	0.653	0.097	0.814	0.439*	0.183 <sup>‡</sup>	0.11
Sera Aqua	0.687	0.165	0.597	0.705	0.590	0.61
NT sensors	6.232	0.811	0.006	0.185 <sup>†</sup>	6.407 <sup>‡</sup>	4.33

\* Marks the slopes significantly different than 1 at alpha = 0.05.

† Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

‡ Marks the intercepts significantly different than 0 at alpha = 0.05.

### 3.4. Phosphate measurements

The analysis of full spectrum light absorption for standard solutions and calibration curves are included in Figure A 24 through Figure A 30. Linear regression details for colorimetric test kit calibration are presented on Table A 9 with R-square values of 0.688 to 0.999.

The data on measurements and their percentage errors can be found in Table A 10 and Table A 11. All QTKs had higher errors at lower concentrations. The comparison of regressions (Table 11, Figure A 31 and Figure A 32) suggests a strong linear correlation between measured and actual values ( $R^2$  above 0.9) for all QTKs except for Seachem and Salifert regarding Hoagland phosphate analysis ( $R^2$  of 0.67 and 0.87). In terms of slope of the regression line, Sera Aqua and API had the closest slope to one for Hoagland (0.981 and 1.078) and Vegbloom (1.021 and 1.007) solutions. Seachem overestimated all measurements, with higher slopes of 1.571 for the Hoagland solution and 1.713 for the Vegbloom solution. The intercept values ranged from 0.98 to -0.386. Fluval (0.034) and Sera Aqua (-0.035) for Vegbloom and Seachem (0.02) for Hoagland solution had the least zero offset.

Overall, API and Sera Aqua QTKs offered very close results to the laboratory measurement for both solutions with total measurement error of  $\pm 0.483$  and  $\pm 0.261$  ppm  $\text{PO}_4^{3-}$  and measurement repeatability of  $\pm 0.725$  and  $\pm 143$  ppm  $\text{PO}_4^{3-}$  in the measurement range of 0.2 to 9 and 0.2 to 4.5 ppm  $\text{PO}_4^{3-}$  respectively.



Table 11. Performance comparison of different brands of Aquarium test kits for Hoagland, Vegbloom, and in total for phosphate.

	Accuracy (ppm)	Precision (ppm)	R <sup>2</sup>	Slope <sup>*†</sup>	Intercept <sup>‡</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
API	0.595	0.880	0.975	1.078	-0.049	0.544
Fluval	0.457	0.106	0.985	1.248	-0.345	0.244
JBL	0.515	0.096	0.979	1.264 <sup>*</sup>	-0.323 <sup>‡</sup>	0.301
Red Sea	0.253	0.059	0.946	1.119	-0.212	0.244
Salifert	0.596	0.074	0.872	0.821	0.098	0.582
Seachem	1.248	0.348	0.670	1.571 <sup>*</sup>	0.020	0.522
Sera Aqua	0.280	0.132	0.967	0.981	0.074	0.297
<b>Vegbloom</b>						
API	0.228	0.166	0.993	1.007	-0.062	0.238
Fluval	0.462	0.059	0.980	0.852 <sup>*</sup>	0.034	0.225
JBL	0.263	0.113	0.979	1.047	-0.190 <sup>‡</sup>	0.227
Red Sea	0.161	0.006	0.969	1.011	-0.163 <sup>‡</sup>	0.034
Salifert	0.219	0.062	0.990	1.044	-0.237 <sup>‡</sup>	0.116
Seachem	1.006	0.527	0.932	1.713 <sup>*</sup>	-0.386	0.309
Sera Aqua	0.242	0.153	0.932	1.021	-0.035	0.244
<b>Total</b>						
API	0.483	0.725	0.977	1.058	-0.066	0.478
Fluval	0.459	0.091	0.933	1.054	-0.168	0.468
JBL	0.398	0.106	0.966	1.154 <sup>*</sup>	-0.252 <sup>‡</sup>	0.294
Red Sea	0.219	0.045	0.959	1.118 <sup>*</sup>	-0.211 <sup>‡</sup>	0.179
Salifert	0.490	0.070	0.901	0.874	-0.012	0.457
Seachem	1.151	0.434	0.797	1.649 <sup>*</sup>	-0.174 <sup>‡</sup>	0.440
Sera Aqua	0.261	0.143	0.961	0.998	0.017	0.268

### 3.5. Potassium measurements

The complete set of measurements and their respective percentage errors is shown in Table A 12. The distribution of errors suggests that percentage error is relatively higher at lower concentrations of potassium measurement for both solutions. Regression analysis shows a good fit

\* Marks the slopes significantly different than 1 at alpha = 0.05.

† Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

‡ Marks the intercepts significantly different than 0 at alpha = 0.05.

between measured and actual potassium concentrations with R-square values above 0.95 for all methods (Table 12, Figure A 33, Figure A 34). All methods had a slope close to one ranging from 0.9 to 1.23. NT sensors (1.05) and Salifert (0.98) with Vegbloom and Red Sea (0.95) with Hoagland analysis had the closest slopes to 1 indicating a good agreement with the actual concentrations. Salifert with intercepts of 2.04 and NT sensors with -22.81 had the closest intercept to zero.

Overall, NT Sensors demonstrated the best performance in terms of accuracy and precision, with the least total measurement error ( $\pm 20.51$  ppm  $K^+$ ), the highest precision ( $\pm 5.84$  ppm  $K^+$ ), and the highest  $R^2$  (0.99). This method also showed a strong linear relationship with a slope close to 1 (1.13), suggesting that its measurements are reliable and well-calibrated.

Table 12. Performance comparison of different brands of aquarium test kits and ISEs for Hoagland, Vegbloom, and in total for potassium.

	Accuracy (ppm)	Precision (ppm)	$R^2$	Slope <sup>*†</sup>	Intercept <sup>‡</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
JBL	62.98	10.00	0.97	1.22 <sup>*</sup>	-102.46 <sup>‡</sup>	34.44
Red Sea	27.11	10.95	0.99	0.95	33.55 <sup>‡</sup>	16.95
Salifert	50.88	7.45	0.99	0.90 <sup>*</sup>	73.39 <sup>‡</sup>	13.05
NT sensors	18.66	4.90	1.00	1.11 <sup>*</sup>	-22.81 <sup>‡</sup>	1.00
<b>Vegbloom</b>						
JBL	25.72	5.00	0.98	1.21 <sup>*</sup>	-16.06	13.65
Red Sea	36.95	5.92	0.97	1.23 <sup>*</sup>	-62.11 <sup>‡</sup>	18.83
Salifert	9.70	5.77	0.99	0.98	2.04	10.91
NT sensors	22.21	6.65	0.99	1.05	-28.67 <sup>‡</sup>	0.99
<b>Total</b>						
JBL	48.11	7.91	0.90	1.07	-29.65	47.43
Red Sea	32.40	8.80	0.96	1.10	-24.05	31.33
Salifert	36.62	6.67	0.95	1.02	19.92	29.52
NT sensors	20.51	5.84	0.99	1.13 <sup>*</sup>	-32.93 <sup>‡</sup>	0.99

\* Marks the slopes significantly different than 1 at alpha = 0.05.

† Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

‡ Marks the intercepts significantly different than 0 at alpha = 0.05.

### 3.6. Calcium measurements

Table A 13 and Table A 14 display the measurements and the corresponding percentage error values. Most of the test kits and  $\text{Ca}^{2+}$  ISE measurements on the Vegbloom solution had lower percent errors at higher calcium concentrations. The reverse relation between error and calcium concentration is more pronounced with API and Sera Aqua measurements on the Vegbloom solution.

The regression analysis showed strong correlations, ranging from 0.921 to 0.988 for the Hoagland measurements and from 0.944 to 0.997 for the Vegbloom measurements (Table 13, Figure A 35 and Figure A 36). For the Hoagland tests, the regression lines for API, Sera Aqua, JBL, Red Sea, and Fluval had slopes of 0.995, 0.999, 1.041, 1.046, and 1.07, respectively, all of which were close to 1. Red Sea, JBL, and Salifert exhibited the closest intercepts to zero, with values of -1.532, -4.262, and -4.329, respectively. In the Vegbloom analysis, Salifert and API, with slopes of 1.083 and 1.099, demonstrated the least sensitivity offset, while JBL, Seachem, and NT Sensors showed the least zero offset, with intercepts of -3.489, 4.326, and 5.736, respectively.

Overall, the combined results of Vegbloom and Hoagland solution show that Red Sea was the most accurate test with a total measurement error of  $\pm 15.85$  ppm  $\text{Ca}^{2+}$  and Sera Aqua was the most precise method with measurement repeatability of  $\pm 6.67$  ppm  $\text{Ca}^{2+}$  (Table 13).

Table 13. Performance comparison of different brands of aquarium test kits and ISEs for Hoagland, Vegbloom, and in total for calcium.

	Accuracy (ppm)	Precision (ppm)	R <sup>2</sup>	Slope <sup>†</sup>	Intercept <sup>‡</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
API	22.36	14.91	0.97	0.995	14.47	20.33
Fluval	18.91	14.91	0.98	1.07	-12.75	19.31
JBL	31.54	17.64	0.93	1.04	-4.26	35.02
Red Sea	18.3	12.8	0.98	1.05	-1.53	17.50
Salifert	94.08	39.09	0.92	1.36*	-4.33	50.81
Seachem	22.98	15.63	0.99	0.86*	17.51	11.97
Sera Aqua	20.41	9.43	0.97	0.999	9.07	20.83
NT sensors	56.22	44.06	0.94	1.35*	-62.48	43.16
<b>Vegbloom</b>						
API	41.71	0	0.997	1.1*	30.07 <sup>‡</sup>	3.93
Fluval	61.25	6.67	0.94	0.37*	23.27 <sup>‡</sup>	6.10
JBL	18.62	6.67	0.99	0.88*	-3.49	5.11
Red Sea	12.94	5.53	0.98	0.89	20.01 <sup>‡</sup>	9.07
Salifert	22.05	8.97	0.98	1.08	10.21	10.30
Seachem	20.31	4.41	0.99	0.82*	4.33	6.69
Sera Aqua	24.12	0	0.99	0.68*	50.04 <sup>‡</sup>	3.67
NT sensors	27.82	3.07	0.97	0.75*	5.74	8.16
<b>Total</b>						
API	33.46	10.54	0.97	0.95	35.76 <sup>‡</sup>	19.79
Fluval	45.32	11.55	0.89	1.05	-31.43	41.16
JBL	25.9	13.33	0.95	1.05	-14.95	26.03
Red Sea	15.85	9.86	0.98	1.01	6.4	14.42
Salifert	68.33	28.36	0.94	1.35*	-11.33	37.50
Seachem	21.69	11.49	0.98	0.89*	2.95	12.59
Sera Aqua	22.34	6.67	0.97	0.93	22.62 <sup>‡</sup>	18.81
NT sensors	44.36	31.23	0.93	1.25*	-45.29 <sup>‡</sup>	38.05

\* Marks the slopes significantly different than 1 at alpha = 0.05.

† Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

‡ Marks the intercepts significantly different than 0 at alpha = 0.05.

### 3.7. Magnesium measurements

Table A 15 lists the measurements, along with their corresponding percentage errors. Salifert and Sera Aqua tests failed to measure magnesium at lower concentrations, resulting in a 100% relative error.

The summary of linear regression is presented in Table 14. The Salifert test kit had the closest slope to the Hoagland samples with the value of 0.918. However, the high intercept of -32.4 caused a wide gap between the results of Salifert test kits and laboratory measurements. As shown in Figure A 37, Salifert and JBL test kits tend to underestimate, and Red Sea tends to overestimate magnesium measurement in the Hoagland solution. For Vegbloom (Figure A 38), Red Sea had the closest slope to one (0.839), and Seachem and Red Sea had the closest intercept to zero (10.356 and 10.042 respectively). The comparison of total measurement error indicates that the most accurate test kits were Seachem ( $\pm 13.5$  ppm  $\text{Mg}^{2+}$ ) for Hoagland and Red Sea ( $\pm 6.2$  ppm  $\text{Mg}^{2+}$ ) for Vegbloom. The most precise test kit for Hoagland solution was Salifert with  $\pm 10$  ppm  $\text{Mg}^{2+}$  measurement repeatability. Red Sea, Salifert, Seachem and Sera Aqua had high precision with measurement repeatability of 0 to  $\pm 5.89$  ppm  $\text{Mg}^{2+}$ .

Table 14. Performance comparison of different brands of aquarium test kits for Hoagland, Vegbloom, and in total for magnesium.

	Accuracy (ppm)	Precision (ppm)	R <sup>2</sup>	Slope <sup>*†</sup>	Intercept <sup>‡</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
JBL	27.44	20.00	0.53	0.55	9.90	18.64
Red Sea	85.59	79.93	0.65	2.29	-22.78	60.04
Salifert	39.39	10.00	0.84	0.92	-32.41 <sup>‡</sup>	14.27
Seachem	13.48	18.63	0.82	0.77	12.84	12.90
Sera Aqua	44.34	48.99	0.24	0.73 <sup>†</sup>	30.28	46.55
<b>Vegbloom</b>						
JBL	20.07	13.33	0.11	0.23 <sup>*†</sup>	22.76	14.68
Red Sea	6.15	0.00	0.96	0.84 <sup>*</sup>	10.04 <sup>‡</sup>	3.56
Salifert	40.48	0.00	#DIV/0!	0.000	0.00	0.00
Seachem	8.62	5.89	0.87	0.64 <sup>*</sup>	10.36 <sup>‡</sup>	5.39
Sera Aqua	19.77	0.00	0.89	1.4	-29.93 <sup>‡</sup>	10.56
<b>Total</b>						
JBL	24.04	17.00	0.44	0.47 <sup>*</sup>	14.57	16.16
Red Sea	60.67	56.52	0.66	2.1 <sup>*</sup>	-23.39	45.65
Salifert	39.94	7.07	0.68	0.72 <sup>*</sup>	-23.05 <sup>‡</sup>	14.98
Seachem	11.32	13.82	0.85	0.79 <sup>*</sup>	8.28	10.13
Sera Aqua	34.33	34.64	0.48	1.14	-7.11	36.17

### 3.8. Copper measurements

The full spectrum light absorption analysis, along with the calibration curves and linear regression summary for the colorimetric test kit calibration, are presented in Table A 16 and Figure A 39 to Figure A 43 . The regression lines had R-square values ranging from 0.97 to 1.

Table A 17 summarizes the measurements and their associated percentage errors. The percent error of Hoagland's measurements was mostly higher than those of Vegbloom, with all methods overestimating copper concentrations in Hoagland (Sera Aqua only overestimated at higher concentrations). API, Salifert, and Seachem (only at higher concentrations) overestimated copper

\* Marks the slopes significantly different than 1 at alpha = 0.05.

† Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

‡ Marks the intercepts significantly different than 0 at alpha = 0.05.

in the Vegbloom solution, while JBL and Sera Aqua underestimated copper concentration (Figure A 44 and Figure A 45).

For the Hoagland solution, the regression analysis shows a lower R-square value for most test kits compared to other methods. Seachem and Sera Aqua had the highest R-squares of 0.763 and 0.984, respectively, while other test kits had R-squared values between 0.298 to 0.33. The API test kit, with a slope of 1.364 had the closest slope to one while Salifert, with an intercept of 0.023, had the closest intercept to zero. Overall, the API test kit demonstrated the best accuracy and precision for Hoagland solution, with a total measurement error of  $\pm 0.059$  ppm Cu(I&II) and measurement repeatability of  $\pm 0.03$  ppm Cu (I&II) (Table 15 -A).

For Vegbloom measurements, the R-square values were higher, ranging from 0.789 to 0.905. None of the test kits achieved a slope close to 1. JBL, Sera Aqua and API had the closest slope to one with values of 0.476, 0.573 and 2.416 respectively. Overall, JBL was the most accurate and precise test with  $\pm 0.027$  ppm Cu (I&II) total measurement error and  $\pm 0.005$  ppm Cu ion measurement repeatability (Table 15 -B).

Table 15. Performance comparison of different brands of aquarium test kits for Hoagland, Vegbloom, and in total for copper.

	Accuracy (ppm)	Precision (ppm)	R <sup>2</sup>	Slope**	Intercept <sup>†</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
API	0.059	0.030	0.309	1.364 <sup>†</sup>	0.040	0.034
JBL	0.062	0.051	0.298	1.653 <sup>†</sup>	0.030	0.043
Salifert	0.201	0.151	0.330	5.566 <sup>†</sup>	0.023	0.134
Seachem	0.507	0.096	0.984	22.058*	-0.177 <sup>‡</sup>	0.048
Sera Aqua	0.739	0.149	0.763	36.653*	-0.556	0.345
<b>Vegbloom</b>						
API	0.106	0.011	0.978	2.416*	0.033 <sup>‡</sup>	0.01
JBL	0.027	0.005	0.905	0.476*	0.001	0.004
Salifert	0.242	0.077	0.789	4.921*	0.029	0.072
Seachem	0.459	0.065	0.864	15.224*	-0.414 <sup>‡</sup>	0.171
Sera Aqua	0.035	0.009	0.808	0.573*	-0.012	0.008
<b>Total</b>						
API	0.085	0.022	0.800	2.394*	0.023	0.029
JBL	0.048	0.036	0.006	0.146 <sup>†</sup>	0.044 <sup>‡</sup>	0.045
Salifert	0.222	0.120	0.583	4.952*	0.034	0.101
Seachem	0.484	0.082	0.586	12.706*	-0.109	0.257
Sera Aqua	0.523	0.106	0.038	4.183 <sup>†</sup>	0.074	0.51

### 3.9. Iron measurements

Table A 18 and Figure A 46 to Figure A 50 illustrate the results of the full spectrum light absorption analysis, the calibration curves, and the linear regression summary for calibrating colorimetric test kits. The regression lines demonstrated strong correlations, with R-square ranging from 0.959 to 0.983.

The measurements and their corresponding percentage error values are listed in Table A 19. The error distribution for the Vegbloom solution indicates higher errors at lower concentrations, whereas this trend is not observed for the Hoagland solution. Seachem test kits exhibited the highest percentage errors among the QTKs, ranging from 63% to 222.6%. The linear regression

\* Marks the slopes significantly different than 1 at alpha = 0.05.

<sup>†</sup> Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

<sup>‡</sup> Marks the intercepts significantly different than 0 at alpha = 0.05.



analysis between laboratory results and QTK measurements is presented in Figure A 51 and Figure A 52 and summarized in Table 16. Fluval and Sera Aqua had the closest slopes to one for both solutions, with values ranging from 0.98 to 1.27. These test kits also demonstrated the best accuracy, with total measurement errors of  $\pm 0.06$  and  $\pm 0.08$  ppm Fe ion for Hoagland and  $\pm 0.03$  ppm  $\text{Fe}^{+2}/\text{Fe}^{3+}$  for Vegbloom. JBL and Sera Aqua showed the best measurement repeatability, with errors of  $\pm 0.02$  ppm  $\text{Fe}^{+2}/\text{Fe}^{3+}$ . All QTKs achieved good precision for Vegbloom tests.

Table 16. Performance comparison of different brands of aquarium test kits for Hoagland, Vegbloom, and in total for iron.

	Accuracy (ppm)	Precision (ppm)	R <sup>2</sup>	Slope <sup>††</sup>	Intercept <sup>‡</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
Fluval	0.06	0.04	0.94	1.16	-0.004	0.046
JBL	0.10	0.02	0.98	1.41*	-0.01	0.034
Red Sea	0.09	0.04	0.94	1.26	0.01	0.050
Seachem	0.23	0.04	0.89	0.57*	-0.13 <sup>‡</sup>	0.032
Sera Aqua	0.08	0.02	0.97	1.27*	0.003	0.032
<b>Vegbloom</b>						
Fluval	0.03	0.01	0.99	0.98	0.04 <sup>‡</sup>	0.012
JBL	0.06	0.01	1.00	1.11*	0.03 <sup>‡</sup>	0.006
Red Sea	0.05	0.01	1.00	0.78*	0.10 <sup>‡</sup>	0.006
Seachem	0.28	0.01	0.86	0.27*	-0.07 <sup>‡</sup>	0.015
Sera Aqua	0.03	0.02	0.99	1.09	0.01	0.017
<b>Total</b>						
Fluval	0.05	0.03	0.95	1.08	0.01	0.034
JBL	0.08	0.02	0.96	1.26*	0.01	0.034
Red Sea	0.07	0.03	0.90	1.04	0.05	0.049
Seachem	0.26	0.03	0.79	0.44*	-0.11 <sup>‡</sup>	0.032
Sera Aqua	0.06	0.02	0.96	1.16*	0.01	0.035

\* Marks the slopes significantly different than 1 at alpha = 0.05.

† Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

‡ Marks the intercepts significantly different than 0 at alpha = 0.05.

### 3.10. pH measurements

The outcomes of the full spectrum light absorption analysis for standard solutions, the calibration curves, and the linear regression summary for colorimetric test kit calibration are detailed in Table A 20 and Figure A 53 to Figure A 56.

All relevant measurements and their percentage errors are included in Table A 21. JBL and Seachem test kits show less error at higher pH levels. NT sensors pH ISE had lower percent error than other methods with values of 0.24% to 3.15%. All QTKs overestimate pH levels in both solutions (Figure A 57 and Figure A 58). Table 17 presents a summary of linear regression between laboratory results and ISE and QTKs.

For the Hoagland solution, API and Fluval had the closest slopes to one (0.936 and 1.018 respectively), and API and NT sensors had the closest intercepts to zero (0.737 and 1.245). NT sensor pH ISE with  $\pm 0.145$  total measurement error was the most accurate, and API with  $\pm 0.034$  measurement repeatability error was the most precise method for pH measurements.

For the Vegbloom solution, Fluval and NT sensors had the most agreement with the laboratory results with slopes of 1.007 and 0.974 and intercepts of 0.352 and 0.099. NT sensors were the most accurate method, with a total measurement error of  $\pm 0.089$ . NT sensors and Fluval both achieved high precision of  $\pm 0.099$  and  $\pm 0.352$ , respectively.

Table 17. Performance comparison of different brands of aquarium test kits and pH probe for Hoagland, Vegbloom, and in total for pH.

	Accuracy (ppm)	Precision (ppm)	R <sup>2</sup>	Slope <sup>*†</sup>	Intercept <sup>‡</sup> (ppm)	SE (ppm)
<b>Hoagland</b>						
API	0.314	0.034	0.988	0.936	0.737 <sup>‡</sup>	0.062
Fluval	0.334	0.065	0.990	1.018	0.204	0.064
JBL	0.496	0.066	0.991	1.408 <sup>*</sup>	-2.322 <sup>‡</sup>	0.080
Sera Aqua	0.559	0.107	0.985	1.469 <sup>*</sup>	-2.681 <sup>‡</sup>	0.111
NT sensor	0.145	0.084	0.962	0.809 <sup>*</sup>	1.245 <sup>‡</sup>	0.098
<b>Vegbloom</b>						
API	0.345	0.089	0.974	0.875 <sup>*</sup>	1.174 <sup>‡</sup>	0.088
Fluval	0.405	0.065	0.988	1.007	0.352	0.069
JBL	0.582	0.140	0.975	1.398 <sup>*</sup>	-2.163 <sup>‡</sup>	0.137
Sera Aqua	0.571	0.121	0.972	1.324 <sup>*</sup>	-1.658 <sup>‡</sup>	0.136
NT sensor	0.089	0.041	0.995	0.974	0.099	0.043
<b>Total</b>						
API	0.330	0.068	0.980	0.906 <sup>*</sup>	0.954 <sup>‡</sup>	0.075
Fluval	0.371	0.065	0.985	1.013	0.277	0.073
JBL	0.541	0.109	0.980	1.403 <sup>*</sup>	-2.243 <sup>‡</sup>	0.117
Sera Aqua	0.565	0.114	0.976	1.397 <sup>*</sup>	-2.172 <sup>‡</sup>	0.128
NT sensor	0.121	0.066	0.972	0.891 <sup>*</sup>	0.675 <sup>‡</sup>	0.089

\* Marks the slopes significantly different than 1 at alpha = 0.05.

† Marks the slopes not significantly different than zero 1 at alpha = 0.05 (non-responsive behavior).

‡ Marks the intercepts significantly different than 0 at alpha = 0.05.

### 3.11. Summary

Figure 1 and Figure 2 provide a fair comparison between all ions and all measurement methods. This figure depicts the standardized accuracy, precision and standard error of regression by division of these numbers by the range of measurements.

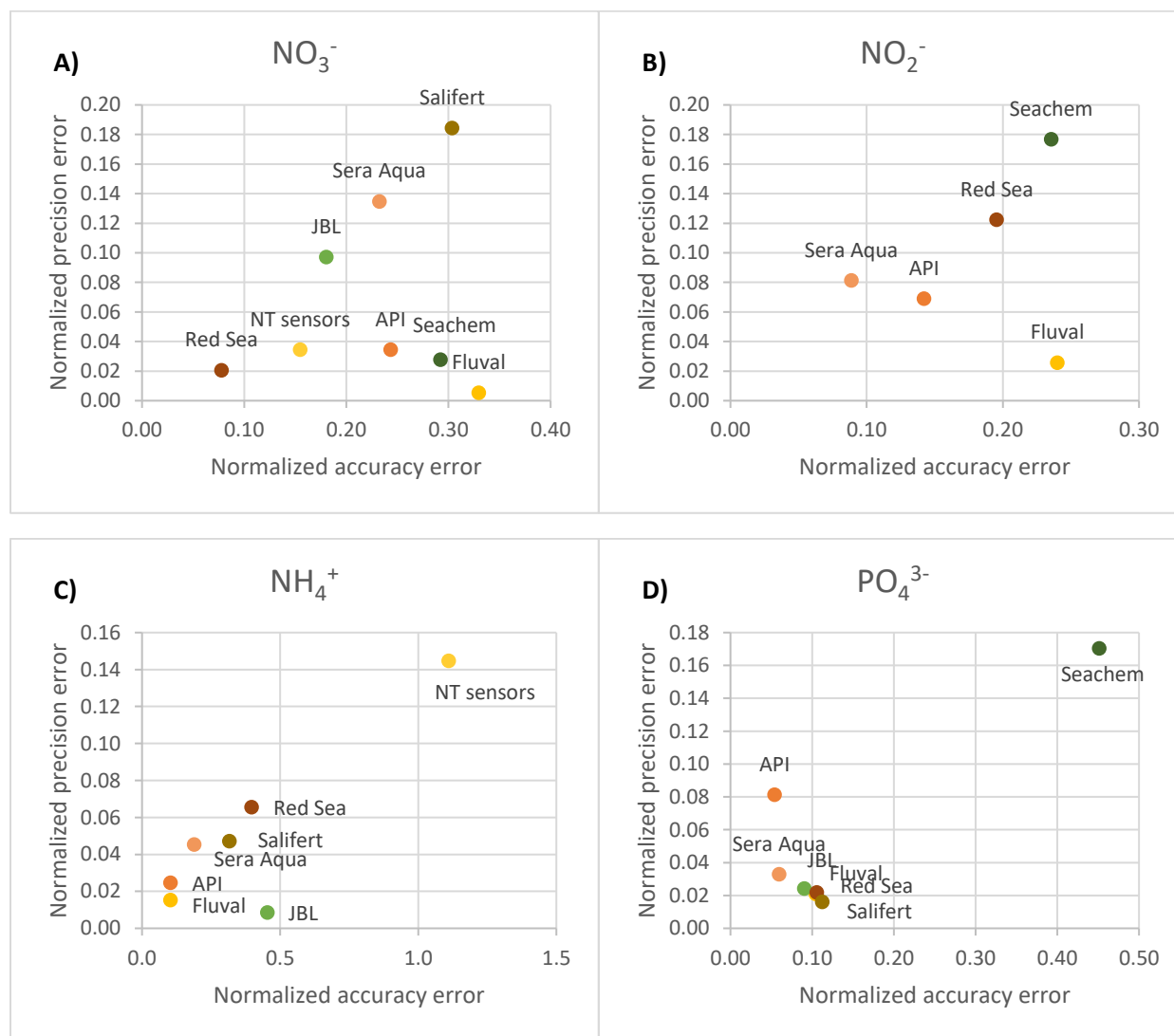


Figure 1. Normalized accuracy (X axis) and precision (Y axis), by divided by the range of measurements for  $\text{NO}_3^-$  (A),  $\text{NO}_2^-$  (B),  $\text{NH}_4^+$  (C),  $\text{PO}_4^{3-}$  (D). Closer value to (0,0) indicates more reliable measurement

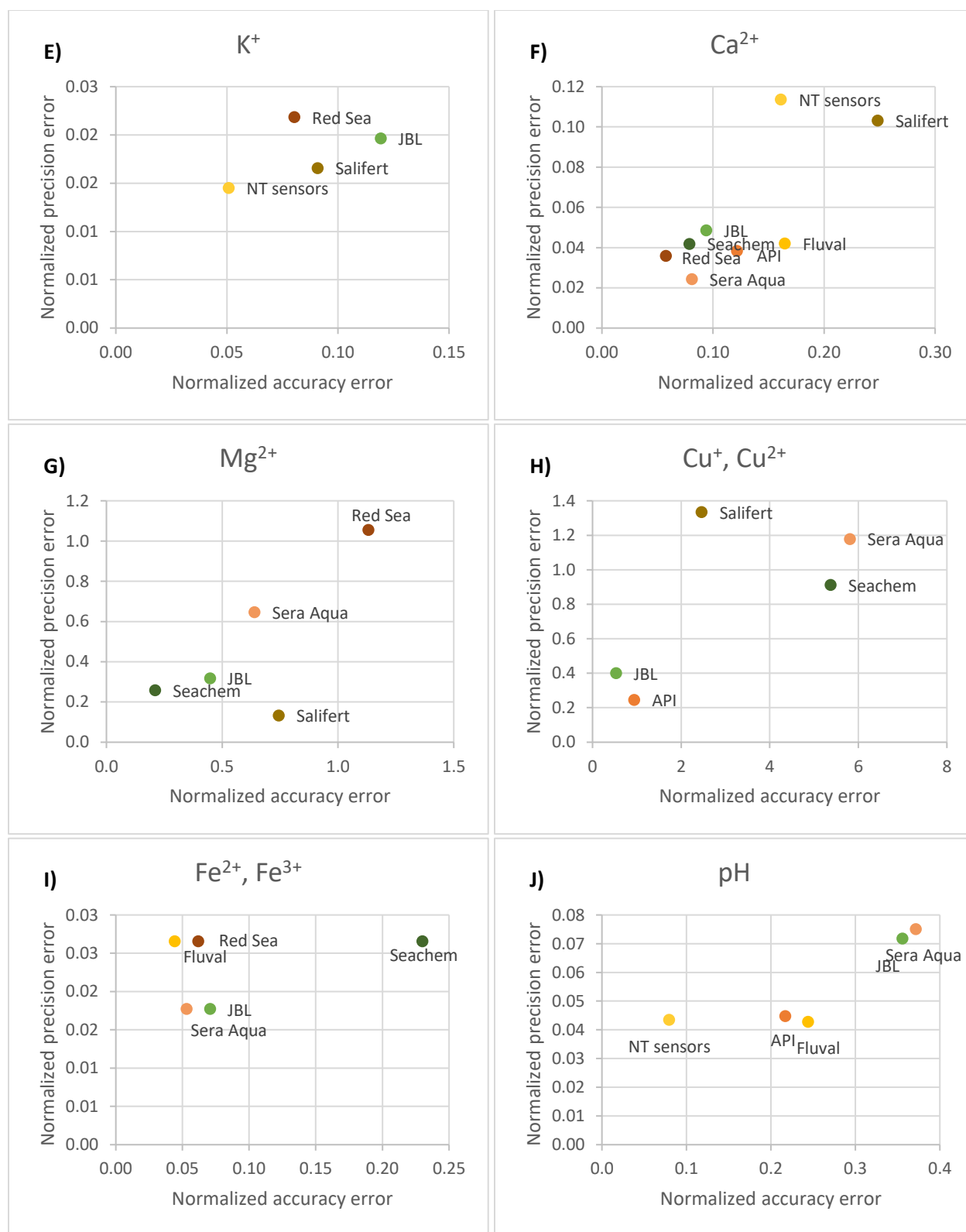


Figure 2. Normalized accuracy (X axis) and precision (Y axis), by divided by the range of measurements for K (E),  $Ca^{2+}$  (F),  $Mg^{2+}$  (G), Cu (*I&II*) (H), Fe (*II&III*) (I), pH (J). Closer value to (0,0) indicates more reliable measurement

## **4. Discussion**

### **4.1. Nitrate measurements**

#### **Measurement ranges**

Acceptable nitrate range in aquariums is 0 - 10 ppm  $\text{NO}_3^-$  (0 to 2.26 ppm  $\text{NO}_3^-$ -N) (Borneman, 2008). The highest range covered by QTKs in this study was offered by JBL and API QTKs of 0-200 and 0-160 ppm  $\text{NO}_3^-$  respectively (45.18 and 36.14 ppm  $\text{NO}_3^-$ -N). Red Sea and Seachem had the upper measurement range of 50 ppm  $\text{NO}_3^-$  (11.3 ppm  $\text{NO}_3^-$ -N), therefore it was necessary to dilute all hydroponic samples before measurements. Nitrate ISE covers the wide range of 0.6 to 30000 ppm  $\text{NO}_3^-$  (0.14 to 6776.90 ppm  $\text{NO}_3^-$ -N).

#### **Hoagland nitrate measurement**

Among the test kits evaluated for Hoagland measurements, the JBL test kit demonstrated the least sensitivity offset. However, it exhibited significant zero offset, which consistently led to overestimation of results. Despite this, JBL QTK showed the least error (<10%) at high nitrate concentrations and proved to be the most suitable choice for testing nitrates at high concentrations (1:5 dilution factor, ~170 ppm  $\text{NO}_3^-$ ). Salifert QTK excelled in mid-range analysis (1:10 dilution factor, ~70 ppm  $\text{NO}_3^-$ ), offering the best performance for this concentration range. The NT Sensors ISE demonstrated the highest correlation with laboratory measurements (>99%), but its high slope resulted in persistent overestimation of results at higher concentrations.

The Red Sea kit displayed the best overall performance, with low zero and sensitivity offsets, along with a strong correlation (>98%) to laboratory measurements. Red Sea, Seachem, and API QTKs performed well in low-range measurements (1:20 to 1:100 dilution factor, ~below 40 ppm  $\text{NO}_3^-$ ). Fluval test kit exhibited the weakest correlation with laboratory results and showed significant zero and sensitivity offsets, making it unsuitable for accurate monitoring of nitrate levels in Hoagland solution.

#### **Vegbloom nitrate measurement**

Similar results were obtained using the Red Sea QTK with the Vegbloom solution, demonstrating the best performance in terms of minimal zero offset, sensitivity offset, and strong

correlation with laboratory measurements. The Red Sea test kit exhibited a total measurement error of only  $\pm 3.8$  ppm  $\text{NO}_3^-$  within the 0 to 50 ppm  $\text{NO}_3^-$  range.

In contrast, all other test kits showed significantly higher sensitivity offset (with slopes below one). While the API, Sera Aqua, and JBL test kits performed well at lower concentrations (1:20 to 1:40 dilution factor,  $\sim$  below 20 ppm  $\text{NO}_3^-$ ) their performance rapidly deteriorated as the sample concentration increased. This resulted in an overestimation of nitrate levels, particularly in less diluted samples. The Fluval test kit performed notably better with the Vegbloom solution, with results falling within 70% of laboratory measurements at higher concentration ranges (1:2 to 1:4 dilution factor,  $\sim$  70 to 180 ppm  $\text{NO}_3^-$ ). NT sensors, which exhibited high sensitivity offset, consistently overestimated nitrate concentrations by more than 50%.

### **Overall performance and important considerations**

The results for both the Hoagland and Vegbloom solutions demonstrate that the Red Sea test kit consistently performed well for both solutions, with a measurement error of  $\pm 3.19$  ppm  $\text{NO}_3^-$  within the manufacturer-recommended range (0 to 50 ppm  $\text{NO}_3^-$ ).

A significant difference in the performance of the Fluval test kit was observed between the Hoagland and Vegbloom solutions, suggesting possible interference from other chemicals present in the Hoagland solution.

The NT sensor consistently overestimated nitrate concentrations in both solutions, with particularly notable overestimation for the Vegbloom solution. However, this sensor provides the advantage of high measurement range compared to the test kits without the need for repetitive dilutions and digitalized measurements allowing automation and computer-based decision making.

Parks and Milham (2017) in their comparison of test strips and ISEs for on-site nitrate monitoring concluded that both can be suitable for hydroponic nutrient management and test strips are a better options for shoot or xylem sap nitrate measurements, they point out that chloride ion effects the performance of both measurement tools. Results obtained by Lee et al. (2017) and Maggini et al. (2010) on using commercial test kits for measuring nitrate in hydroponic nutrient solution confirms that nitrate test kits can be successfully used for in situ measurement with close agreement to chromatography methods.

Rius-Ruiz et al. (2014) designed a computer-operated analytical platform using nitrate NT Sensors ISEs, which allowed them to successfully make all the required decisions to correct nutritional imbalances in hydroponic solutions. They reported inconsistencies in the slope and standard electrode potential ( $E_0$ ) of the nitrate NT Sensors ISEs compared to other electrodes, along with a potential drift of -1.8 to -2.3 mV/day over a 3-month measurement period. They concluded that this electrode needs to be calibrated with at least two solutions before measuring each sample.

## **4.2.Nitrite measurements**

### **Measurement ranges**

In this study nitrite was manually added to both Hoagland and Vegbloom solution in range of 0.1 to 1 ppm  $\text{NO}_2^-$ , which is covered by all QTKs.

### **Hoagland nitrite measurement**

A comparison of the performance of QTKs for Hoagland solution revealed that the Fluval test kit outperformed the others, demonstrating the least sensitivity offset (slope of 0.944), as well as the highest precision ( $\pm 0.029$  ppm  $\text{NO}_2$  measurement repeatability) and accuracy ( $\pm 0.041$  ppm  $\text{NO}_2$  total measurement error). The Sera Aqua test kit ranked second, offering competitive performance in terms of minimal zero and sensitivity offset, with an accuracy of  $\pm 0.105$  ppm  $\text{NO}_2$ . The Seachem test kit exhibited the lowest zero offset and delivered the best results for near-zero measurements. While Seachem, API, and Red Sea kits performed well at lower concentrations, their higher zero offset (slope above one) caused the measured values to deviate more significantly from true concentrations at higher levels, leading to overestimation of nitrite concentrations.

### **Vegbloom nitrite measurement**

The results of the Quick Test Kits (QTKs) for Vegbloom solution showed that the Sera Aqua test kit was the top performer, exhibiting the least zero and sensitivity offset, along with the highest accuracy, achieving a total measurement error of  $\pm 0.08$  ppm  $\text{NO}_2$ . The Fluval test kit excelled in precision, with a repeatability of  $\pm 0.16$  ppm  $\text{NO}_2$ , and ranked second for near-zero measurements. However, its high sensitivity offset resulted in a wider gap between the measured and actual



concentrations as nitrite levels increased, with all Fluval measurements exceeding the added amount. In contrast, the Seachem test kit demonstrated an opposite trend, with results becoming closer to the true concentration at higher nitrite levels. However, it performed poorly at the 0.5 ppm concentration, showing low precision ( $\pm 0.21$  ppm  $\text{NO}_2$ ) and a weak correlation ( $R^2 = 0.66$ ).

### **Overall performance and important considerations**

The combined results from tests on both Hoagland and Vegbloom solutions indicate that the Sera Aqua test kit provided the most accurate results, with a total measurement error of  $\pm 0.08$  ppm  $\text{NO}_2$ , as well as the least zero and sensitivity offset overall. The Fluval test kit was the most precise, with a measurement repeatability of  $\pm 0.023$  ppm  $\text{NO}_2$ . API ranked second in both accuracy and precision.

Nitrite can pose significant challenges in aquaponic systems (Yep & Zheng, 2019), organic hydroponic solutions (Tikász, 2019), and any hydroponic setups characterized by high ammonia concentrations and elevated pH levels (Barbouch et al., 2012). Monitoring nitrite levels in such systems is crucial, as nitrite can cause severe damage to plants, and consequently to human health through the consumption of contaminated produce (Anjana & Iqbal, 2007). Since laboratory analysis doesn't always provide nitrite analysis, making QTKs valuable alternative for assessing the safety of these systems. Ormaza-González and Villalba-Flor (1994) compared portable test kits (Hach DR/2000) to laboratory method with natural water reported that nitrite levels measured by the test kit are reliable for monitoring nitrite in both fresh and saline waters.

## **4.3. Ammonium/Ammonia measurements**

### **Measurement ranges**

Sera Aqua and API QTKs with measurement range of 0 to 10 and to 8 ppm  $\text{NH}_4^+$  have the widest measurement range among all the test kits. Ammonium ISE had the measurement range of 0.2 to 9000 ppm  $\text{NH}_4^+$ .

## Hoagland ammonium measurement

Comparison of the test kits and ISE revealed that the Fluval test kit demonstrated the best performance when measuring the Hoagland solution. It exhibited the least zero and sensitivity offsets, along with the high correlation to laboratory results. Furthermore, it had the best accuracy, with a total measurement error of  $\pm 0.195$  ppm  $\text{NH}_4^+$ . This test kit also showed the lowest percent error across all concentrations within the 0 to 5 ppm  $\text{NH}_4^+$  range.

In terms of precision, the JBL, Fluval, and API test kits provided the most consistent measurements. The API kit had the second-best performance in terms of sensitivity offset and accuracy, delivering results that were closely aligned with laboratory measurements for concentrations up to 1.2 ppm  $\text{NH}_4^+$ . All other test kits exhibited significant sensitivity offset, yielding acceptable results only at lower concentrations (0 to 0.5 ppm  $\text{NH}_4^+$ ).

Ammonium ISE showed a poor performance while measuring Hoagland solution, with lowest accuracy, precision and highest zero offset among all measured data. One possible explanation for this poor performance could be interference from other ions present in the Hoagland solution.

## Vegbloom ammonium measurement

Most of the test kits and the NT sensor ISE demonstrated better performance when measuring ammonium in the Vegbloom solution compared to the Hoagland solution. The API test kit showed the least zero offset and ranked second in terms of sensitivity offset, with a total measurement error of  $\pm 0.717$  ppm  $\text{NH}_4^+$  in the 0 to 6 ppm  $\text{NH}_4^+$  range. The NT sensors exhibited the least sensitivity error, along with high precision and accuracy ( $\pm 0.751$  ppm  $\text{NH}_4^+$  in range of 0 to 6 ppm  $\text{NH}_4^+$ ). Both the NT sensors and the Red Sea test kit consistently overestimated ammonium concentrations (slope above one), while all other test kits underestimated ammonium concentrations (slope below one).

## Overall performance and important considerations

Considering the results for both solutions, the API and Fluval test kits demonstrated the best overall performance, achieving high accuracy and precision while covering a wide measurement range. The NT sensors and Sera Aqua test kits exhibited significantly different behaviors when measuring the Hoagland and Vegbloom solutions, resulting in poor correlation ( $R^2$  below 6). This

inconsistency may be due to potential interference. The JBL test kit exhibited the poorest performance for both solutions. It failed to show a visible color change during calibration and nutrient solution measurements, possibly due to corruption of test.

Tikász (2019) compared, ISE and API test kits and Lachat flow injection for monitoring ammonium concentration in manure solution, reported more than 300% error in the results of API test kit due to initial color, turbidity and presence of unknown ions. Results of both QTK and ISE were statistically different than laboratory measurements. Maggini et al. (2010) compared the performance of a ammonium test kit with IC, reported a good agreement for concentrations below 1 ppm, but under estimation of ammonium readings at higher concentrations. Naigaga et al. (2017) compared the performance of the Seneye slide and by the Seachem ammonia alert test kits with standard methods on aquaculture solution, reported moderate agreement (58% level of agreement) between the mentioned measurement methods.

#### **4.4. Phosphate measurements**

##### **Measurement ranges**

The acceptable phosphate range in an aquarium 0 – 1 ppm (Borneman, 2008). Hence why the majority of test kits in this study has the measurement range below 3 ppm (JBL, Red Sea, Salifert, Seachem, Sera Aqua). API and Fluval test kits had the highest measurement range of up to 10 ppm and up to 5 ppm respectively.

##### **Hoagland phosphate measurement**

Analyzing the results of phosphate aquarium test kits for Hoagland solution, two test kits standing out in terms of zero and sensitivity offset compared to laboratory measurements. API and Sera Aqua QTKs, both had slopes and intercepts very close to 1 and 0, which correlated very close to laboratory measurements. Studying the correlation between laboratory results and QTK measurement shows that better performance was observed for Sera Aqua and Red Sea at relatively higher concentrations (40 to 70 times dilution of Hoagland solution  $\sim 1.5$  to 3 ppm  $\text{PO}_4^{3-}$ ), for Fluval and JBL at mid-range measurements (1:100 dilution factor  $\sim 1$  to 0 ppm  $\text{PO}_4^{3-}$ ), and for

API and Salifert for lower concentrations (1:200 dilution factor  $\sim 1$  to 0 ppm  $\text{PO}_4^{3-}$ ). Seachem had better results in near zero measurements but overestimated phosphate concentration at all times.

### **Vegbloom phosphate measurement**

Similar results were observed using the Vegbloom solution, with high performance in terms of both sensitivity offset and zero offset from API and Sera Aqua QTK. Fluval test kit had the best performance at near 0 concentration, However, its performance rapidly declining by drastically underestimating phosphate levels as concentrations increased (slope below 1). Seachem closely follows Fluval in terms of high performance near 0 ppm, but it degraded even more rapidly compared to control measurements at higher concentrations, overestimating by more than 70%. The Vegbloom nutrient solution was best analyzed through API and Sera Aqua test kits, as they demonstrate the highest consistency to determine accurate levels of phosphate throughout the whole range of concentrations. Observations on the regression line of QTKs and laboratory results shows that API, JBL, Red Sea and Salifert had better performance at higher phosphate concentrations (10 to 40 times dilution  $\sim 4$  to 7 ppm  $\text{PO}_4^{3-}$ ). Sera Aqua at mid-range (100 times dilution  $\sim 1$  to 4 ppm  $\text{PO}_4^{3-}$ ) and Seachem and Fluval at lower concentrations (200 to 500 times dilution  $\sim 0$  to 1 ppm  $\text{PO}_4^{3-}$ ) had the most accurate results.

### **Overall performance and important considerations**

Overall, the combination of samples on Hoagland and Vegbloom solution shows Sera Aqua had the closest results to the control analysis and was within its measurement range (0 to 2 ppm  $\text{PO}_4^{3-}$ ). Fluval and API test kit had the closest results to laboratory measurement after Sera Aqua.

There was a large gap between Seachem aquarium test kit and laboratory results for both solutions. A possible reason for this might be due to the difficulty at finding the proper wavelength for calibration and low correlation between light absorption and standard solutions ( $R^2 = 0.688$ ). API, JBL, Salifert and Seachem calibration equation resulted in negative concentration numbers for high dilutions for Hoagland (1:500) and Vegbloom solution (1:500). One explanation for this might be non-linearity of calibration curve at very low concentrations. Some measurements were taken at concentrations higher than the recommended range specified by the manufacturer.

The results indicate that the QTKs can still provide accurate measurements at higher concentrations than upper limit of test kits mentioned by the manufacturers. However, it is important to note that higher errors may occur in spectrophotometer readings for darker solutions.

Faber et al. (2007) evaluated the performance of five different brand of test kits for measurement of phosphorus as  $P_2O_5$  on soil extracts. Their results showed the categorical value provided by three test kits (La Motte Soil, Rapitest, Quick Soiltest) can be beneficial for growers while two other brands (Soil Kit and NittyGritty) can result in underestimating the nutrient and excessive use of fertilizers. Maggini et al. (2010) suggest  $Cl$  and  $SO_4$  might interfere with the results of QTKs. Their experiments show a strong correlation between the results from IC and the QTK for hydroponic solutions with phosphate levels above 30ppm. However, phosphate content of soil solutions was underestimated by 25% at higher concentrations. The study done by Lee et al. (2017) concludes that the  $PO_4^{3-}$  concentration in the hydroponic solution does not follow the same trend as EC and therefore needs to be monitored separately in the hydroponic solution. The comparison of IC and  $PO_4^{3-}$  QTKs in this study were not significantly different ( $p\text{-value} > 0.05$ ), However did not closely match due to interference during some time intervals.

## **4.5.Potassium measurement**

### **Measurement ranges**

It is recommended to maintain potassium levels in reef aquariums between 380 and 200 ppm (Seachem, 2024). The Salifert and Red Sea test kits are both titration-based methods that measure potassium concentrations within the ranges of 250 to 470 ppm and 150 to 540 ppm, respectively. The volume of titration solution required for each test had a reverse relation to corresponding potassium concentrations, making potassium measurement at lower concentrations less economically feasible. The Salifert test kit uses a dropper to add the titrant solution, where each drop corresponds to 10 ppm  $K^+$  (smallest measurable unit). The Red Sea test kit uses a syringe, with each 0.01 ml of titrant solution representing a 3ppm change in potassium (the smallest measurable unit). JBL is a turbidity test that can measure potassium in range of 2 to 15 ppm. It is recommended by the manufacturer to dilute marine water samples 30 times before conducting the JBL test. The accuracy of this turbidity test depends on the viewer's angle, vision, and the lighting

conditions which might be a source of error in the results of this test kit. Finally, the NT Sensors potassium ion-selective electrode (ISE) can measure potassium levels across a wide range, from 0.4 to 39,000 ppm.

### **Hoagland potassium measurement**

The results from the QTKs for the Hoagland solution revealed a noticeable reduction in measurement error at higher potassium concentrations, (double Hoagland solution~ 430 to 450 ppm K<sup>+</sup>). The potassium ISE demonstrated the opposite trend, performing exceptionally well at medium and lower concentrations, but slightly drifting off at double Hoagland measurements. The NT sensor potassium ISE maintained a percent error of less than 10% across all concentrations and outperformed the other methods in terms of minimal zero offset, high R<sup>2</sup> values, and an accuracy with a total measurement error of  $\pm 18.66$  ppm K<sup>+</sup>. Among the test kits evaluated, the Red Sea test kit displayed the least sensitivity offset and ultimately provided the most consistent and reliable performance. JBL test kit was the most precise measurement method (measurement repeatability of  $\pm 5$  ppm K<sup>+</sup>) but had the highest zero and sensitivity offsets and total measurement error.

### **Vegbloom potassium measurement**

The Salifert test kit exhibited a high correlation with laboratory measurements, demonstrating minimal zero and sensitivity offsets, as well as the smallest total measurement error ( $\pm 9.7$  ppm K<sup>+</sup>). The JBL test kit performed well at lower potassium concentrations, especially with a 1:2 dilution factor (~ below 100 ppm K<sup>+</sup>). However, its accuracy decreased at higher concentrations. In contrast, the NT sensors and Red Sea kits showed lower accuracy at lower potassium concentrations but performed better as the potassium concentration increased, with less than 8% error at higher concentrations (double Vegbloom ~ above 250 ppm K<sup>+</sup>). The NT sensors ISE demonstrated the second least sensitivity offset and achieved the highest precision among all methods, with a measurement repeatability of  $\pm 4.9$  ppm K<sup>+</sup>.

### **Overall performance and important considerations**

Considering the results for both Hoagland and Vegbloom solutions, the NT sensors demonstrated the best overall performance, with a total measurement error of  $\pm 20.51$  ppm and measurement repeatability of  $\pm 5.84$  ppm K<sup>+</sup> in the 60 to 450 ppm K<sup>+</sup> range. The JBL test kit, in

contrast, showed the lowest accuracy within the same concentration range. Although the JBL test kit did not rank as the top performer among the tested kits for either solution, it remains the only test kit allowing of feasible measurements at lower potassium concentrations in the samples. While Red Sea and Salifert test kits can technically measure potassium at lower concentrations, they require large volumes of titrant solution, resulting in a limited number of measurements possible per kit.

Rius-Ruiz et al. (2014) designed a computer-operated analytical platform using NT sensors for hydroponic solution testing. They reported standard electrode potential ( $E_0$ ) of  $K^+$  ISE showed poor precision and reasonable stability during 120 days of study. They concluded that the high slope stability of  $K^+$  ISEs enables a one-point calibration for standardizing the  $E_0$  value.

Faber et al. (2007) evaluated the performance of five commercially available colorimetric test kits with laboratory analysis for potassium ( $K_2O$ ) measurement in soil. They reported Rapitest, Quick Soiltest, La Motte and NittyGritty test kits provided similar accuracy, aligning with laboratory measurements 82% of the time.

## **4.6. Calcium measurement**

### **Measurement ranges**

The acceptable calcium concentration in saltwater aquariums is between 350 to 500 ppm  $Ca^{2+}$  (Borneman, 2008). This is 2-3 times higher than the calcium concentrations found in Hoagland solution and 4-5 times higher than those in Vegbloom solution. Although manufacturers of calcium aquarium test kits do not specify a lower measurement range, testing for calcium at these lower concentrations may be challenging. This is because, at very low concentrations, the titration endpoint color may appear before the titration process even begins. Among the test kits, API, Fluval, JBL, and Sera Aqua use a dropper to add the titrant solution, with each drop corresponding to 10 ppm  $Ca^{2+}$ . Red Sea, Salifert, and Seachem test kits use a syringe for titrant addition, where each 0.01 mL of titrant solution equals 5 ppm  $Ca^{2+}$  (the smallest measurable unit). The NT Sensors calcium ISE has a measurement range of 0.4 to 4000 ppm  $Ca^{2+}$ .

## Hoagland calcium measurement

The results for Hoagland's solution can be grouped into three categories based on the performance. The first group includes API and Sera Aqua, both showing minimal sensitivity offset compared to the control. With slopes close to 1 (0.995 for API and 0.999 for Sera Aqua), their regression lines are nearly perpendicular to the ideal control line. Sera Aqua stands out for its high precision, the best among all kits. While both kits slightly overestimate calcium concentrations, they excel at all concentration levels.

The second group consists of Fluval, JBL, and Red Sea which show similar behavior. These kits overestimate calcium concentrations at higher ranges but perform exceptionally well at lower concentrations. Red Sea and JBL had the very least zero offset among all tests. Red Sea and Fluval were the most accurate, with total measurement errors of  $\pm 18.3$  and  $\pm 18.9$ , respectively in the measurement range of 80 to 400 ppm  $\text{Ca}^{2+}$ .

The final group includes Seachem, Salifert, and NT sensors. Seachem performs well at mid and low concentrations (2:1 and 1:1 dilution factor  $\sim 200$  ppm  $\text{Ca}^{2+}$  and below) but underestimates calcium at higher ranges. Salifert exhibits the highest sensitivity offset, while NT sensors show a notable zero offset, resulting in lower accuracy and precision overall.

## Vegbloom calcium Measurement

Similar to the results for the Hoagland solution, the Red Sea test kit demonstrated the highest accuracy for the Vegbloom solution, with a total measurement error of  $\pm 12.94$  ppm  $\text{Ca}^{2+}$  in the 40 to 200 ppm  $\text{Ca}^{2+}$  range. It showed excellent performance at higher calcium concentrations, with errors remaining below 6%. Sera Aqua also performed well at higher concentrations, but its accuracy decreased at lower calcium levels, due to a significant sensitivity offset. Both of these tests overestimate calcium concentrations at lower levels.

JBL, Seachem, Fluval test kits and NT sensors had very close results to laboratory values at lower concentrations, but their accuracy declined as calcium concentrations increased. These kits exhibited a tendency to underestimate calcium concentrations in the solution (Slope below 1). Notably, Fluval, with the highest sensitivity offset and a total measurement error of  $\pm 61.25$  ppm  $\text{Ca}^{2+}$ , exhibited the most significant underestimation, almost 50%, at double Vegbloom



concentrations. Fluval's slope of 0.367 further indicates a significant underestimation, as it deviates far from the ideal value of one.

### **Overall Performance and Important Considerations**

The combined results from testing both the Hoagland and Vegbloom solutions highlight that the Red Sea test kit offers the most consistent performance, with the least sensitivity offset, highest accuracy (total measurement error of  $\pm 15.85$  ppm  $\text{Ca}^{2+}$ ), and good precision (measurement repeatability of  $\pm 9.86$  ppm) for calcium measurements in hydroponic solutions. This makes it the most reliable option for monitoring calcium concentrations in these solutions.

Additionally, it's crucial to consider that test kits produce discrete or stepped results based on the type of titrant dispenser used, which can limit the accuracy of measurements, especially in solutions with concentrations that fall between these steps. This discrete measurement approach can introduce a potential source of error or bias in precision.

Rius-Ruiz et al. (2014) in their 120 days calcium measurements of hydroponic solution using  $\text{Ca}^{2+}$  NT sensors ISE, reported high slope precision for this electrode. They pointed out that the response of the  $\text{Ca}^{2+}$  ISE can be considered stable enough to yield reliable results with single point calibration.

## **4.7. Magnesium measurement**

### **Measurement ranges**

The typical magnesium concentration in natural seawater is around 1,300 ppm. For optimal reef aquarium health, it is generally recommended to maintain magnesium levels between 1,200 and 1,400 ppm (Seachem Laboratories, accessed 2024/12). This is more than 30 times higher than the magnesium concentration in hydroponic solutions. While manufacturers of magnesium test kits for aquariums do not define a lower limit for measurements, testing magnesium at these lower levels can be difficult. At very low concentrations, the color change marking the endpoint of the titration may occur prematurely, before the start of titration process.

Among the test kits, Salifert, Red Sea and Seachem use a syringe to measure magnesium in one titration process where each 0.01 ml titrant solution equals to 15, 20 and 12.5 ppm  $\text{Mg}^{2+}$

respectively. Sera Aqua and JBL test kits use a different method consisting of two titration tests: one to measure the combined amount of magnesium and calcium, and another to measure the amount of calcium in the solution. The final magnesium concentration is determined by subtracting the calcium value from the combined result. These test kits provide discrete results, with JBL offering intervals of 20 ppm and Sera Aqua 60 ppm for magnesium.

### **Hoagland Magnesium measurement**

The Seachem test kit performed the best in measuring magnesium in Hoagland solution, achieving the lowest total measurement error of  $\pm 13.5$  ppm  $\text{Mg}^{2+}$  in the 20 to 120 ppm  $\text{Mg}^{2+}$  range, making it the most accurate. Salifert showed the least sensitivity offset and best precision, but it was not able to measure magnesium concentrations in Hoagland and half Hoagland solution, causing a high zero offset and resulting in underestimation of all measurements. JBL and Red Sea offer closer values to laboratory measurements at lower concentrations (1:2 dilution factor  $\sim$  20 to 30 ppm  $\text{Mg}^{2+}$ ) but drift apart at higher magnesium concentrations. Sera Aqua had a poor correlation with laboratory measurements ( $R^2 = 0.2$ ), while Red Sea had the lowest overall accuracy and precision.

### **Vegbloom Magnesium measurement**

In contrast to its performance with the Hoagland solution, the Red Sea test kit was the top performer for magnesium measurement in Vegbloom, particularly at higher concentrations (double Vegbloom  $\sim$  60 ppm  $\text{Mg}^{2+}$ ). It excelled in minimizing zero and sensitivity offsets, with the lowest total measurement error ( $\pm 6.15$  ppm  $\text{Mg}^{2+}$ ) and the best  $R^2$  value. Seachem followed as the second most accurate test kit, with a total measurement error of  $\pm 8.6$  ppm  $\text{Mg}^{2+}$ . Data from the Salifert and Sera Aqua test kits were not obtainable at lower concentrations due to premature endpoint color development. However, Sera Aqua performed well at higher concentrations (2:1 dilution factor  $\sim$  60 ppm  $\text{Mg}^{2+}$ ), with a percent error below 5%. The JBL test kit was accurate at mid and low concentrations (1:1 and 1:2 dilution factors  $\sim$  below 40 ppm  $\text{Mg}^{2+}$ ) but showed high inaccuracy while measuring magnesium in double Vegbloom solution, which caused highest sensitivity offset and poor  $R^2$  values.

## **Overall performance and important considerations**

Based on the results from both solutions, the Seachem test kit was the most accurate, with a total measurement error of  $\pm 11.3$  ppm  $\text{Mg}^{2+}$ , the least zero offset, and low sensitivity offset. The Red Sea test kit showed significant variability between Hoagland and Vegbloom solutions, likely due to ion interference. While Sera Aqua and Salifert test kits exhibited poor measurement sensitivity at lower magnesium levels, they performed well at higher concentrations. The discrete results provided by these kits, especially those with two step titrations (Sera Aqua and JBL), can cause significant errors, highlighting the need for more sensitive magnesium tests with smaller steps to better cover lower magnesium concentrations in hydroponic solutions.

## **4.8.Copper measurement**

### **Measurement ranges**

The copper test kits used in this study have upper measurement ranges varying from 0.8 to 4 ppm. Among the brands tested, API offers the widest measurement range, spanning from 0 to 4 ppm, while other kits like Seachem and JBL have narrower ranges, with Seachem measuring up to 0.8 ppm and JBL up to 1.6 ppm.

### **Hoagland copper measurement**

API test kit achieved the closest results to the laboratory measurements by achieving the least sensitivity offset, best accuracy ( $\pm 0.06$  ppm Cu(I&II) total measurement error) and best precision ( $\pm 0.03$  ppm Cu(I&II) measurement repeatability) in range of 0.01 to 0.05 ppm Cu(I&II). JBL followed closely, demonstrating strong performance in terms of zero and sensitivity offset, accuracy, and precision. In contrast, Salifert, Seachem, and Sera Aqua exhibited high sensitivity offset, significantly overestimating results at higher concentrations, producing unreliable data at lower concentrations, and displaying poor precision.

### **Vegbloom copper measurement**

Both JBL and Sera Aqua test kits exhibited similar behavior when measuring copper in the Vegbloom solution, significantly underestimating the copper concentrations while maintaining

relatively high accuracy and precision. JBL demonstrated slightly better performance, with a total measurement error of  $\pm 0.03$  ppm Cu(I&II) and precision of  $\pm 0.005$  in the copper range of 0.02 to 0.08 ppm copper. In contrast, API and Salifert test kits both significantly overestimated copper readings at all concentrations. Seachem, was the most inaccurate, with nearly a 1000% error at double the Vegbloom copper concentration.

### **Overall performance and important considerations**

The JBL test kit demonstrated the highest accuracy overall, with  $\pm 0.048$  ppm Cu (I&II) total measurement error in range of 0.01 to 0.08 ppm Cu(I&II). This error relative to the copper concentration in the solution is misleading and might lead to improper adjustments to the nutrient solution. Other test kit provided unreliable data for one or both solutions.

There was barely any visible color change while conducting the copper test kits, making Cu QTKs very challenging to interpret the results with unarmored eye. Copper test kits can act as an indicator for detecting the presence of copper in hydroponic solution, but they do not offer sufficient sensitivity for measurement and adjustment of copper in the hydroponic solution.

Lin et al. (2013) designed and synthesized Cu ion colorimetric chemosensors and tested on DMSO/H<sub>2</sub>O solutions. They reported high selectivity and sensitivity of one of the sensors without being interfered with other metal ions. Xiong et al. (2016) tested a new compound (4-aminoantipyrine derivative) to detect copper ions (I&II) in water. Their results show this test are highly selective and cover a proper range for environmental and biomedical applications.

## **4.9.Iron measurement**

### **Measurement ranges**

Iron plays a crucial role in planted aquaria, where it should be in range of 0.1 to 0.2 ppm (Seachem Laboratories, accessed 2024/12). Seachem, JBL, Fluval, Sera Aqua and Red Sea have the highest to lowest upper measurement range of 2, 1.5, 1, 1 and 0.5 ppm Fe<sup>+2</sup>/Fe<sup>3+</sup>, respectively.

### **Hoagland iron measurement**

During the iron measurements of Hoagland solution, four test kits—Fluval, JBL, Red Sea, and Sera Aqua— demonstrated a similar behavior, all of these tests tend to overestimate iron concentrations, with greater error at higher concentrations. Among these, the Fluval test kit excelled in terms of sensitivity offset and accuracy, with a total measurement error of  $\pm 0.06$  ppm  $\text{Fe}^{+2}/\text{Fe}^{3+}$  in the 0 to 0.5 ppm  $\text{Fe}^{+2}/\text{Fe}^{3+}$  range. JBL had the highest measurement repeatability, while Sera Aqua demonstrated the second-best performance in both precision and accuracy, along with minimal zero offset. Seachem test kit consistently underestimated iron concentrations and had noticeably higher error compared to the others.

### **Vegbloom iron measurement**

The same trend was observed with the Vegbloom solution among four test kits of Fluval, JBL, Red Sea, and Sera Aqua, with a tendency to overestimate iron readings in Vegbloom solution. Red Sea and Fluval showed improved performance at higher concentrations (2:1 dilution factor  $\sim 0.4$  to 0.5 ppm  $\text{Fe}^{+2}/\text{Fe}^{3+}$ ). As with the Hoagland solution, Fluval provided the highest accuracy and least sensitivity offset. JBL was the most precise, with a measurement repeatability of  $\pm 0.01$  ppm  $\text{Fe}^{+2}/\text{Fe}^{3+}$ , while Sera Aqua demonstrated the second-best accuracy and precision with minimal zero offset. The Seachem test kit, however, had the poorest accuracy and consistently underestimated iron concentrations.

### **Overall performance and important considerations**

Overall, Fluval and Sera Aqua demonstrated the highest accuracy for measuring iron in hydroponic solutions, with total measurement errors of  $\pm 0.05$  and  $\pm 0.06$  ppm  $\text{Fe}^{+2}/\text{Fe}^{3+}$ , respectively, in the 0 to 0.5 ppm  $\text{Fe}^{+2}/\text{Fe}^{3+}$  range. JBL and Sera Aqua excelled in precision, with measurement repeatability of  $\pm 0.016$  and  $\pm 0.021$  ppm  $\text{Fe}^{+2}/\text{Fe}^{3+}$ , respectively. Seachem test kit had a poor performance and was not reliable for iron measurement in hydroponic solution.

## **4.10. pH measurement**

### **Measurement ranges**

Different types of aquariums require different pH ranges. Recommended pH for freshwater aquariums are around 7, for garden ponds between 7.5 to 8.5 and for marine aquariums between 7.8 to 8.5 (JBL, Accessed 2024/12). Recommended pH range in Hydroponic is 5.5 to 6.5 (Singh et al., 2019) which is higher than aquariums levels. In this study, API and Fluval with measurement range of 6-7.5, JBL with measurement range of 3 -10 and Sera Aqua with measurement range of 6.5 to 9 and NT sensors pH electrode with measurement range of 0 to 14, were tested and compared with hydroponic solution with pH levels of 6 to 7.5.

### **Hoagland pH measurement**

The NT Sensors pH electrode was the most accurate method for measuring pH in the Hoagland solution, with a total measurement error of  $\pm 0.145$ . Among the test kits, API and Fluval demonstrated high precision with minimal zero and sensitivity offsets, although they tended to overestimate pH levels by 2.5 to 6.5%. JBL and Sera Aqua exhibited higher sensitivity offsets, consistently overestimating pH values. They provided more accurate results at lower pH levels (6–6.5) but became less reliable at higher pH values.

### **Vegbloom pH measurement**

The NT Sensors pH electrode was the top performer for Vegbloom solution, with a low measurement error of  $\pm 0.09$  and high precision (measurement repeatability of  $\pm 0.04$ ). It exhibited minimal zero and sensitivity offsets (percent error  $< 2\%$ ). All test kits overestimated pH readings. Similar to Hoagland solution results, JBL and Sera Aqua performed better at lower pH levels (6–6.5), but their error increased at higher pH. API and Fluval maintained stable sensitivity and good precision but overestimated all readings due to higher zero offset.

### **Overall performance and important considerations**

The combined results of both solutions indicated that pH electrode offers the maximum accuracy, and high precision while offering a much wider measurement range for both solutions. Aquarium test kits over estimated pH readings in both solutions at all times with a noticeable higher absolute error.

Chioma et al. (2015) compared pH meters and pH water test kit on samples from tap water, stream and air conditioner. The study found that the pH meter consistently measures lower pH values compared to the pH kit, with both methods showing acceptable variability. However, there was a statistically significant difference between their readings. Naigaga et al. (2017) compared the reliability of three different pH test kits for aquaculture, reported that the API test strips were considered the most reliable for pH measurements among the evaluated kits. Tetra EasyStrips demonstrated moderate agreement and Seneye slide had only fair agreement with the standard laboratory method.

#### **4.11. Limitation and future work**

This study was conducted in experimental conditions, controlled in a laboratory setting and may not fully reflect real-world hydroponic environment. The effectiveness of dyes and titrants used in aquarium test kits may be impacted by the presence of proteins, amino acids, and other chelating substances (Seachem, accessed 2024/12). Consequently, it is essential to validate these results in an ongoing hydroponic production system. One limitation of this study was the relatively small sample size, which may restrict the generalizability of the findings. To strengthen the validity and applicability of the results, future research should aim to replicate this study with a larger sample size and a broader range of hydroponic solutions, including both organic and inorganic types.

Some of the measurement methods demonstrated varying performance depending on the solution being tested. For example, calcium NT Sensors ISE performed significantly better with the Vegbloom solution, exhibiting higher precision and lower zero offset. Another example is Fluval calcium test kit with excellent performance with the Hoagland solution but performed poorly with Vegbloom. This variation in performance could be due to several factors such as the interference of other ions, the pale pink color of the Vegbloom solution which may complicate the titration or colorimetric process, and issues such as turbidity and precipitation in the sample or after conducting the test that impact spectrophotometer readings.

In order to choose a measurement method, it is crucial to consider other factors such as measurement frequency, price per measurement, equipment in hand, safety, and service life. The

accuracy of ISEs can be compromised by signal drift and decreased sensitivity over time (Han et al., 2020). Biofilm accumulation, interference of other ions are some other problems that can affect the results of ISEs. moreover, Temperature, mobility state in a hydroponic solution, pH, and nutrient mixing time can all have an impact on the accuracy and precision of ISEs (Chowdhury et al., 2019).

Some QTKs offer a very limited shelf life. Using QTKs requires access to dH<sub>2</sub>O water for dilution and cleaning the sample vials; failure to do so could lead to contamination of future samples. Limited range of QTKs for some ions, especially for nitrate and phosphate, requires serial dilution to bring the sample within the test kit's measurable range. Determining the appropriate dilution factors for unknown solutions can be challenging, often requiring multiple trial-and-error measurements with different dilution factors to obtain a valid reading.

Most of the test kits enclose two different color charts for fresh and marine water. Factors such as salinity, pH, temperature, and buffer strength of the water samples can affect the dye response when using QTKs (Seachem, accessed 2024/12). The color changes observed in the samples during this study did not always align with either of the color charts for fresh or marine water. If the tests kits are being used by visual color matching only, it is important to have a color chart specifically corresponding to the color changes in hydroponic solutions. It is challenging to compare all shades of color with an untrained eye. Interpretation of the final color of colorimetric tests can be influenced by various factors such as: lighting conditions, the shape and material of the sample container, the background used for comparison, the observer's color perception, and the viewing angle. To reduce potential biases from these variables and improve precision, a spectrophotometer was used to numerically quantify test outcomes. However, it is important to note that spectrophotometers have upper limits for light absorption readings. Absorption measurements above three optical units (AU) were excluded, as they do not yield reliable results. Generally, quantifying results from the test kits requires a spectrophotometer, colorimeter, or reflectometer, which can be costly for small-scale hydroponic users or hobbyists.



## 5. Conclusion

This study investigated the reliability of water test kits and ion-selective electrodes for use in hydroponic systems for pH and nine ions of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^+$ , and  $\text{Fe}^{2+}$ .

The result for nitrate ions shows that among QTKs the Red Sea kit emerged as the most reliable for both solutions, however this test kit offers a very narrow measurement range of 0 to 50 ppm  $\text{NO}_3^-$  and requires 20 times dilution for full strength Hoagland solution and 7 times dilution for Vegbloom solution. JBL and Salifert QTKs performed well at high ( $\sim 170$  ppm  $\text{NO}_3^-$ ) and mid-range ( $\sim 70$  ppm  $\text{NO}_3^-$ ) nitrate concentrations of Hoagland, respectively, while Fluval displayed poor performance with Hoagland but improved with Vegbloom.  $\text{NO}_3^-$  ISE offers a much wider range of measurements, but significantly over estimated nitrate concentrations specifically with Vegbloom solution.

Nitrite analysis on hydroponic solutions indicates that Sera Aqua test kit performed best overall, demonstrating the highest accuracy and minimal offset. Fluval test kit offered excellent results with Hoagland but poor results with Vegbloom. Results highlighted that performance varied by kit, concentration, and solution type, with Sera Aqua being the most reliable choice. Nitrite QTKs become of importance in systems with high pH and ammonia especially since laboratory analysis usually do not analysis nitrite in water samples.

For ammonium measurements, The Fluval test kit demonstrated superior accuracy and reliability for Hoagland, while NT sensors and other kits exhibited inconsistencies. For Vegbloom solution, API test kit had the closest result to the laboratory measurement with a tendency to underestimate the results.  $\text{NH}_4^+$  ISE demonstrated a very poor performance for Hoagland solution but was the second-best measurement method for Vegbloom solution.  $\text{NH}_4^+$  ISE overestimated the results for both solutions.

For phosphate measurements, API and Sera Aqua demonstrated the best overall accuracy for both hydroponic solutions. API offers a wider measurement range of 0 to 10 ppm  $\text{PO}_4^{3-}$  compared to those for Sera Aqua 0 to 2 ppm  $\text{PO}_4^{3-}$ . Measurement of phosphate within the hydroponic solution using aquarium test kit will require serial dilution and among the test kits compared in this study, API and Fluval offer the widest measurement range. Seachem test kit had noticeably higher error

for both solutions compared to other test kits possibly due to difficulty at finding the proper wavelength for calibration.

For potassium measurements, the NT Sensors potassium ISE demonstrated the best overall performance, with minimal offset, high precision and accuracy across a broad range of measurements. The Red Sea kit excelled in reliability and consistency for Hoagland, while the Salifert kit showed superior accuracy for Vegbloom. JBL provided precise measurements at low concentrations but suffered from high errors and sensitivity offset. Red Sea and Salifert kits were less practical for lower concentrations due to their high titrant usage, while the NT sensor and JBL were more suited for diverse concentration ranges.

The calcium test kits evaluated showed varying performance across Hoagland and Vegbloom solutions, with the Red Sea kit emerging as the most reliable for both. Fluval for Hoagland and JBL for Vegbloom were second best performers. The comparison of performance between those two solutions shows that calcium test kits had a better performance with Hoagland solution, with higher margins of error for Vegbloom. The discrete measurement method in titration QTKs introduced potential errors. While the calcium ISE proved reliable, its accuracy and precision were inferior to those of most quick test kits QTKs.

The Seachem test kit demonstrated the highest overall accuracy for magnesium measurements in both Hoagland and Vegbloom solutions, followed closely by Red Sea kit which performed exceptionally for Vegbloom magnesium, particularly at higher concentrations. The results obtained highlight challenges in testing low magnesium concentrations, especially due to low measurement sensitivity of Sera Aqua and Salifert test kits, as well as test kits with two-step titration methods. Test kits with discrete measurements and wide intervals, such as Sera Aqua, lack the precision needed for fine magnesium adjustments in hydroponic solutions.

The JBL Cu QTK demonstrated the best overall performance across both solutions. The API test kit performed well for the Hoagland solution in terms of accuracy and precision, while the Sera Aqua test kit showed good accuracy for the Vegbloom solution. However, other test kits failed at providing reliable data. Without the use of a spectrophotometer, the minimal visible color changes associated with copper concentrations in hydroponic solutions make these kits more suitable for detecting the presence of copper rather than providing precise measurements and enabling accurate adjustments.

For measuring iron concentrations, the Fluval and Sera Aqua test kits demonstrated the highest overall accuracy, despite overestimating iron measurements, which all QTKs except for Seachem tend to accomplish. However, the latter suffered a poor performance by underestimating the iron concentration in both Vegbloom and Hoagland solutions by a large margin and therefore was not reliable for iron measurement in hydroponic solutions.

For pH, the NT Sensors pH electrode outperformed all test kits, with noticeably higher accuracy and precision at a wide measurement range (0 to 14). Aquarium test kits consistently overestimated pH levels, with errors increasing at higher pH values. Among test kits, API and Fluval demonstrated better precision and accuracy overall, while JBL and Sera Aqua were more reliable at lower pH levels (6–6.5).

When selecting a measurement method, it is important to consider other factors such as measurement frequency, cost, available equipment, safety, and service life. ISEs face challenges like signal drift and reduced sensitivity over time, biofilm accumulation in long term, interference with other ions, and being affected by environmental conditions such as temperature, pH, nutrient mixing time, and mobility in hydroponic solutions. ISEs offer a wide range of measurements, are fast and easy to use and allow for automation.

Aquarium test kits present issues, including limited shelf life, dependence on dH<sub>2</sub>O for dilution and cleaning, and narrow measurement ranges for certain ions like nitrate and phosphate. Additionally, discrepancies in color charts for fresh and marine water complicate visual interpretation in hydroponic solutions, with color perception influenced by lighting, container material, background, and observer bias. Quantifying results from the test kits requires a spectrophotometer, colorimeter, or reflectometer, which can be costly for small-scale hydroponic users or hobbyists.

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## 7. Appendix

### 7.1. Nitrate ( $\text{NO}_3^-$ ) Tests

#### Calibration

Table A 1. Linear regression parameters and  $R^2$  values of calibration for  $\text{NO}_3^-$  test kits.

	Identified wavelength	$R^2$	Slope	Intercept
<b>Standard solution</b>				
API	544	0.989	0.023	0.119
Fluval	544	0.994	0.004	0.033
JBL	450	0.979	0.016	-0.065
Red Sea	534	0.998	0.032	0.051
Salifert	534	0.915	0.010	0.105
Seachem	552	0.974	0.063	0.157
Sera Aqua	548	0.902	0.011	-0.037

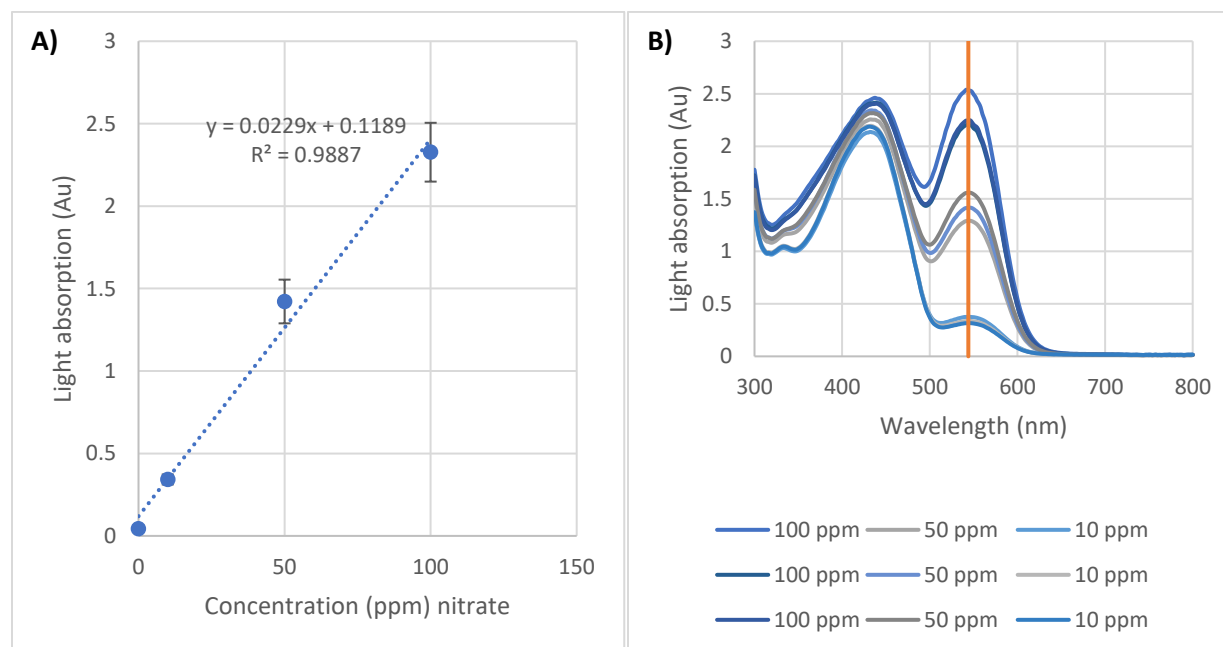


Figure A 1. Light absorption graph (A) and calibration curve (B) of nitrate API test kit



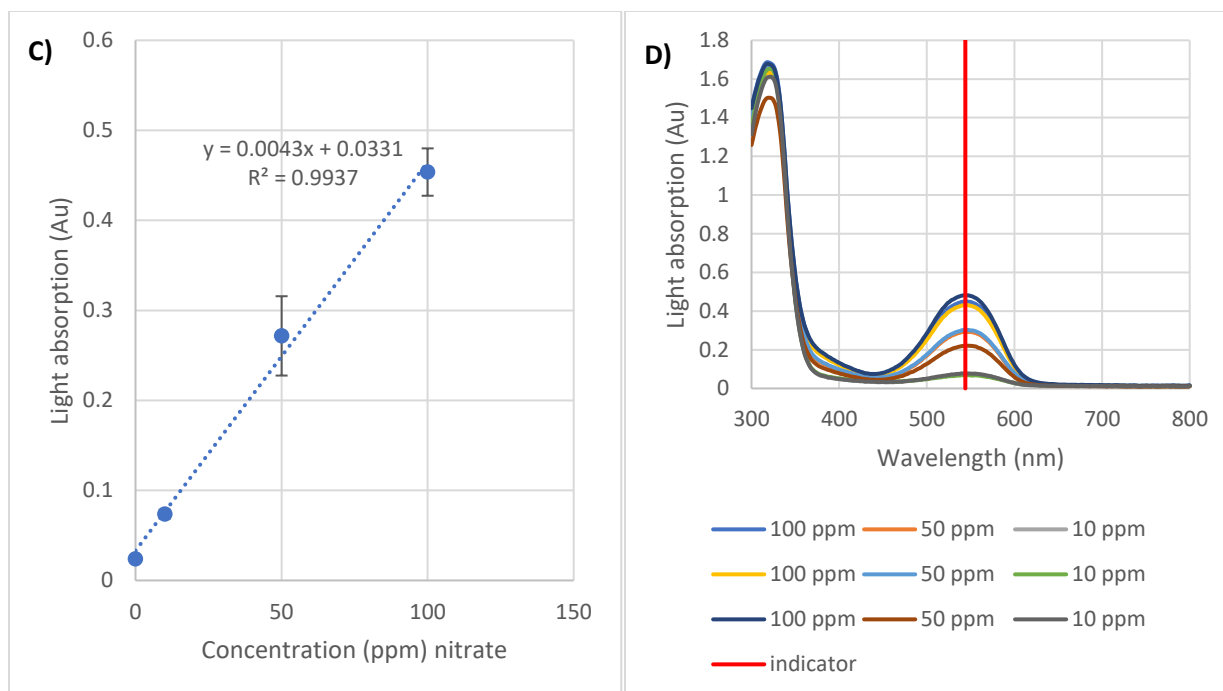


Figure A 2. Light absorption graph (C) and calibration curve (D) of nitrate Fluval test kit

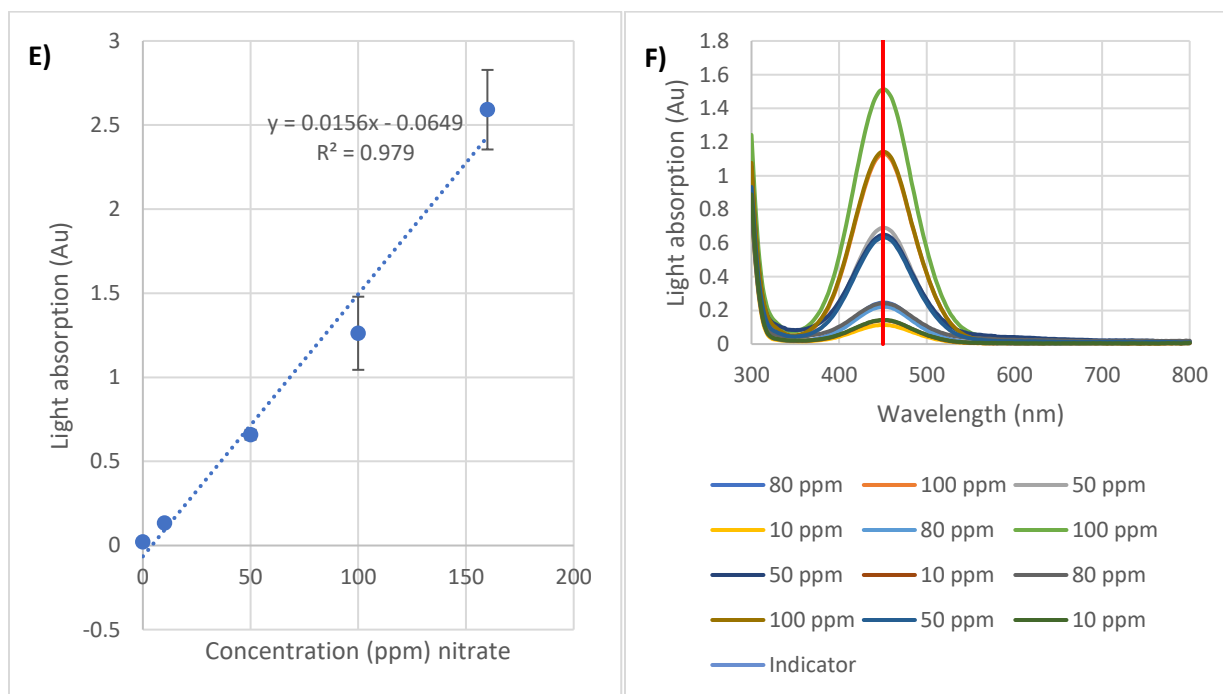


Figure A 3. Light absorption graph (E) and calibration curve (F) of nitrate JBL test kit

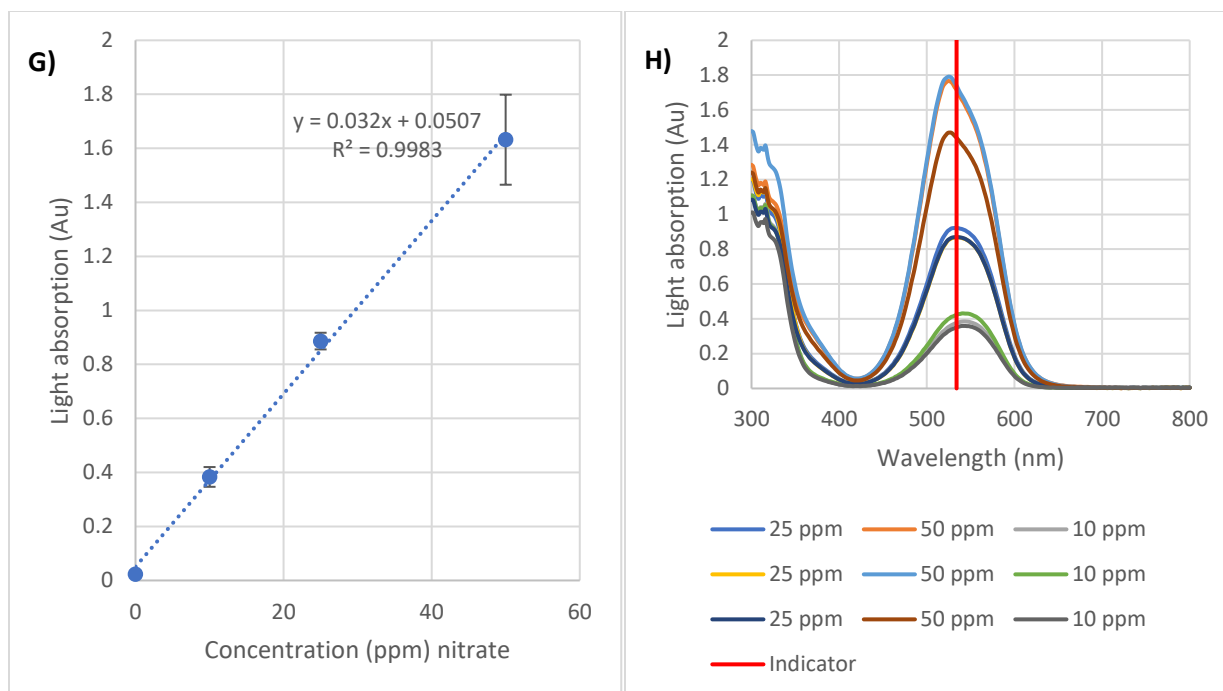


Figure A 4. Light absorption graph (G) and calibration curve (H) of nitrate Red Sea test

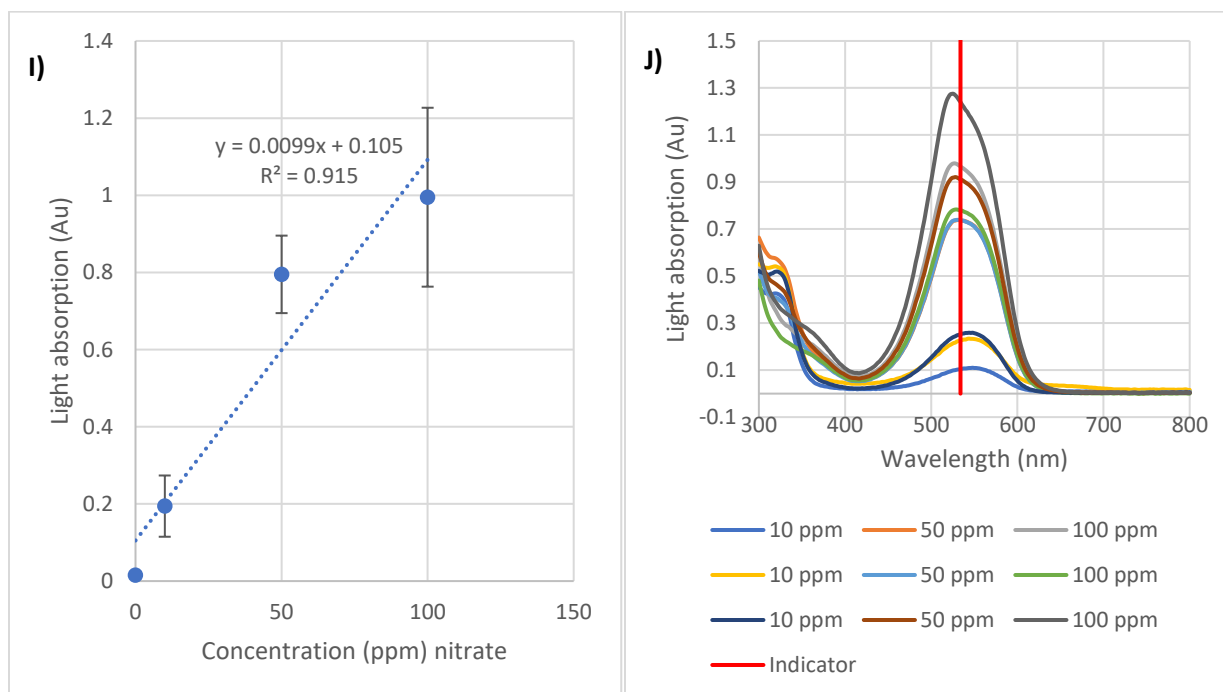


Figure A 5. Light absorption graph (I) and calibration curve (J) of nitrate Salifert test kit

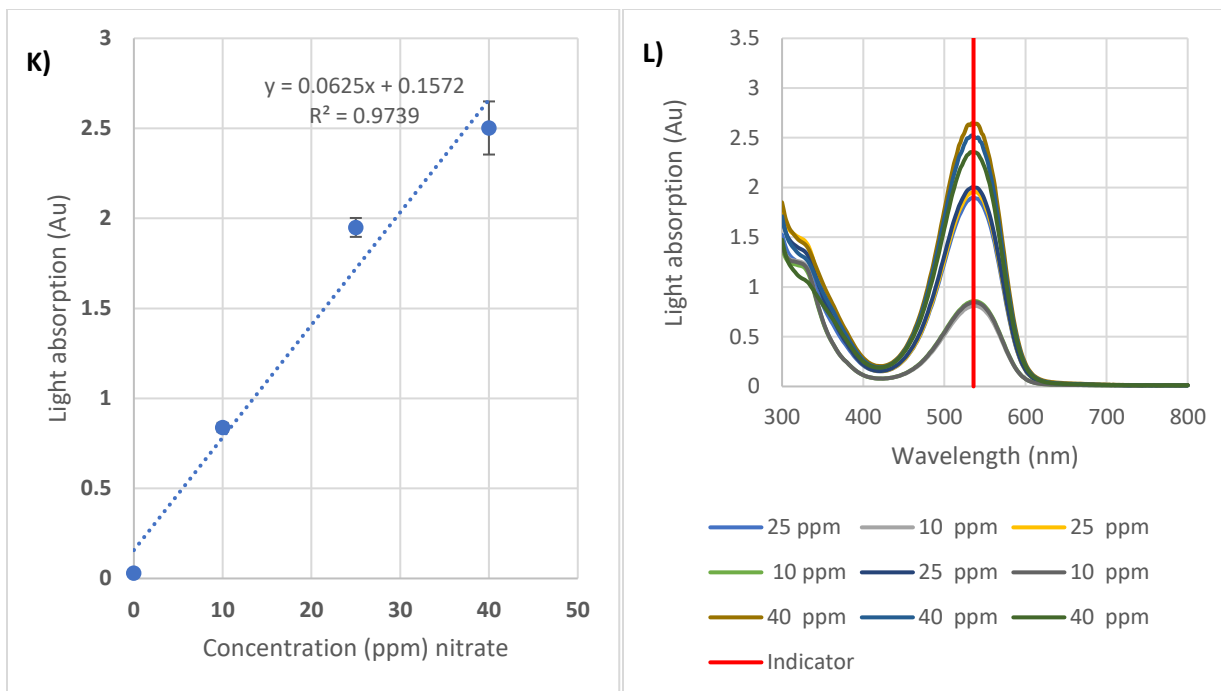


Figure A 6. Light absorption graph (K) and calibration curve (L) of nitrate Seachem test kit

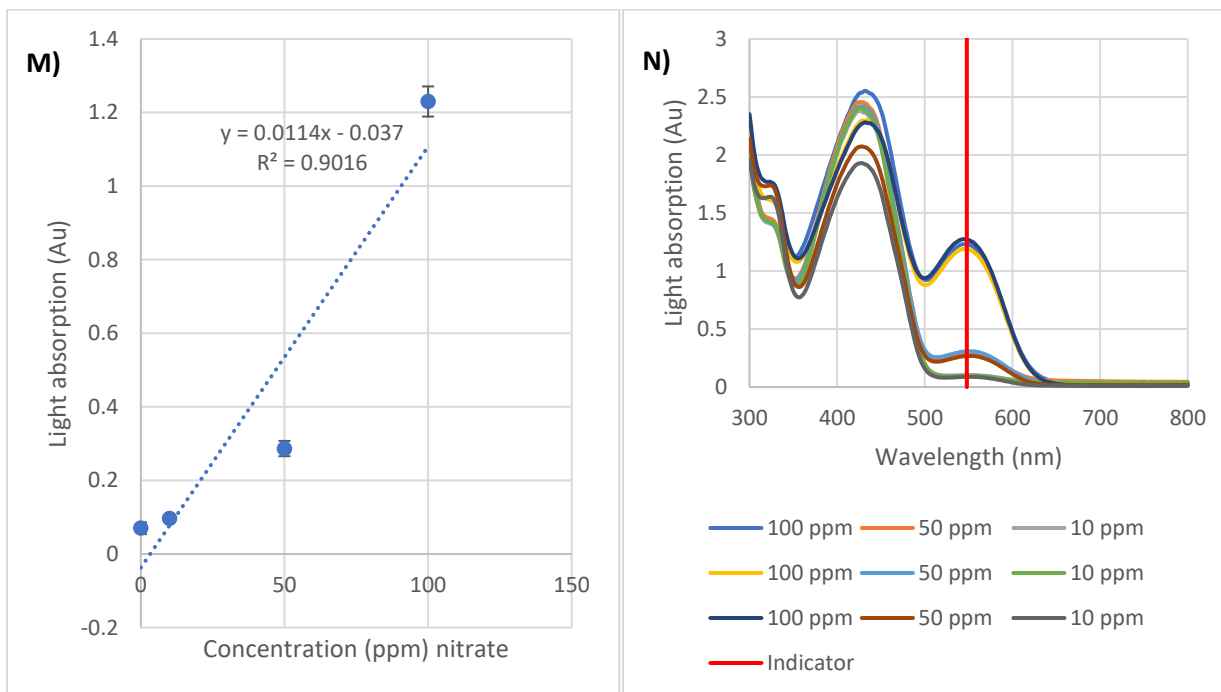


Figure A 7. Light absorption graph (M) and calibration curve (N) of nitrate Sera Aqua test kit

Table A 2. Results of aquarium test kits and ISE for **nitrate** measurements of **Hoagland** solution at different concentrations followed by the percent error. Darker color indicates higher error. N.A. = Not analyzed. ALD = Above limit of detection.

Target value (ppm)	Dilution factor	Laboratory results	API		Fluval		JBL		Red Sea		Salifert		Seachem		Sera aqua		NT sensors	
			Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
930	1:1	863.2	ALD		34.2*	96.0	ALD		ALD		ALD		ALD		ALD		1043	20.8
	1:1	845.5	ALD		37.2*	95.6	ALD		ALD		ALD		ALD		ALD		1142	35.1
	1:1	858.8	ALD		37.4*	95.6	ALD		ALD		ALD		ALD		ALD		1137	32.4
186	1:5	172.6	97.1*	43.8	32.8*	81.0	183.8	6.4	ALD		163.7*	5.2	ALD		ALD		204	18.2
	1:5	169.1	72.7*	57.0	26.0*	84.6	180.8	6.9	ALD		144.8*	14.3	ALD		ALD		188	11.2
	1:5	171.8	89.3*	48.0	31.4*	81.7	189.8	10.5	ALD		108.4*	36.9	ALD		ALD		209	21.7
116	1:8	107.9	78.1	27.6	31.4	70.9	130.1	20.5	ALD		132.8*	23.1	ALD		124*	15.0	140	29.7
	1:8	105.7	70.1	33.7	24.4	76.9	114.9	8.7	ALD		90.0*	14.8	ALD		79.7*	24.6	132	24.9
	1:8	107.3	74.1	31.0	20.9	80.5	120.8	12.5	ALD		82.2*	23.4	ALD		74.1*	31.0	121	12.7
46.5	1:20	40.7	34.5	15.3	19.5	52.1	64.3	57.9	36.1	11.3	96.2	136.1	35.0	14.1	30.2	25.9	63	54.7
	1:20	40.9	38.6	5.8	15.3	62.6	59.7	45.7	37.4	8.6	69.4	69.5	33.6	17.9	26.1	36.4	54	31.9
	1:20	39.4	44.0	11.6	17.0	57.0	122.2	210.1	35.8	9.2	23.9	39.2	31.7	19.6	21.5	45.5	57	44.7
18.6	1:50	17.3	13.7	20.6	6.7	61.1	28.0	62.2	16.6	3.8	28.8	66.7	18.7	8.3	21.1	22.4	26	50.6
	1:50	16.9	14.3	15.3	19.0	12.6	27.9	64.9	17.3	2.1	23.0	36.2	18.3	8.0	14.1	16.5	26	53.8
	1:50	17.2	17.2	0.1	6.7	60.9	21.5	25.4	14.9	13.0	5.5	68.2	17.0	1.3	15.5	9.6	31	80.5
9.3	1:100	8.6	N.A.		N.A.		N.A.		8.9	2.6	N.A.		8.9	3.4	N.A.		N.A.	
	1:100	8.5	N.A.		N.A.		N.A.		9.0	6.6	N.A.		9.0	6.9	N.A.		N.A.	
	1:100	8.6	N.A.		N.A.		N.A.		7.1	16.9	N.A.		8.7	1.5	N.A.		N.A.	

\* This measurement is outside of the measurement range of the test kit.

Table A 3.. Results of aquarium test kits and ISE for **nitrate** measurements of **Vegbloom** solution at different concentrations followed by the percent error. Darker color indicates higher error. N.A. = Not analyzed. ALD = Above limit of detection.

Target value (ppm)	Dilution factor	Laboratory results	API		Fluval		JBL		Red Sea		Salifert		Seachem		Sera Aqua		NT sensors	
			Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
158.6	1:2	172.9	ALD		125.3*	27.5	100.4	41.9	ALD		141.3*	18.3	ALD		ALD		470	171.9
	1:2	170.7	ALD		137.9*	19.2	144.4	15.4	ALD		109.2*	36.0	ALD		ALD		519	204.1
	1:2	167.1	ALD		135.3*	19.0	125.4	24.9	ALD		203.4*	21.7	ALD		ALD		405	142.4
79.3	1:4	86.4	48.9	43.4	93.9	8.7	63.3	26.8	ALD		123.5	42.9	ALD		46.5	46.2	140	62.0
	1:4	85.3	45.8	46.4	90.0	5.4	53.8	37.0	ALD		172.7	102.4	ALD		61.8	27.5	136	59.4
	1:4	83.6	46.2	44.6	98.1	17.4	64.0	23.4	ALD		185.2	121.6	ALD		41.4	50.4	201	140.6
45.3	1:7	49.4	32.3	34.7	66.7	35.1	39.3	20.5	53.7	8.7	114.2	131.3	44.4	10.1	29.5	40.3	147	197.6
	1:7	48.8	31.2	36.0	67.7	38.7	44.9	8.0	53.5	9.8	116.4	138.7	43.3	11.2	26.7	45.3	132	170.7
	1:7	47.7	32.0	33.0	70.9	48.5	46.3	3.1	54.9	15.0	141.9	197.2	44.4	7.0	24.1	49.5	132	176.5
15.9	1:20	17.3	15.7	9.0	27.0	55.9	14.0	19.2	19.6	13.2	23.5	36.1	44.7	158.8	18.6	7.6	62	258.7
	1:20	17.1	17.0	0.2	27.9	63.4	14.1	17.4	20.0	17.4	25.1	46.8	45.1	164.1	20.8	21.8	38	122.7
	1:20	16.7	16.6	0.4	27.4	64.1	14.5	13.0	18.9	13.0	32.4	94.0	44.8	168.4	17.9	7.1	80	378.7
7.9	1:40	8.6	N.A.		N.A.		N.A.		6.0	30.1	N.A.		13.0	50.5	N.A.		61	605.7
	1:40	8.5	N.A.		N.A.		N.A.		6.5	24.1	N.A.		12.9	50.7	N.A.		61	614.9
	1:40	8.4	N.A.		N.A.		N.A.		5.8	30.3	N.A.		9.6	15.0	N.A.		40	378.7

\* This measurement is outside of the measurement range of the test kit.

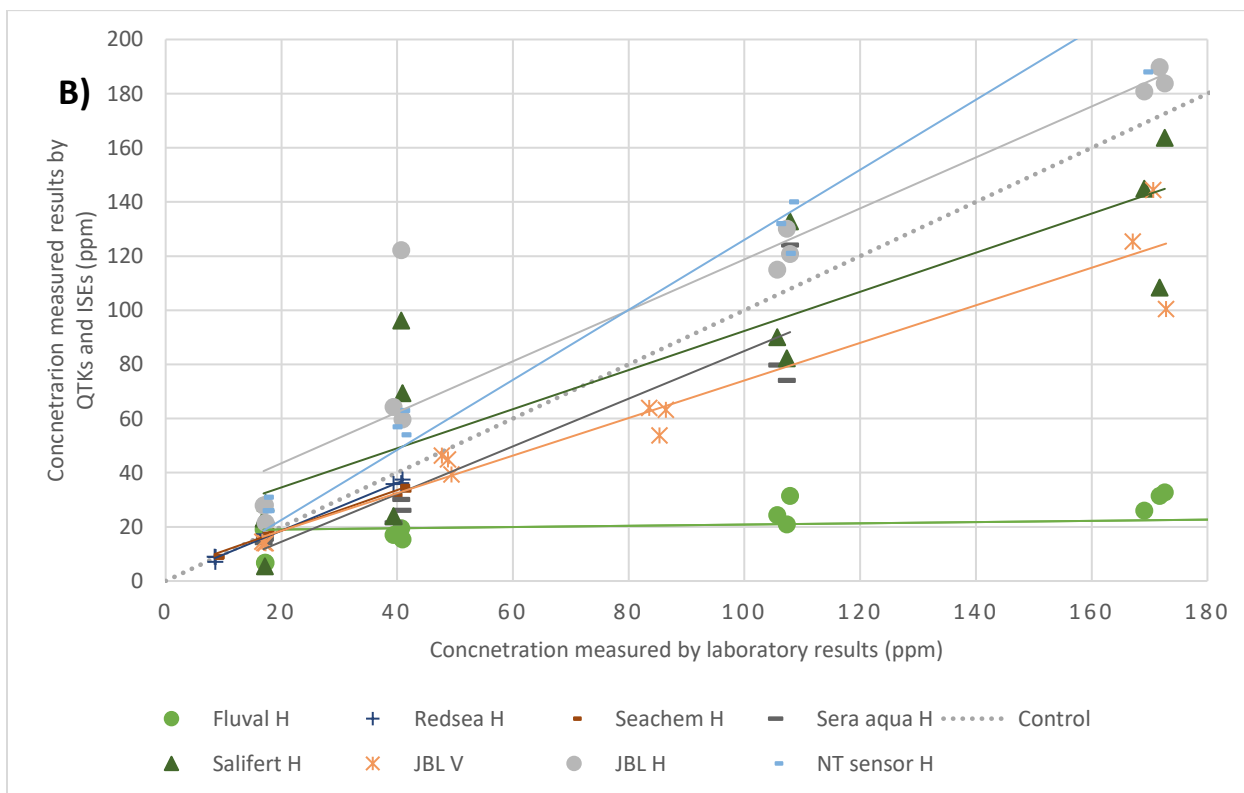
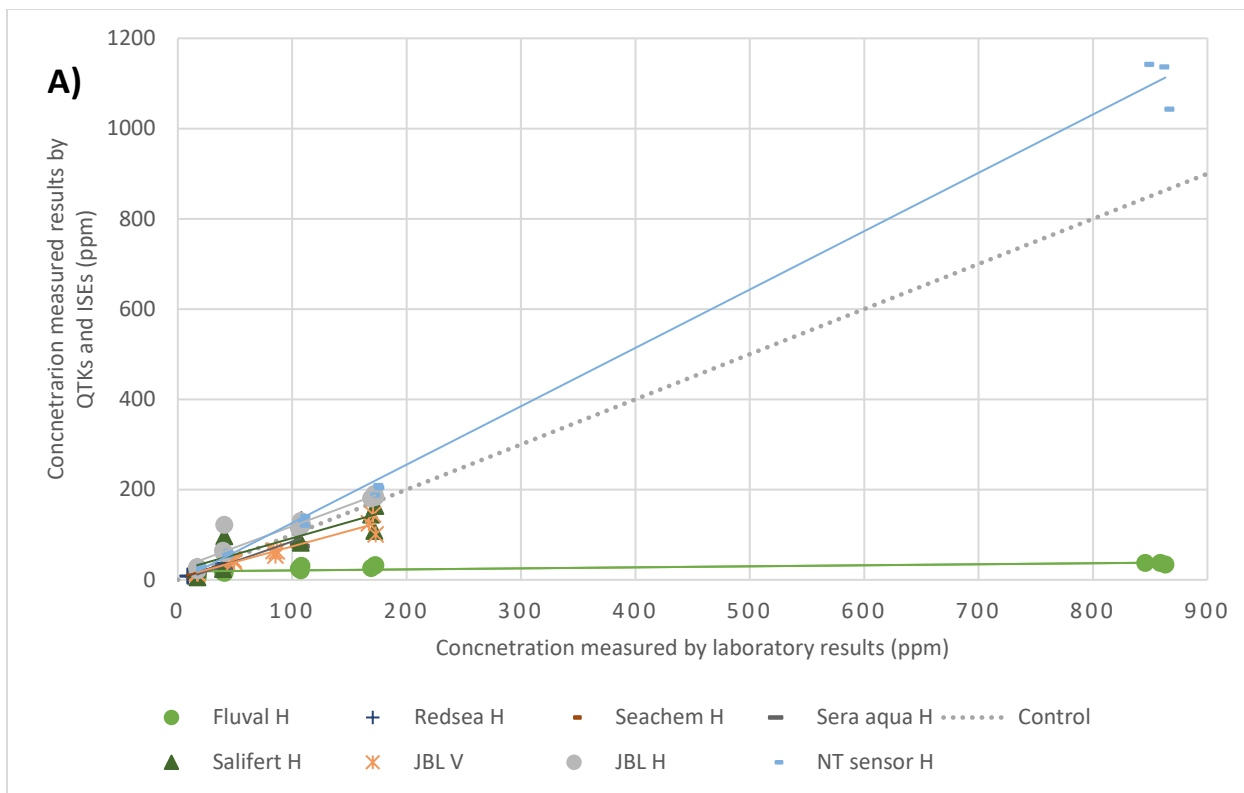


Figure A 8. Regression fits between laboratory analysis and the results of the **nitrate** test kits and ISE for **Hoagland** solution. Figure B is a closed-up version of Figure A.

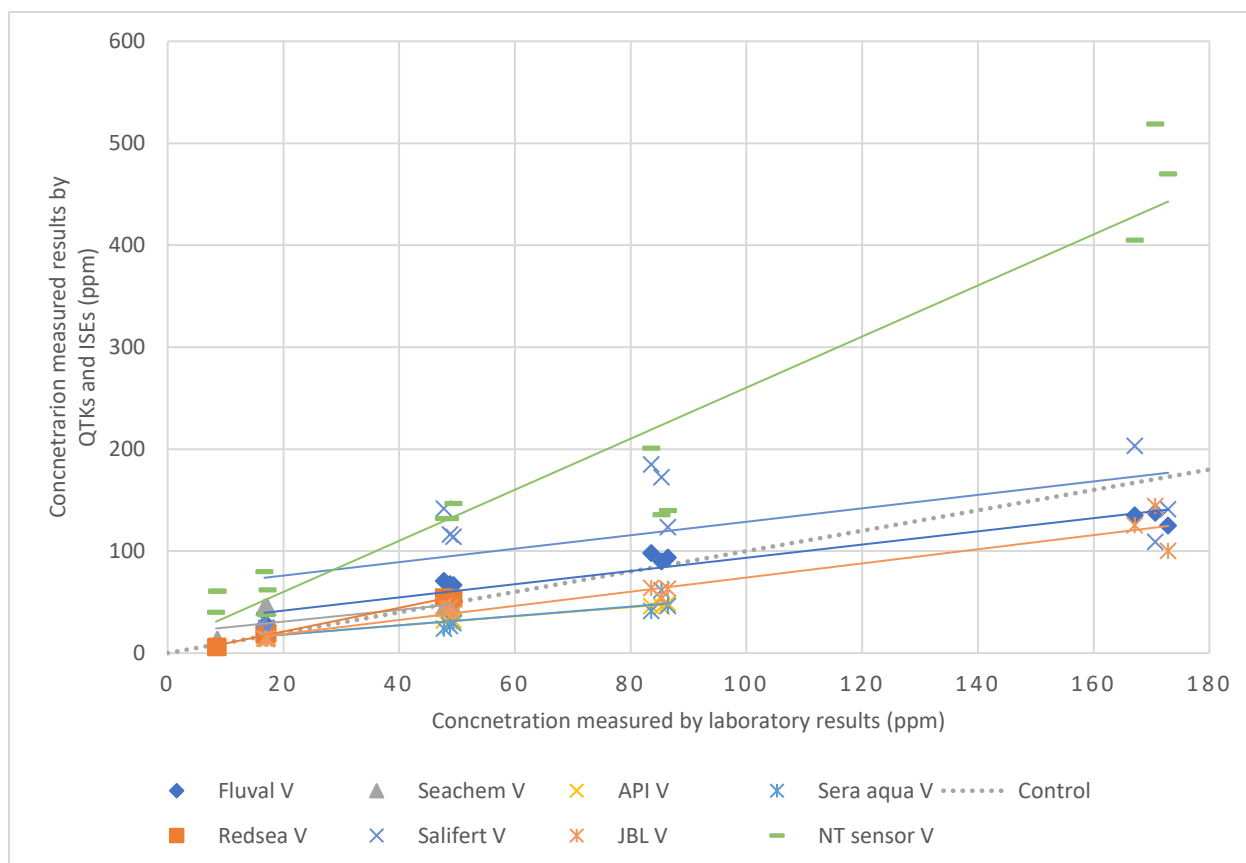


Figure A 9. Regression fits between laboratory analysis and the results of the **nitrate** test kits and ISE for **Vegbloom** solution.

## 7.2. Nitrite (NO<sub>2</sub><sup>-</sup>) Tests

### Calibration

Table A 4. Linear regression parameters and R<sup>2</sup> values of calibration for NO<sub>2</sub><sup>-</sup> test kits.

	Identified wavelength	R <sup>2</sup>	Slope	Intercept
<b>Standard solution</b>				
API	544	1.000	0.774	0.039
Fluval	536	0.998	0.579	0.028
Red Sea	540	0.993	0.177	0.013
Seachem	540	1.000	0.525	0.022
Sera Aqua	548	1.000	0.614	0.022

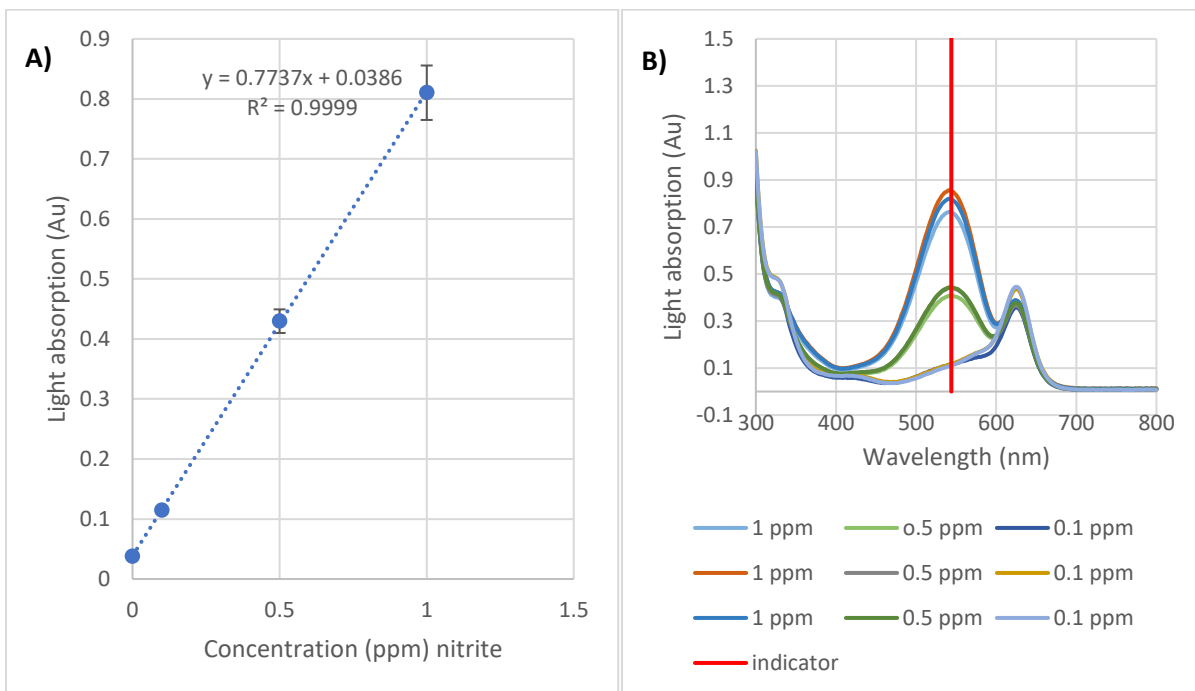


Figure A 10. Light absorption graph (A) and calibration curve (B) of nitrite API test kit.



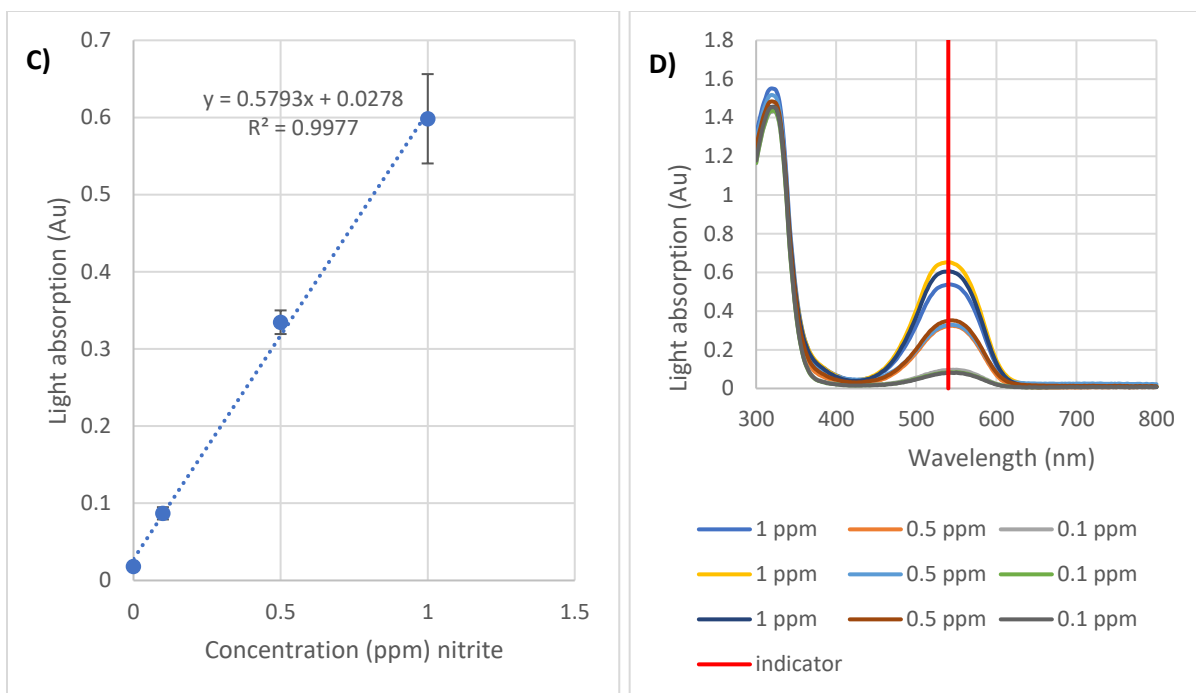


Figure A 11. Light absorption graph (C) and calibration curve (D) of nitrite Fluval test kit.

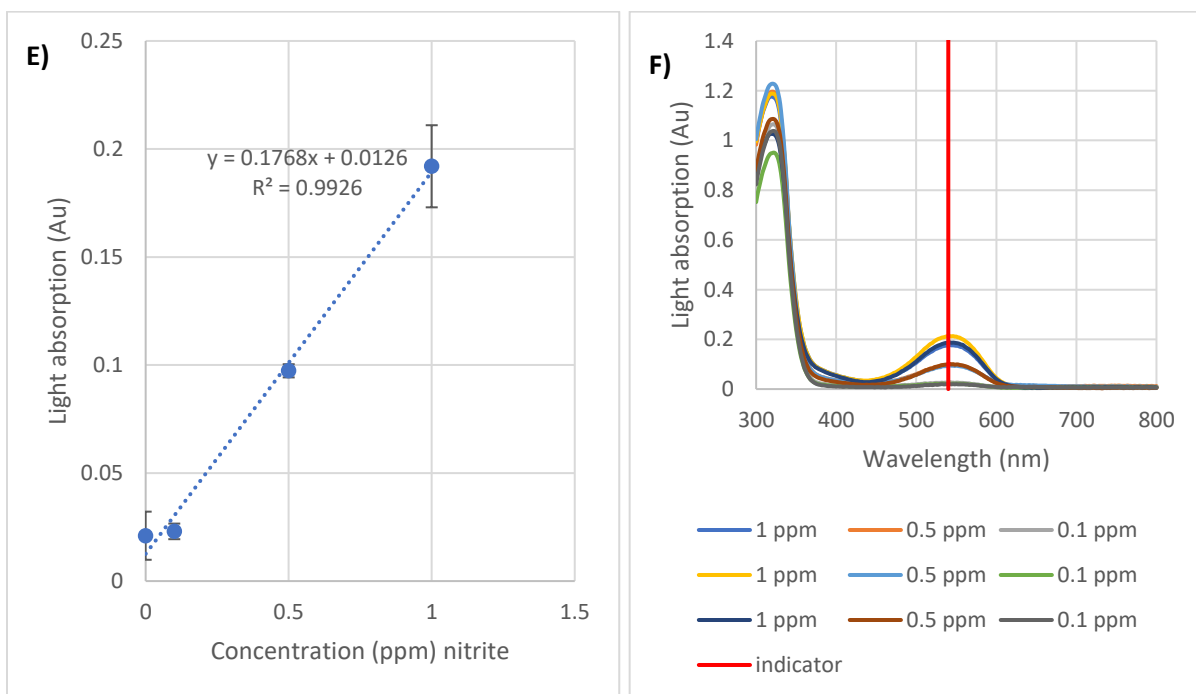


Figure A 12.. Light absorption graph (E) and calibration curve (F) of nitrite Red Sea test kit.

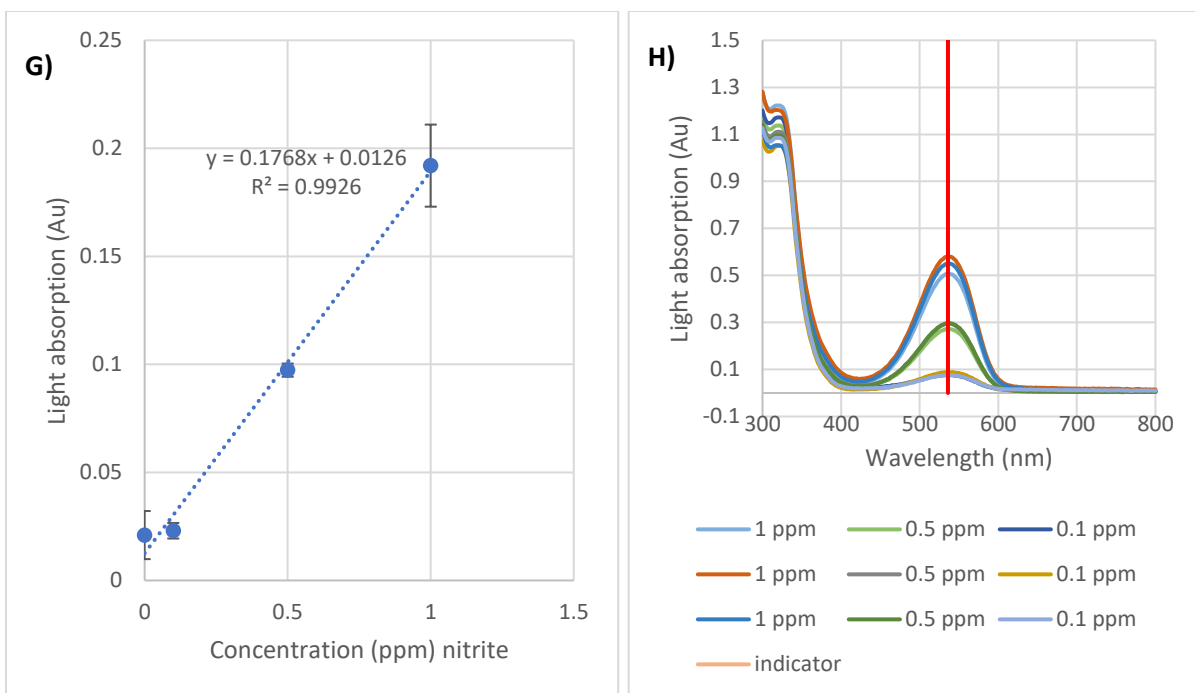


Figure A 13. Light absorption graph (G) and calibration curve (H) of nitrite Seachem test kit.

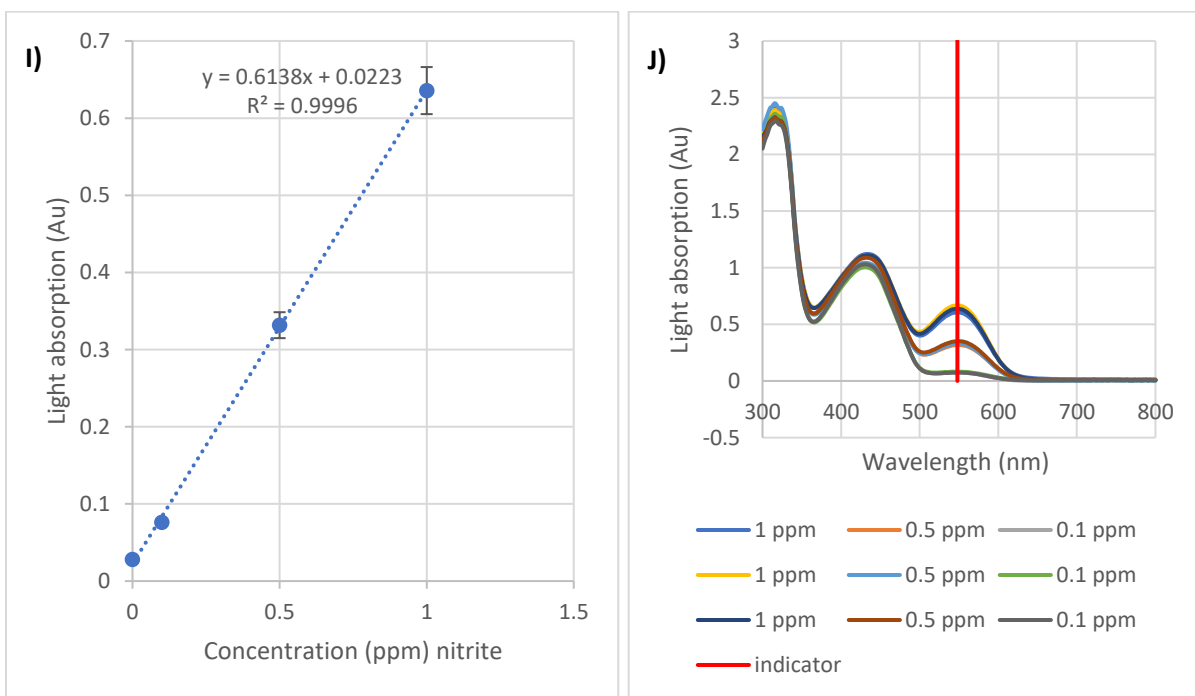


Figure A 14. Light absorption graph (I) and calibration curve (J) of nitrite Sera Aqua test kit.

Table A 5. Results of aquarium test kits for **nitrite** measurements of **Hoagland and Vegbloom** solutions at different concentrations followed by the percent error. Darker color indicates higher error.

Solution	Target value (ppm)*	API		Fluval		Red Sea		Seachem		Sera Aqua	
		Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
Hoagland	1	1.33	32.8	0.94	5.5	1.17	17.3	1.25	25.3	0.96	4.1
	1	1.21	20.9	0.98	2.1	1.17	16.7	1.11	11.4	1.00	0.5
	1	1.07	6.7	0.90	9.5	1.04	3.7	1.03	3.0	0.72	28.2
	0.5	0.64	27.3	0.50	0.5	0.90	79.2	0.65	30.9	0.50	0.9
	0.5	0.62	23.1	0.54	8.5	0.67	33.9	0.60	19.1	0.52	3.8
	0.5	0.53	5.1	0.48	4.6	0.60	20.3	0.51	2.7	0.37	25.5
	0.1	0.11	14.3	0.08	15.0	0.08	24.2	0.11	7.9	0.09	10.9
	0.1	0.15	46.6	0.10	1.2	0.13	26.7	0.14	42.2	0.11	10.3
	0.1	0.08	15.5	0.09	11.6	0.08	24.2	0.06	43.6	0.07	27.2
Vegbloom	1	1.13	13.3	1.46	45.6	1.15	15.0	0.97	3.5	1.05	5.2
	1	1.18	18.3	1.43	42.8	1.43	43.3	1.02	1.9	1.05	4.5
	1	1.21	20.6	1.46	45.7	1.21	21.2	1.00	0.1	1.05	4.5
	0.5	0.54	8.2	0.77	53.0	0.70	39.6	0.49	3.0	0.50	0.9
	0.5	0.54	8.4	0.75	50.6	0.44	11.3	0.86	71.7	0.53	6.8
	0.5	0.57	14.6	0.78	56.8	0.47	6.8	1.21	141.4	0.58	15.9
	0.1	0.07	27.1	0.15	45.4	0.06	41.2	0.24	137.4	0.14	36.3
	0.1	0.08	20.6	0.15	50.6	0.06	41.2	0.25	145.0	0.11	13.5
	0.1	0.08	16.8	0.17	73.0	0.10	4.0	0.26	162.2	0.11	13.5

\* This amount of nitrite was manually added to the solutions.

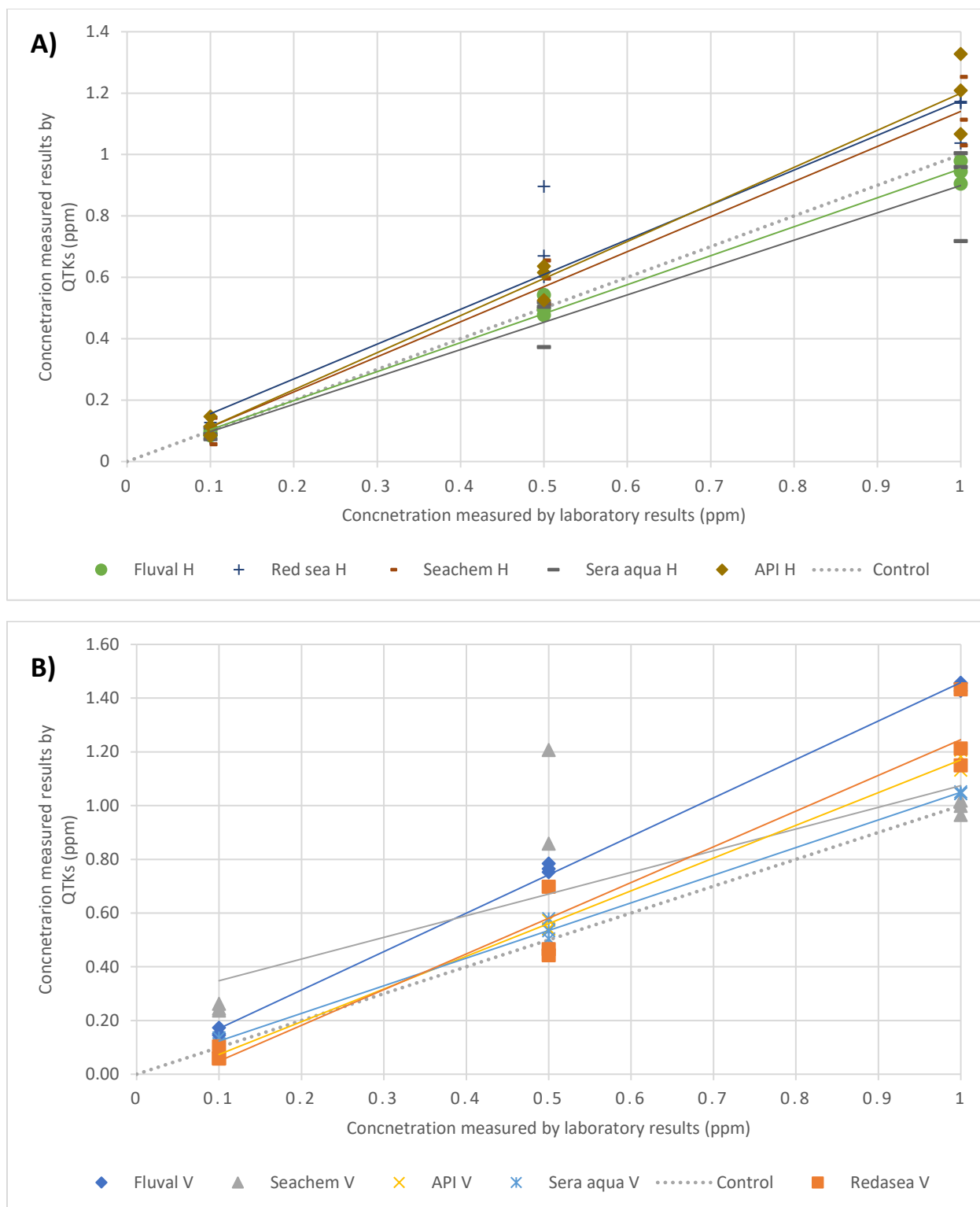


Figure A 15. Regression fits between laboratory analysis and the results of the nitrite test kits for A) Hoagland and B) Vegbloom solution.

### 7.3. Ammonium ( $\text{NH}_4^+$ ) and Ammonia ( $\text{NH}_3$ ) Tests

#### Calibration

Table A 6. Linear regression parameters and  $R^2$  values of calibration for  $\text{NH}_4^+$  test kits.

	Identified wavelength	$R^2$	Slope	Intercept
<b>Standard solution</b>				
API	680	0.998272	0.589667	0.0455
Fluval	656	0.99948	0.449905	0.078286
JBL	396	0.921166	-0.07133	0.694333
Red Sea	694	0.956319	0.257365	0.128294
Salifert	376	0.796798	0.475133	-0.00227
Sera Aqua	696	0.999846	0.818032	0.017627

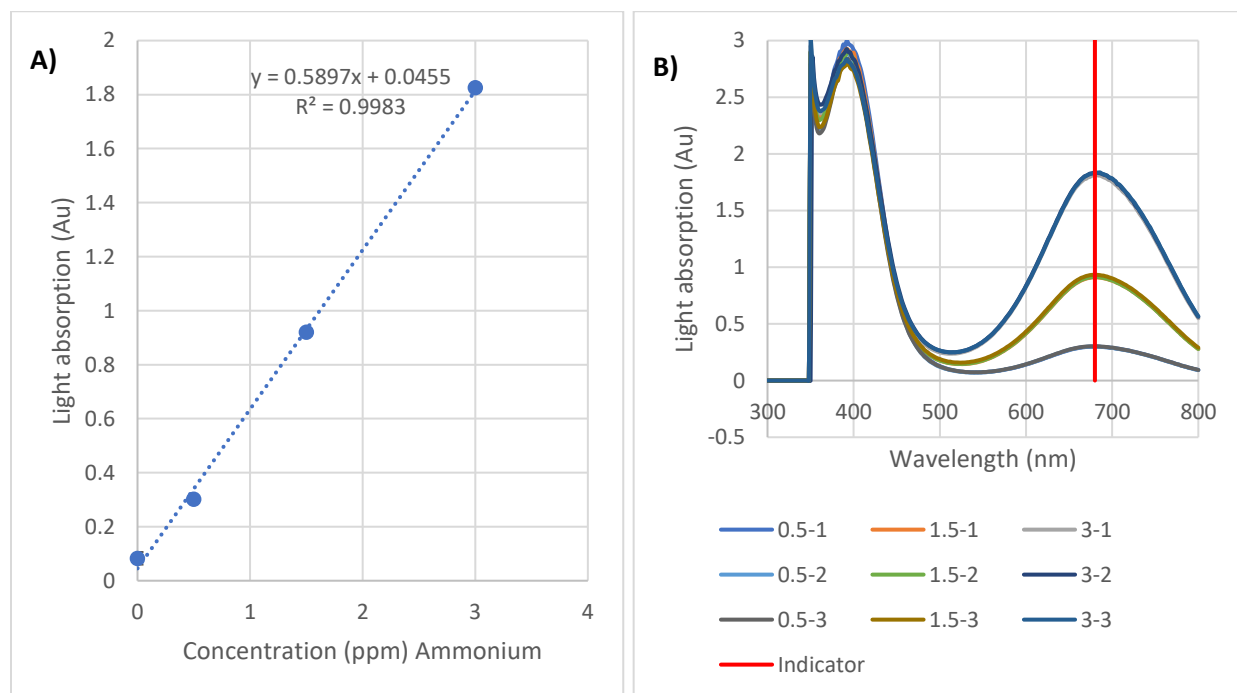


Figure A 16. Light absorption graph (A) and calibration curve (B) of ammonium API test kit.

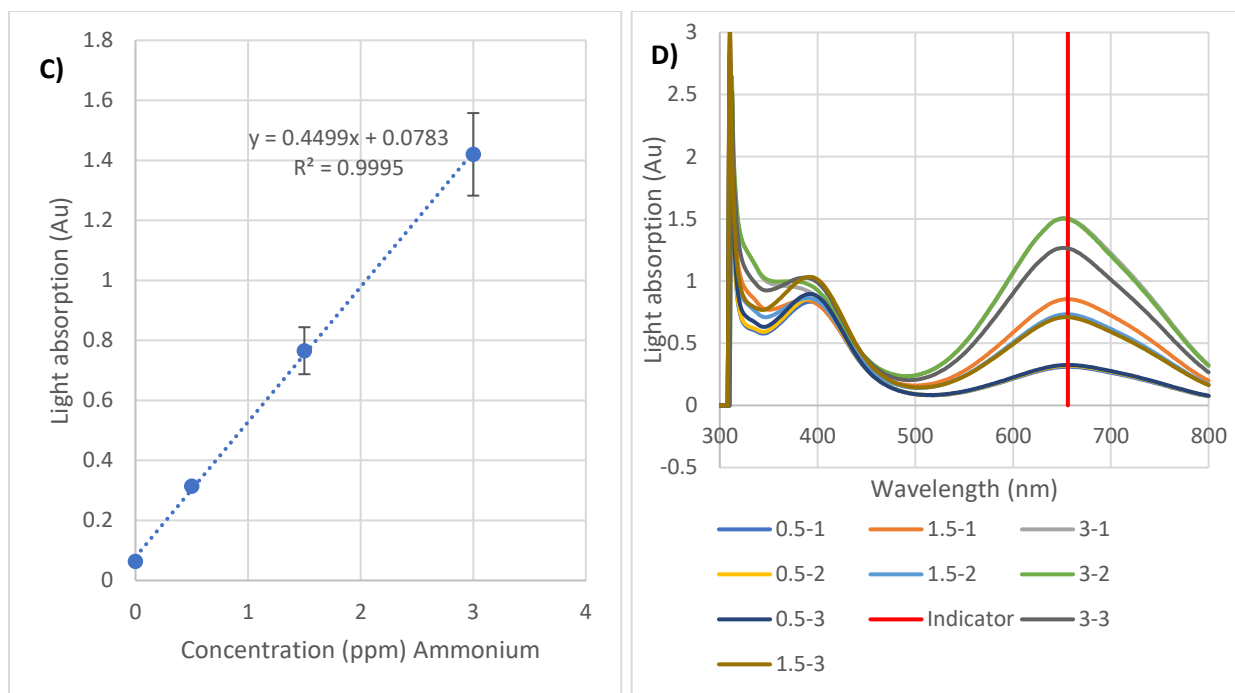


Figure A 17. Light absorption graph (C) and calibration curve (D) of ammonium Fluval test kit.

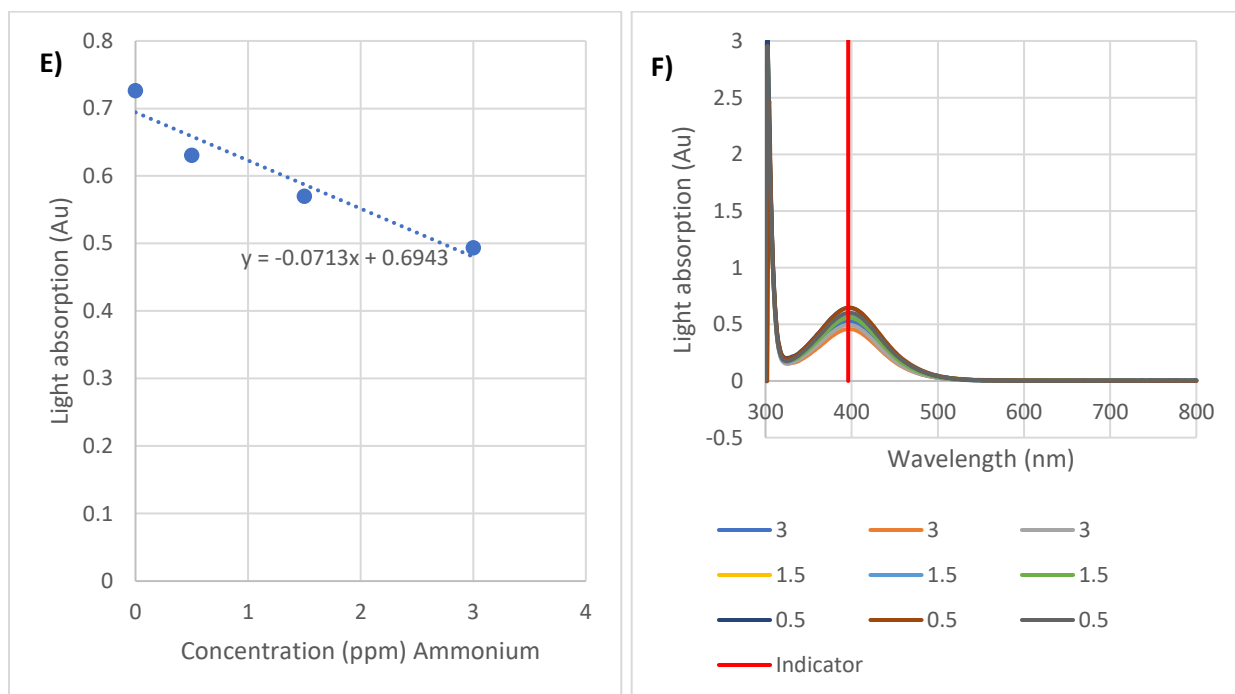


Figure A 18. Light absorption graph (E) and calibration curve (F) of ammonium JBL test kit.

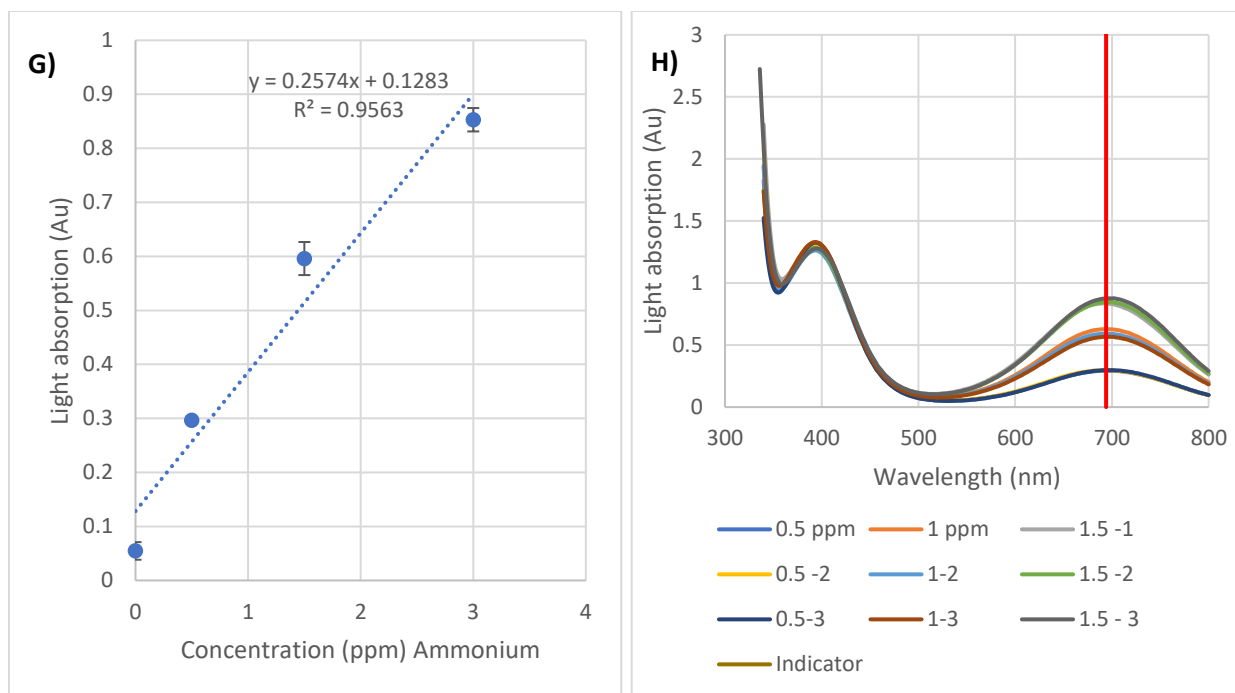


Figure A 19. Light absorption graph (G) and calibration curve (H) of ammonium Red Sea test.

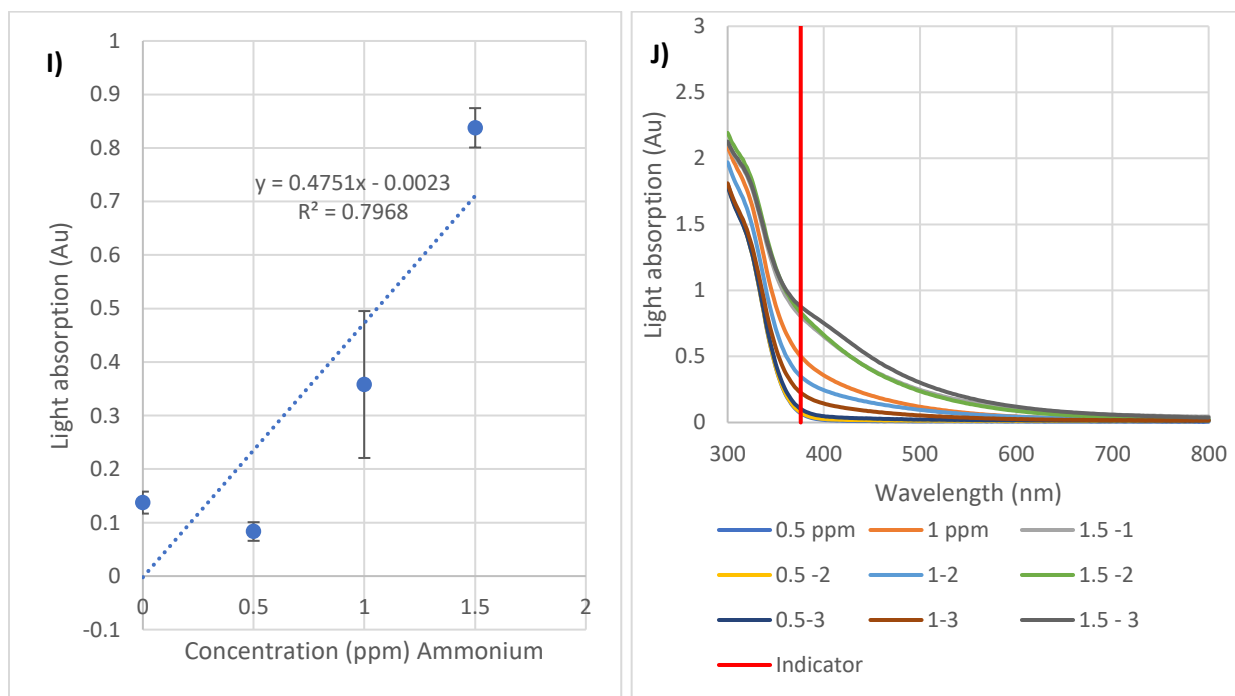


Figure A 20. Light absorption graph (I) and calibration curve (J) of ammonium Salifert test kit.

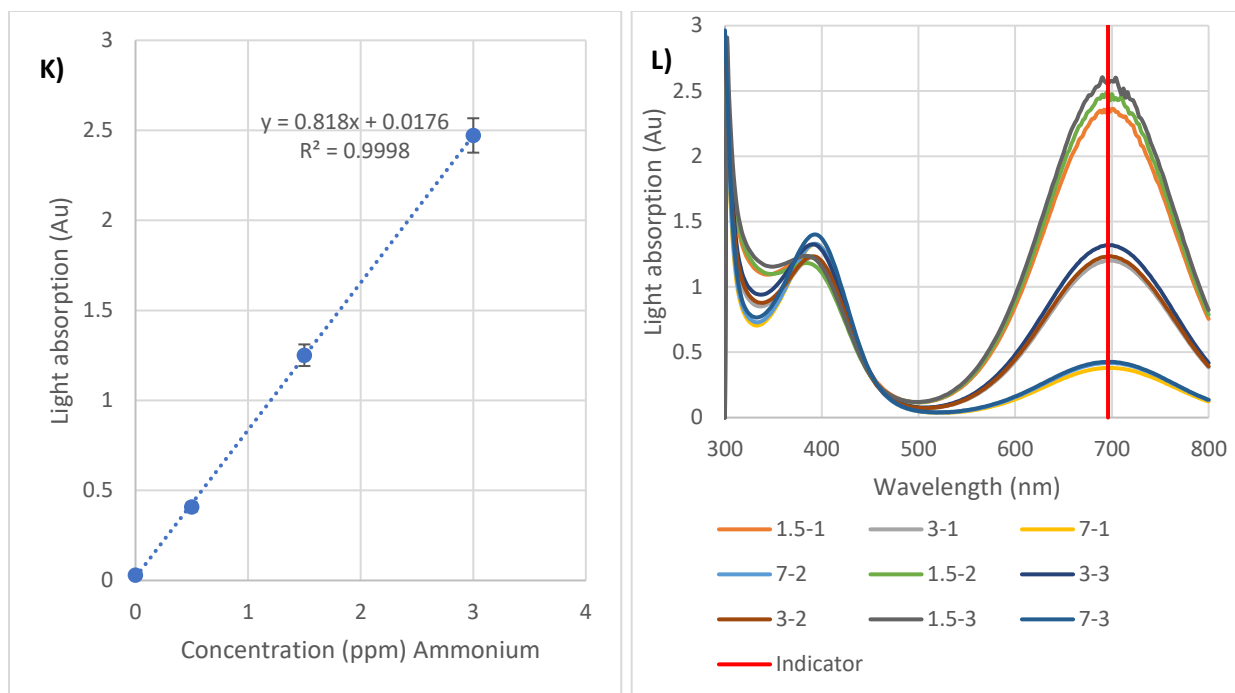


Figure A 21. Light absorption graph (K) and calibration curve (L) of ammonium Sera Aqua test kit.



Table A 7. Results of test kits and NT sensor ISE for **ammonium** measurements of **Hoagland** solution at different concentrations followed by the percent error. Darker color indicates higher error. N.A. = Not analyzed. ALD = Above limit of detection.

	API		Fluval		JBL		Red Sea		Salifert		Sera Aqua		NT sensors	
Target value (ppm)*	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
5.10	ALD		5.32	4.2	0.63 <sup>†</sup>	87.6	ALD		ALD		ALD		12	135.2
5.15	ALD		5.21	1.1	0.66*	87.1	ALD		ALD		ALD		12	132.8
5.13	ALD		5.32	3.7	0.67*	87.0	ALD		ALD		ALD		11	114.5
1.60	0.86	46.3	1.95	21.6	0.69	56.7	2.88	79.5	0.83	48.2	2.66	66.0	13	711.0
1.65	0.97	41.5	2.05	24.1	0.81	51.0	2.75	66.4	0.79	52.1	2.78	67.9	13	685.7
1.63	0.96	41.2	1.92	18.1	0.79	51.5	2.86	75.5	0.86	47.1	2.78	70.7	12	636.7
1.10	1.11	0.3	1.19	8.0	0.90	18.4	1.79	62.3	0.67	39.0	1.94	76.1	8.59	678.8
1.15	1.25	7.9	1.19	3.1	0.96	16.6	1.97	70.9	0.61	47.4	1.78	53.9	9.77	746.2
1.13	1.17	3.4	1.13	0.2	0.96	15.1	1.85	64.1	0.70	38.0	2.02	79.1	9.6	750.5
0.30	0.35	16.1	0.30	0.5	0.92	203.1	0.19	37.5	0.45	47.1	0.40	30.9	8.62	2744.5
0.35	0.39	10.3	0.36	2.0	0.88	148.9	0.38	7.1	0.28	20.0	0.41	14.9	13	3566.6
0.33	0.32	1.2	0.33	1.2	1.01	208.7	0.18	44.8	0.27	18.2	0.13	59.3	11	3245.5

\* The ammonium amount of Hoagland solution were minimal therefore higher concentrations were manually added to the solution.

<sup>†</sup> This measurement is outside of the measurement range of the test kit.

Table A 8. Results of test kits and NT sensor ISE for **ammonium** measurements of **Vegbloom** solution at different concentrations followed by the percent error. Darker color indicates higher error. N.A. = Not analyzed. ALD = Above limit of detection.

Target value (ppm)	Dilution factor	Laboratory results	API		Fluval		JBL		Red Sea		Salifert		Sera Aqua		NT sensors	
			Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
4.51	1:2	4.94	4.30	12.9	4.03	18.4	0.71	85.6	ALD		ALD		ALD		6.52	32.1
	1:2	5.42	4.37	19.3	4.09	24.5	0.72*	86.6	ALD		ALD		ALD		6.41	18.3
	1:2	5.91	4.83	18.3	4.34	26.5	0.63*	89.3	ALD		ALD		ALD		6.47	9.6
3	1:3	3.29	N.A.		N.A.		N.A.		ALD		ALD		2.82	14.4	4.39	33.4
	1:3	3.61	N.A.		N.A.		N.A.		ALD		ALD		2.73	24.4	4.39	21.5
	1:3	3.94	N.A.		N.A.		N.A.		ALD		ALD		3.34	15.2	4.44	12.8
1.8	1:5	1.97	1.66	16.1	1.65	16.4	0.90	54.5	3.05	54.2	1.16	41.3	1.73	12.6	2.54	28.6
	1:5	2.17	1.69	22.1	1.68	22.5	0.88	59.4	3.20*	47.7	1.04*	52.2	1.75	19.3	2.57	18.6
	1:5	2.36	1.91	19.0	1.84	22.0	0.86	63.5	3.46*	46.5	1.35*	42.9	1.87	21.0	2.81	19.0
1.29	1:7	1.41	N.A.		N.A.		N.A.		2.23	58.1	0.97	31.4	N.A.		2.15	52.4
	1:7	1.55	N.A.		N.A.		N.A.		2.46	59.0	1.06	31.4	N.A.		2.01	29.8
	1:7	1.69	N.A.		N.A.		N.A.		2.12	25.9	0.81	51.9	N.A.		2.16	28.0
0.9	1:10	0.99	0.79	19.9	0.81	17.7	1.01	2.4	1.44	45.9	0.56	43.3	0.79	20.3	1.67	69.2
	1:10	1.08	0.84	22.8	0.83	23.2	1.03	4.9	1.39	27.9	0.66	39.1	0.83	23.7	1.63	50.4
	1:10	1.18	0.93	21.0	0.91	22.9	0.93	21.3	1.58	33.5	0.61	48.2	0.93	21.1	1.47	24.5

\* This measurement is outside of the measurement range of the test kit.

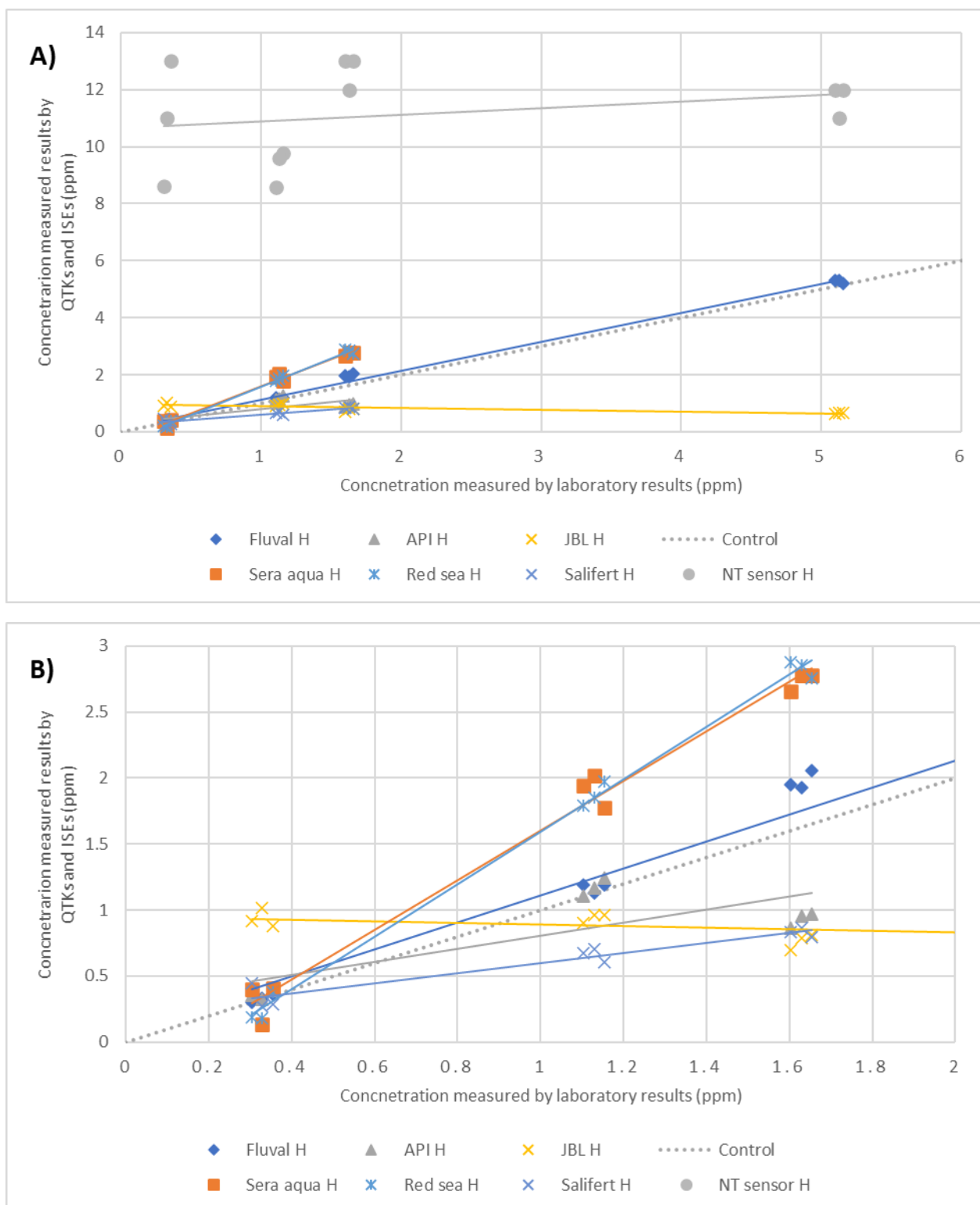


Figure A 22. Regression fits between laboratory analysis and the results of the **ammonium** test kits and ISE for **Hoagland** solution. Figure B is a closed-up version of Figure A

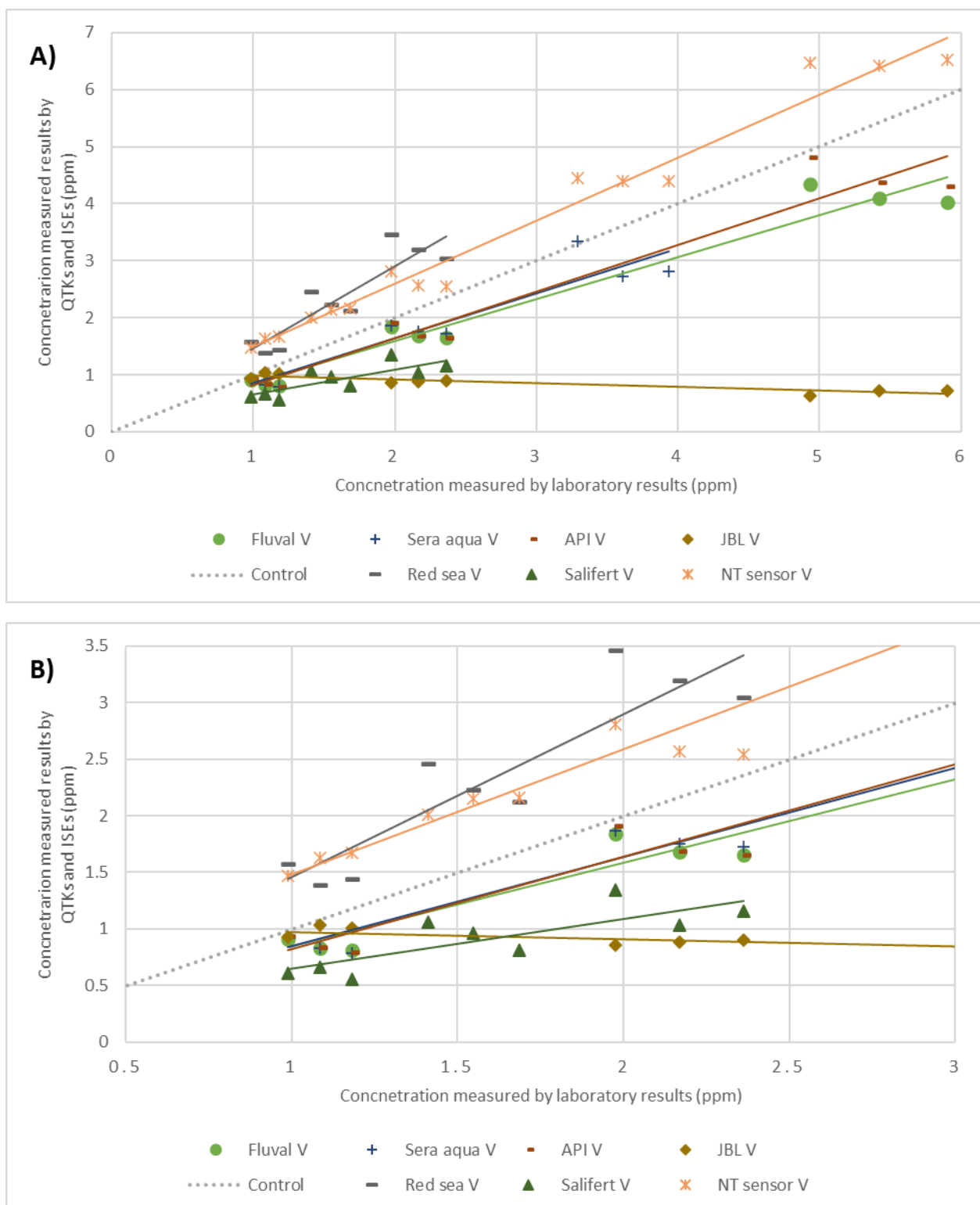


Figure A 23. Regression fits between laboratory analysis and the results of the **ammonium** test kits and ISE for **Vegbloom** solution. Figure B is a closed-up version of Figure A.

## 7.4. Phosphate ( $\text{PO}_4^{3-}$ ) Tests

### Calibration

Table A 9. Linear regression parameters and  $R^2$  values of calibration for  $\text{PO}_4^{3-}$  test kits.

	Identified wavelength	$R^2$	Slope	Intercept
<b>Standard solution</b>				
API	694	0.984	0.144	0.156
Fluval	700	0.999	0.150	0.033
JBL	710	0.977	0.122	0.043
Red Sea	700	0.977	0.236	0.035
Salifert	700	0.822	0.126	0.084
Seachem	640	0.688	0.180	0.279
Sera Aqua	710	0.945	0.093	0.040

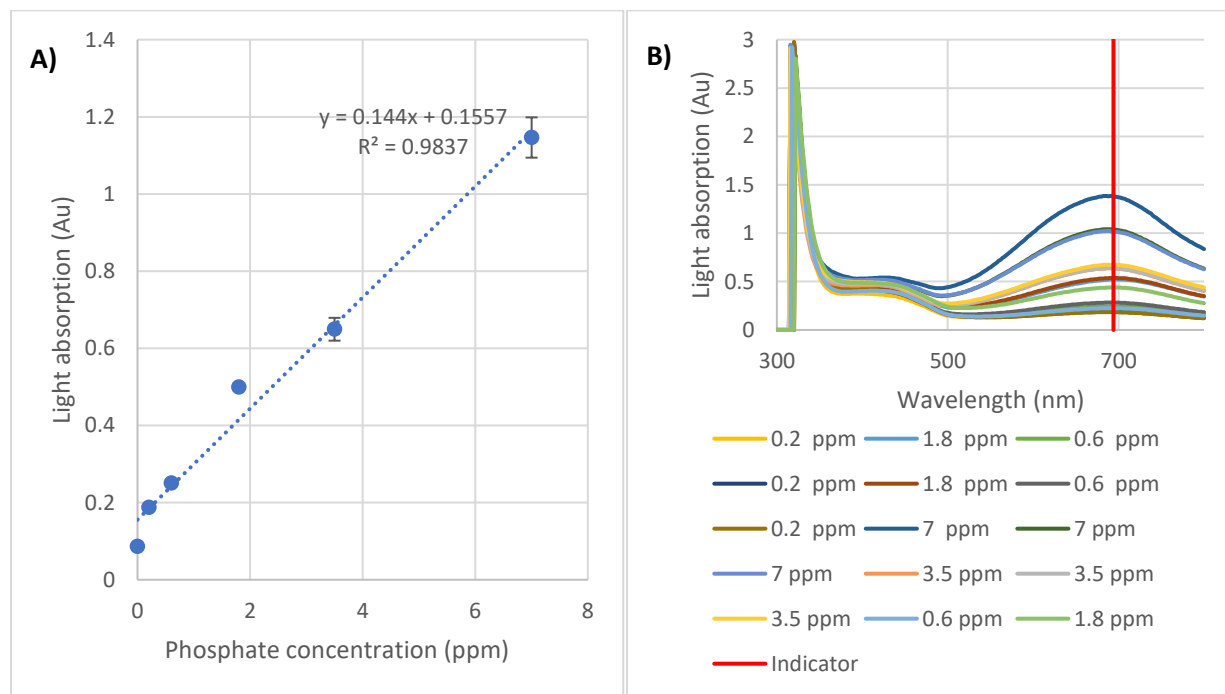


Figure A 24. Light absorption graph (A) and calibration curve (B) of phosphate API test kit.

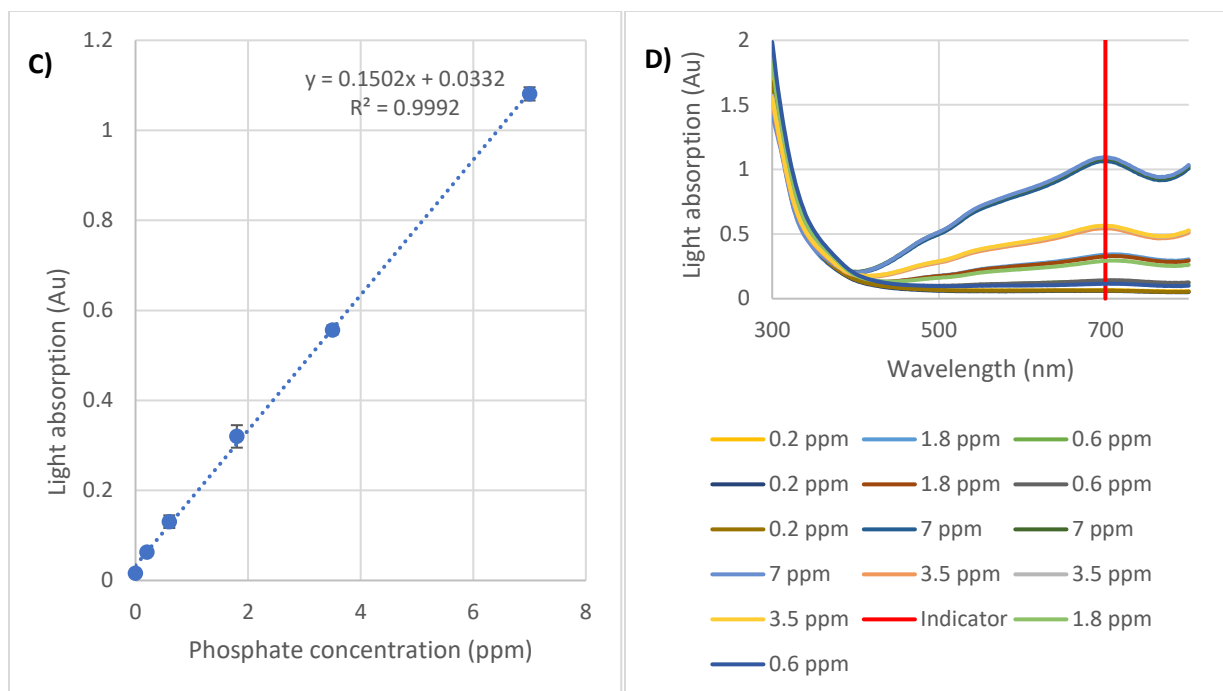


Figure A 25 . Light absorption graph (C) and calibration curve (D) of phosphate Fluval test kit.

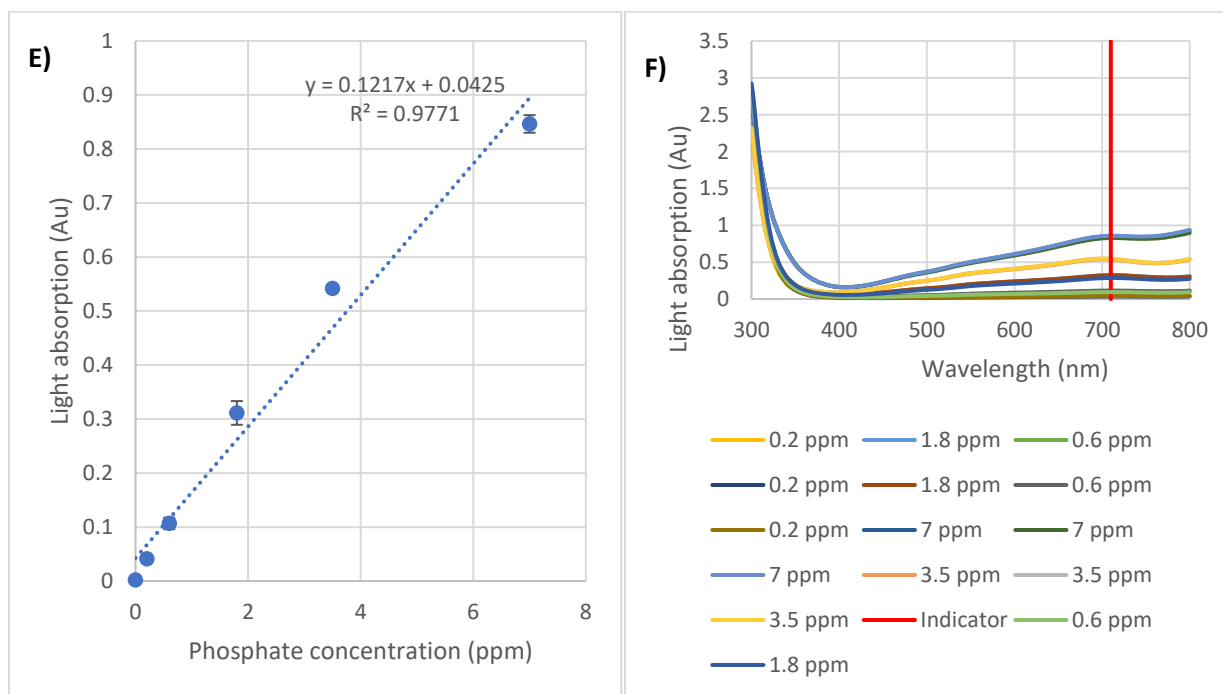


Figure A 26 Light absorption graph (E) and calibration curve (F) of phosphate JBL test kit.

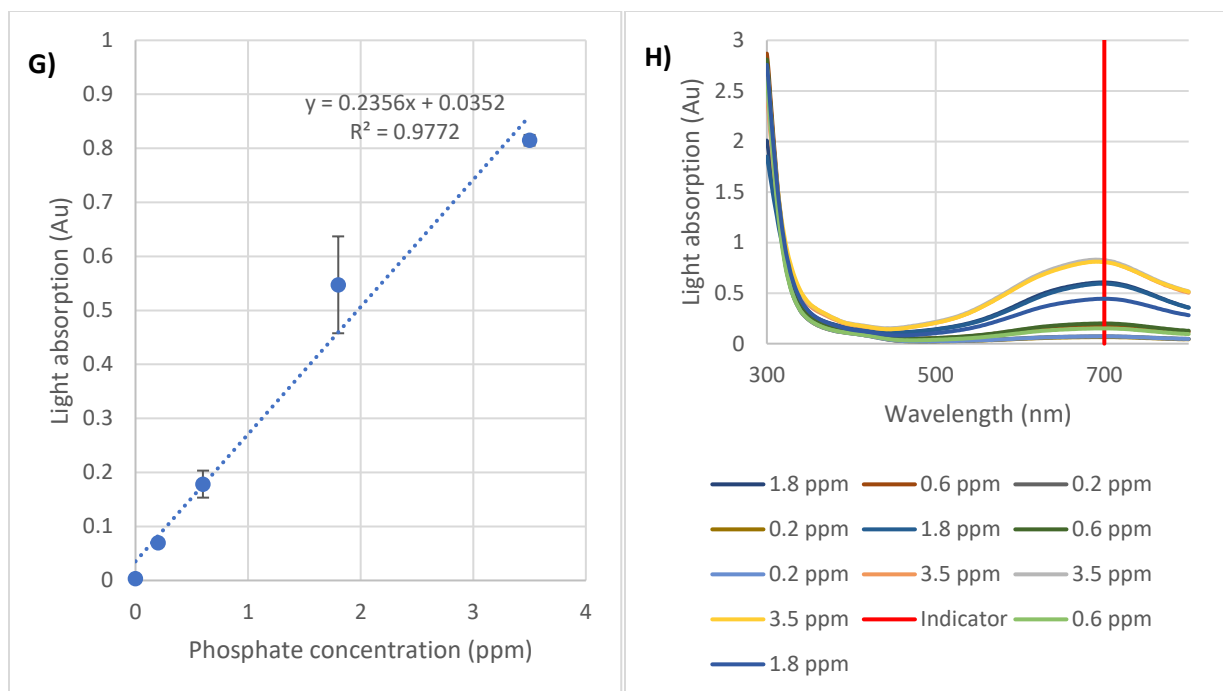


Figure A 27. Light absorption graph (G) and calibration curve (H) of phosphate Red Sea test kit

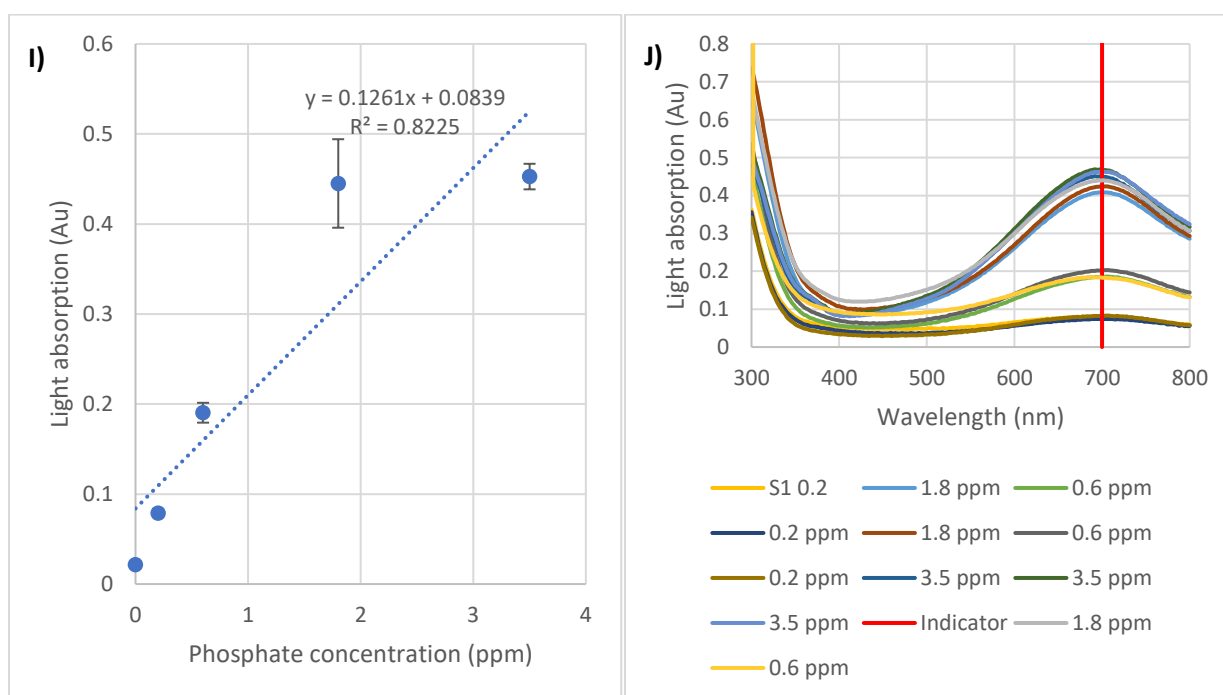


Figure A 28. Light absorption graph (I) and calibration curve (J) of phosphate Salifert test kit.

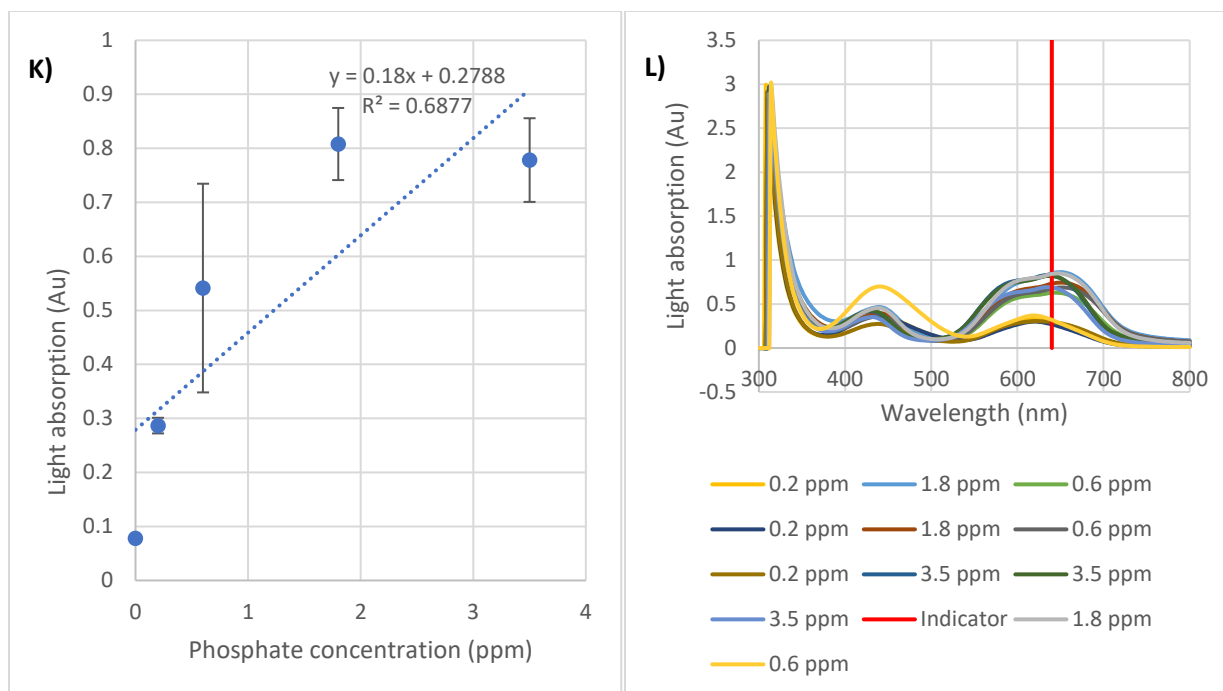


Figure A 29. Light absorption graph (k) and calibration curve (L) of phosphate Seachem test kit

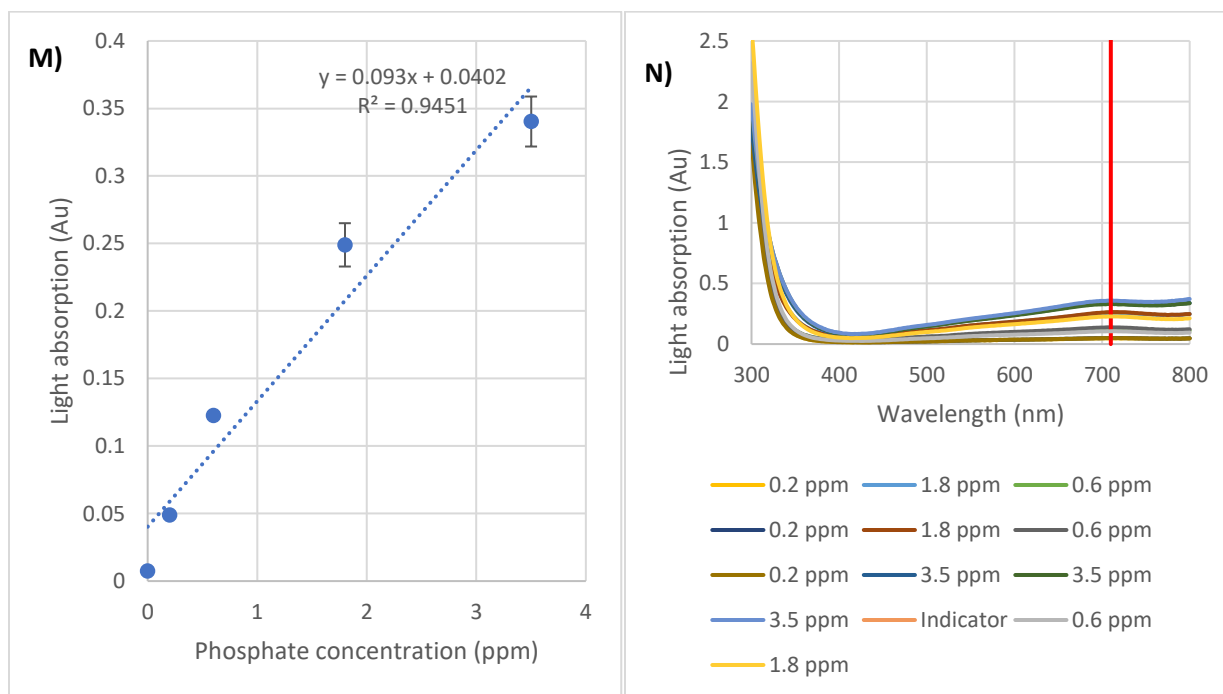


Figure A 30. Light absorption graph (M) and calibration curve (N) of phosphate Sera Aqua test kit



Table A 10 Results of test kits for **phosphate** measurements of **Hoagland** solution at different concentrations followed by the percent error. Darker color indicates higher error. N.A. = Not analyzed. ALD = Above limit of detection

Target value	Dilution	Laboratory results	API		Fluval		JBL		Red Sea		Salifert		Seachem		Sera aqua	
			Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
9.505	1:10	9.01	9.20	2.10	ALD		ALD		ALD		ALD	ALD	ALD	ALD	ALD	
	1:10	9.14	9.34	2.22	ALD		ALD		ALD		ALD	ALD	ALD	ALD	ALD	ALD
	1:10	8.79	9.10	3.52	ALD		ALD		ALD		ALD	ALD	ALD	ALD	ALD	ALD
4.753	1:20	4.50	5.53	22.8	5.56	23.6	5.27*	17.0	ALD		3.28*	27.3	ALD		4.38*	2.8
	1:20	4.57	5.36	17.4	5.26	15.2	5.11*	11.8	ALD		3.35*	26.7	ALD		4.14*	9.4
	1:20	4.39	5.46	24.2	5.17	17.7	5.32*	21.1	ALD		3.36*	23.6	ALD		4.25*	3.4
2.376	1:40	2.25	3.22	42.9	2.69	19.4	3.12*	38.5	2.66*	18.1	2.54	12.7	2.43	8.1	2.90*	28.9
	1:40	2.28	3.09	35.0	2.58	13.0	2.95*	29.3	2.52*	10.3	2.65	16.0	2.71	18.7	2.57*	12.4
	1:40	2.20	3.04	38.2	2.57	17.2	2.91*	32.6	2.48*	13.0	2.67	21.3	2.58	17.4	2.64	20.3
1.426	3:200	1.75	1.52	13.4	1.33	24.0	1.68	4.0	1.38*	21.0	2.09	19.2	3.27	87.1	1.84	5.0
	3:200	1.81	1.34	25.8	1.48	18.1	1.55*	14.4	1.40*	22.7	1.88	3.9	4.02	122.0	1.80	0.3
	3:200	1.68	1.70	1.0	1.40	16.5	1.57	6.3	1.44*	14.4	1.88	11.9	4.61	174.2	1.97	17.0
0.475	1:200	0.58	0.27	52.9	0.35	39.4	0.37	37.0	0.47	18.9	0.38	34.2	1.49	156.9	0.65	12.7
	1:200	0.60	0.11	82.3	0.44	25.9	0.24	59.6	0.39	34.4	0.43	28.5	1.22	103.9	0.40	34.1
	1:200	0.56	0.44	21.5	0.47	15.8	0.46	17.1	0.51	8.5	0.49	12.1	1.33	137.3	0.70	24.4
0.171	1:555	0.21	-0.15	171.7	0.07	68.9	-0.05	125.5	0.10	52.0	-0.26	224.3	-0.29	237.1	0.17	19.3
	1:555	0.22	-0.31	241.0	0.09	58.2	-0.16	172.9	0.06	73.4	-0.16	171.8	-0.26	218.3	0.00	101.2
	1:555	0.21	-0.07	132.0	0.06	72.1	-0.03	113.8	0.11	47.9	-0.25	220.5	-0.32	253.0	0.01	96.1

\* This measurement is outside of the measurement range of the test kit.

Table A 11. Results of test kits for **phosphate** measurements of **Vegbloom** solution at different concentrations followed by the percent error. Darker color indicates higher error. N.A. = Not analyzed. ALD = Above limit of detection.

Target value	Dilution	Laboratory results	API		Fluval		JBL		Red Sea		Salifert		Seachem		Sera Aqua	
			Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
6.267	1:20	6.89	6.76	2	ALD		ALD		ALD		ALD		ALD		ALD	
	1:20	6.50	6.55	0.7	ALD		ALD		ALD		ALD		ALD		ALD	
	1:20	6.55	6.34	3.3	ALD		ALD		ALD		ALD		ALD		ALD	
4.178	1:30	4.60	N.A.		3.71	19.4	4.22*	8.2	ALD		ALD		ALD		ALD	
	1:30	4.34	N.A.		3.58	17.4	4.23*	2.5	ALD		ALD		ALD		ALD	
	1:30	4.37	N.A.		3.71	15.0	4.25*	2.7	ALD		ALD		ALD		ALD	
2.507	1:50	2.76	2.89	4.8	2.56	7.4	2.96*	7.4	ALD		2.59	6.2	3.97	44.1	2.53*	8.4
	1:50	2.60	2.73	5	2.57	1.3	3.00*	15.4	ALD		2.47	5.2	3.75	44.0	2.51*	3.3
	1:50	2.62	2.96	12.9	2.56	2.3	2.95*	12.7	ALD		2.50	4.7	4.71	79.7	2.53*	3.7
1.253	1:100	1.38	N.A.		N.A.		1.30	5.6	ALD		N.A.		N.A.		1.72	24.6
	1:100	1.30	N.A.		N.A.		1.24	4.3	ALD		N.A.		N.A.		1.70	30.5
	1:100	1.31	N.A.		N.A.		1.32	0.6	ALD		N.A.		N.A.		1.70	29.4
0.627	1:200	0.69	N.A.		N.A.		0.48	30.3	0.53	23.2	0.68	1.0	0.46	33.8	0.71	2.6
	1:200	0.65	N.A.		N.A.		0.44	32.4	0.53	18.6	0.58	10.9	1.85	183.8	0.35	45.8
	1:200	0.66	N.A.		N.A.		0.43	34.2	0.52	20.5	0.51	22.5	0.63	4.1	0.76	16.1
0.418	1:300	0.46	0.10	78.4	0.25	45.3	0.10	77.7	0.25	45.7	N.A.		N.A.		0.28	39.7
	1:300	0.43	0.18	59.5	0.37	14.3	0.08	82.0	0.25	41.5	N.A.		N.A.		0.72	65.6
	1:300	0.44	0.40	7.3	0.25	42.4	0.07	84.0	0.24	44.9	N.A.		N.A.		0.27	39.1
0.251	1:500	0.28	N.A.		N.A.		0.41	47.4	0.12	57.3	-0.08	128.5	-0.06	121.8	0.06	77.6
	1:500	0.26	N.A.		N.A.		-0.05	117.4	0.13	49.8	-0.06	124.1	-0.12	144.5	0.03	88.6
	1:500	0.26	N.A.		N.A.		-0.08	129.8	0.13	51.8	-0.07	127.0	-0.20	175.9	0.06	76.4

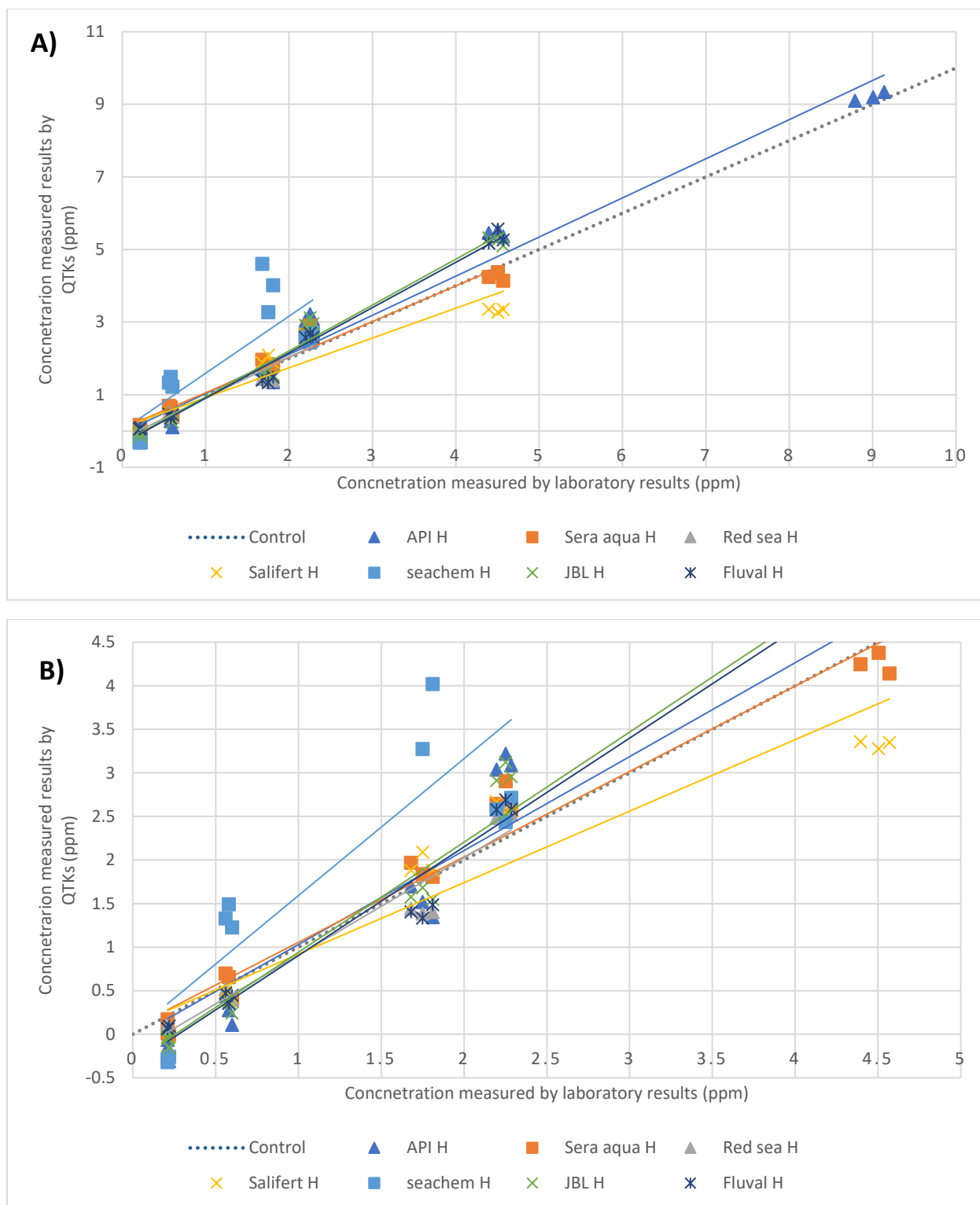


Figure A 31. Regression fits between laboratory analysis and the results of the **phosphate** test kits for **Hoagland** solution. Figure B is a closed-up version of Figure A.

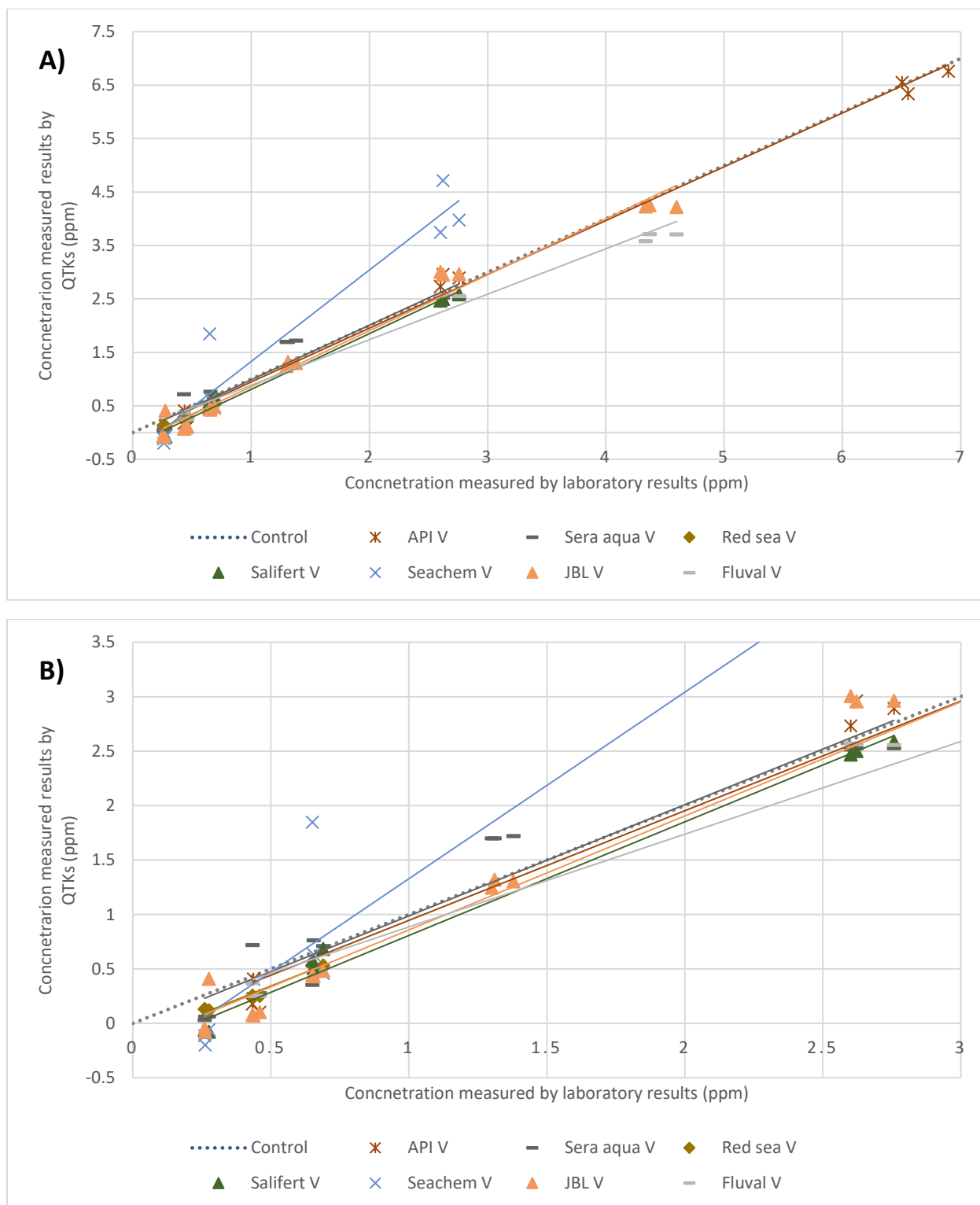


Figure A 32. Regression fits between laboratory analysis and the results of the **phosphate** test kits for **Vegbloom** solution. Figure B is a closed-up version of Figure A.

## 7.5. Potassium (K) Tests

Table A 12. Results of test kits and ISE for **potassium** measurements of **Hoagland** and **Vegbloom** solution at different concentrations followed by the percent error. Darker color indicates higher error.

Solution	Target value	Dilution	Laboratory results	JBL		Red Sea		Salifert		NT sensors	
				Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
Hoagland	468	2:1	443.8	450	1.4	446	0.5	460	3.7	468	5.5
		2:1	445.1	450	1.1	449	0.9	470	5.6	465	4.5
		2:1	437.8	450	2.8	452	3.2	470	7.4	480	9.6
	234	1:1	221.9	120	45.9	260	17.2	290	30.7	220	0.8
		1:1	222.5	135	39.3	269	20.9	290	30.3	209	6.1
		1:1	218.9	120	45.2	263	20.1	280	27.9	224	2.3
	117	1:2	110.9	60	45.9	131	18.1	160	44.2	107	3.5
		1:2	111.3	60	46.1	131	17.7	160	43.8	103	7.4
		1:2	109.5	60	45.2	116	6.0	170	55.3	101	7.7
Vegbloom	259.6	2:1	254	300	18.1	260	2.4	260	2.4	250	1.5
		2:1	264	280	6.3	272	3.2	250	5.1	248	5.9
		2:1	255	300	17.6	254	0.5	250	2.0	236	7.5
	129.8	1:1	127.0	160	26.0	74	41.7	150	18.1	103	18.9
		1:1	131.8	140	6.3	83	37.0	130	1.3	98	25.6
		1:1	127.6	140	9.7	71	44.4	130	1.9	100	21.6
	64.9	1:2	63.5	60	5.5	14	77.9	60	5.5	45	29.1
		1:2	65.9	60	8.9	35	46.9	60	8.9	45	31.7
		1:2	63.8	50	21.6	44	31.0	60	5.9	40	37.3

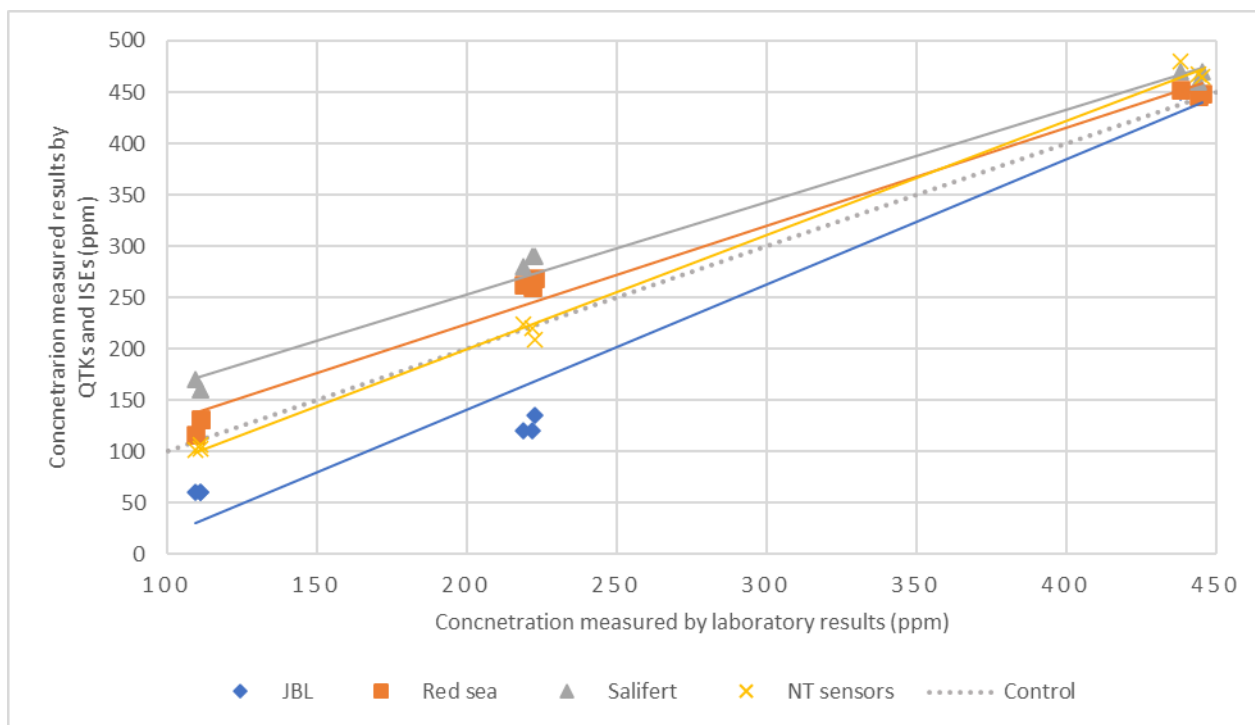


Figure A 33. Regression fits between laboratory analysis and the results of the **potassium** test kits and ISE for **Hoagland** solution.

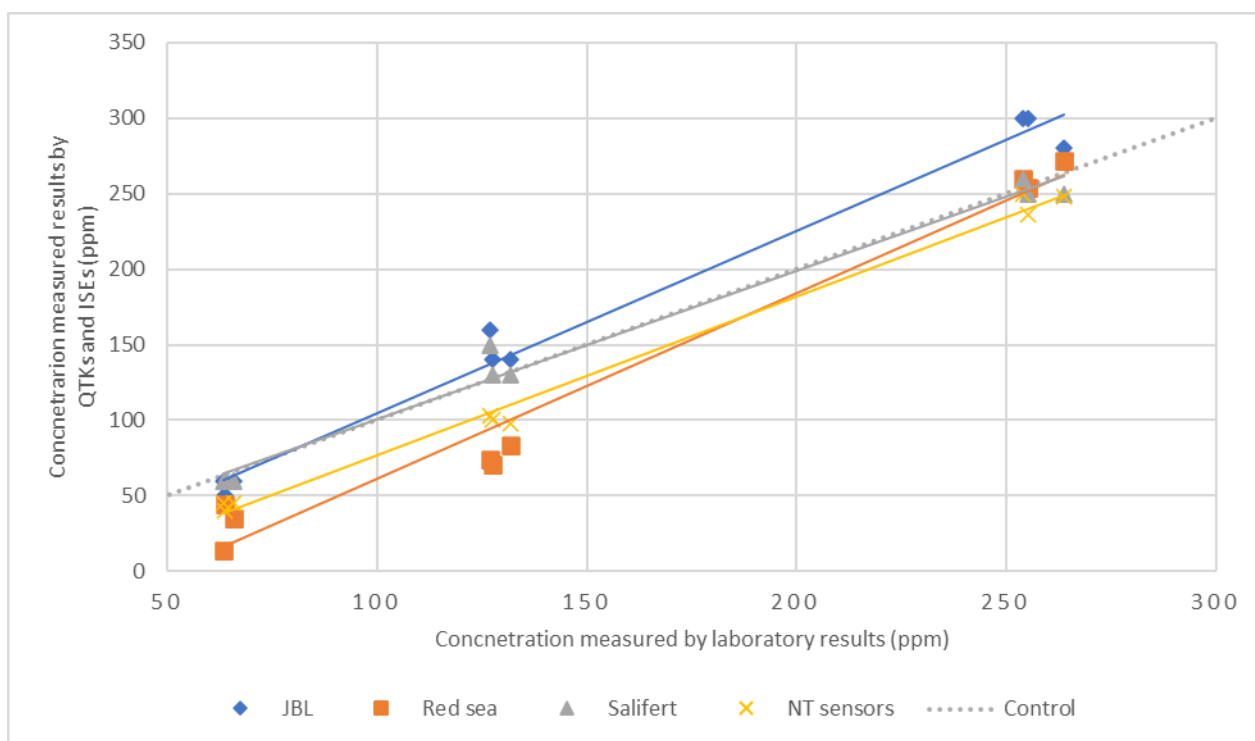


Figure A 34. Regression fits between laboratory analysis and the results of the **potassium** test kits and ISE for **Vegbloom** solution.

## 7.6. Calcium (Ca) Tests

Table A 13. Results of API, Fluval, JBL and Red Sea test kits for **calcium** measurements of **Hoagland** and **Vegbloom** solutions at different concentrations followed by the percent error. Darker color indicates higher error.

Solution	Target value	Dilution	Laboratory results	API		Fluval		JBL		Red Sea	
				Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
Hoagland	320	2:1	400.30	400	0.1	400	0.1	360	10.1	400	0.1
		2:1	335.57	360	7.3	360	7.3	380	13.2	370	10.3
		2:1	345.91	380	9.9	380	9.9	400	15.6	370	7.0
	160	1:1	200.15	180	10.1	180	10.1	180	10.1	175	12.6
		1:1	185.60	180	3.0	160	13.8	160	13.8	195	5.1
		1:1	172.96	200	15.6	180	4.1	200	15.6	195	12.7
	80	1:2	100.08	120	19.9	100	0.1	80	20.1	105	4.9
		1:2	92.80	100	7.8	80	13.8	100	7.8	95	2.4
		1:2	86.48	120	38.8	100	15.6	100	15.6	90	4.1
		1:2	86.48	120	38.8	100	15.6	100	15.6	90	4.1
Vegbloom	179.52	2:1	191.10	240	25.6	80	58.1	160	16.3	180	5.8
		2:1	195.40	240	22.8	100	48.8	180	7.9	190	2.8
		2:1	190.50	240	26.0	100	47.5	160	16.0	195	2.4
	89.76	1:1	95.55	140	46.5	60	37.2	80	16.3	115	20.4
		1:1	97.70	140	43.3	60	38.6	80	18.1	120	22.8
		1:1	95.25	140	47.0	60	37.0	80	16.0	110	15.5
	44.88	1:2	47.78	80	67.5	40	16.3	40	16.3	60	25.6
		1:2	48.85	80	63.8	40	18.1	40	18.1	55	12.6
		1:2	47.63	80	68.0	40	16.0	40	16.0	55	15.5
		1:2	47.63	80	68.0	40	16.0	40	16.0	55	15.5

Table A 14. Results of Salifert, Seachem, Sera Aqua test kits and NT sensor ISE for **calcium** measurements of **Vegbloom** and **Hoagland** solutions at different concentrations followed by the percent error. Darker color indicates higher error.

Solution	Target value	Dilution	Laboratory results	Salifert		Seachem		Sera Aqua		NT sensors	
				Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
Hoagland	320	2:1	400.30	470	17.4	350	12.6	380	5.1	451	12.7
		2:1	335.57	490	46.0	310	7.6	360	7.3	419	24.9
		2:1	345.91	515	48.9	330	4.6	380	9.9	440	27.2
	160	1:1	200.15	285	42.4	170	15.1	180	10.1	204	1.9
		1:1	185.60	180	3.0	185	0.3	200	7.8	178	4.1
		1:1	172.96	285	64.8	160	7.5	200	15.6	92	46.8
	80	1:2	100.08	115	14.9	115	14.9	100	0.1	124	23.9
		1:2	92.80	95	2.4	95	2.4	100	7.8	91	1.9
		1:2	86.48	135	56.1	90	4.1	100	15.6	33	61.8
Vegbloom	179.52	2:1	191.10	215	12.5	160	16.3	180	5.8	144	24.6
		2:1	195.40	210	7.5	155	20.7	180	7.9	147	24.8
		2:1	190.50	225	18.1	165	13.4	180	5.5	150	21.3
	89.76	1:1	95.55	135	41.3	95	0.6	120	25.6	91	4.8
		1:1	97.70	115	17.7	85	13.0	120	22.8	86	12.0
		1:1	95.25	110	15.5	85	10.8	120	26.0	84	11.8
	44.88	1:2	47.78	60	25.6	40	16.3	80	67.5	38	20.5
		1:2	48.85	60	22.8	40	18.1	80	63.8	33	32.4
		1:2	47.63	55	15.5	40	16.0	80	68.0	36	24.4



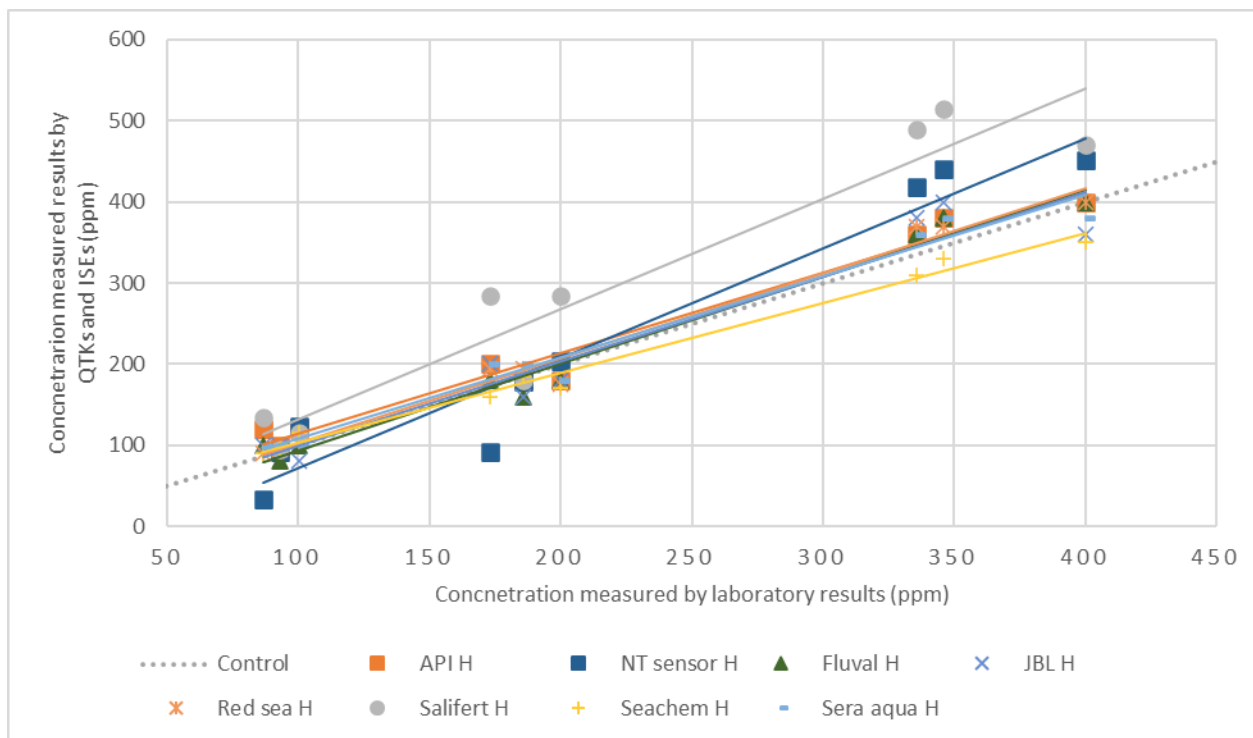


Figure A 35. Regression fits between laboratory analysis and the results of the **calcium** test kits and ISE for **Hoagland** solution.

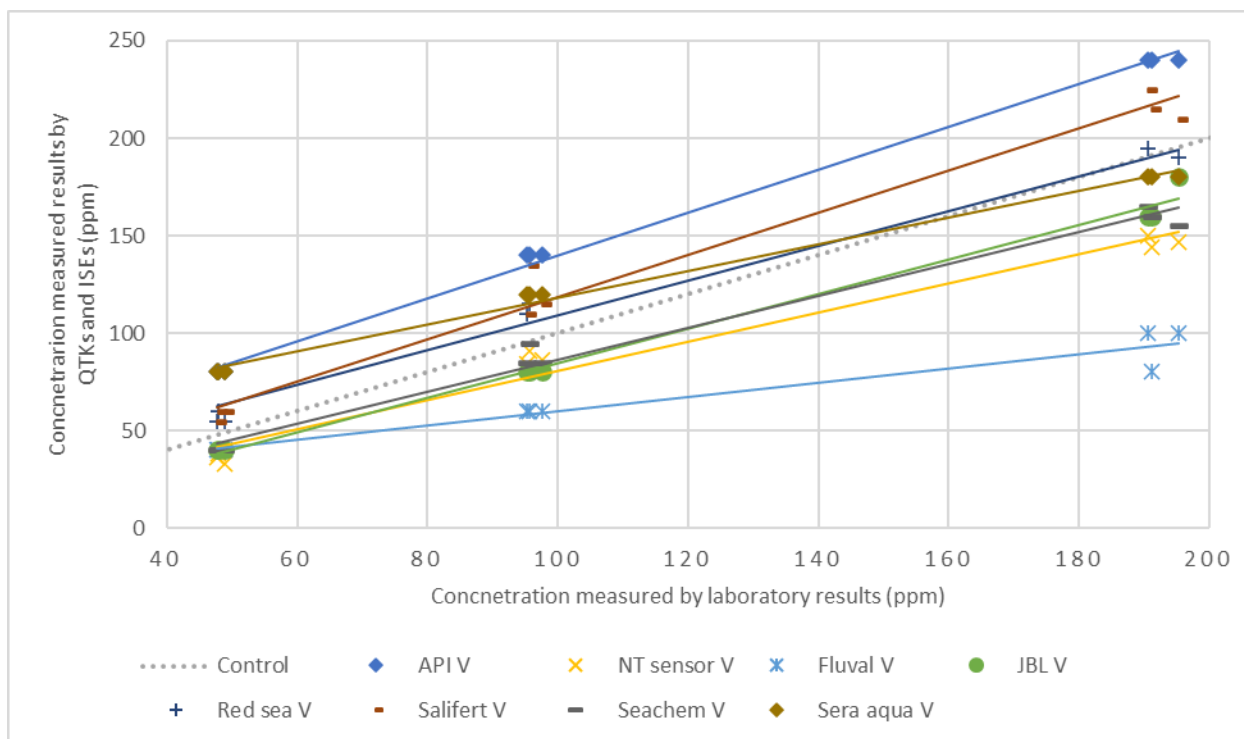


Figure A 36. Regression fits between laboratory analysis and the results of the **calcium** test kits and ISE for **Vegbloom** solution.

## 7.7. Magnesium (Mg<sup>2+</sup>) Tests

Table A 15. Results aquarium test kits for **magnesium** measurements of **Vegbloom** and **Hoagland** solutions at different concentrations followed by the percent error. Darker color indicates higher error.

Solution	Target value	Dilution	Laboratory results	JBL		Red Sea		Salifert		Seachem		Sera Aqua	
				Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
Hoagland	68	2:1	113.2	60	47	340	200.4	75	33.7	112.5	0.6	120	6
		2:1	93.7	60	36	120	28.1	45	52	75	20	120	28.1
		2:1	94.4	80	15.3	120	27.1	75	20.6	75	20.6	60	36.5
	34	1:1	56.6	60	6	160	182.7	0	100	75	32.5	60	6
		1:1	48.7	0	100	80	64.4	0	100	50	2.7	120	146.6
		1:1	47.2	40	15.3	60	27.1	0	100	37.5	20.6	60	27.1
	17	1:2	28.3	40	41.3	60	112	0	100	50	76.7	0	100.0
		1:2	24.3	20	17.8	30	23.3	0	100	25	2.7	120	393.1
		1:2	23.6	20	15.3	40	69.4	0	100	25	5.9	0	100.0
Vegbloom	57.56	2:1	60	20	66.6	60	0.2	0	100	50	16.5	60	0.2
		2:1	63	60	4	60	4.0	0	100	50	20.0	60	4
		2:1	61	20	67.3	60	1.9	0	100	50	18.2	60	1.9
	28.78	1:1	29.9	40	33.6	40	33.6	0	100	25	16.5	0	100.0
		1:1	31.3	40	28	40	28	0	100	37.5	20.0	0	100.0
		1:1	30.6	40	30.8	40	30.8	0	100	25	18.2	0	100.0
	14.39	1:2	15.0	20	33.6	20	33.6	0	100	25	67	0	100.0
		1:2	15.6	20	28	20	28	0	100	25	60	0	100.0
		1:2	15.3	20	30.8	20	30.8	0	100	12.5	18.2	0	100.0

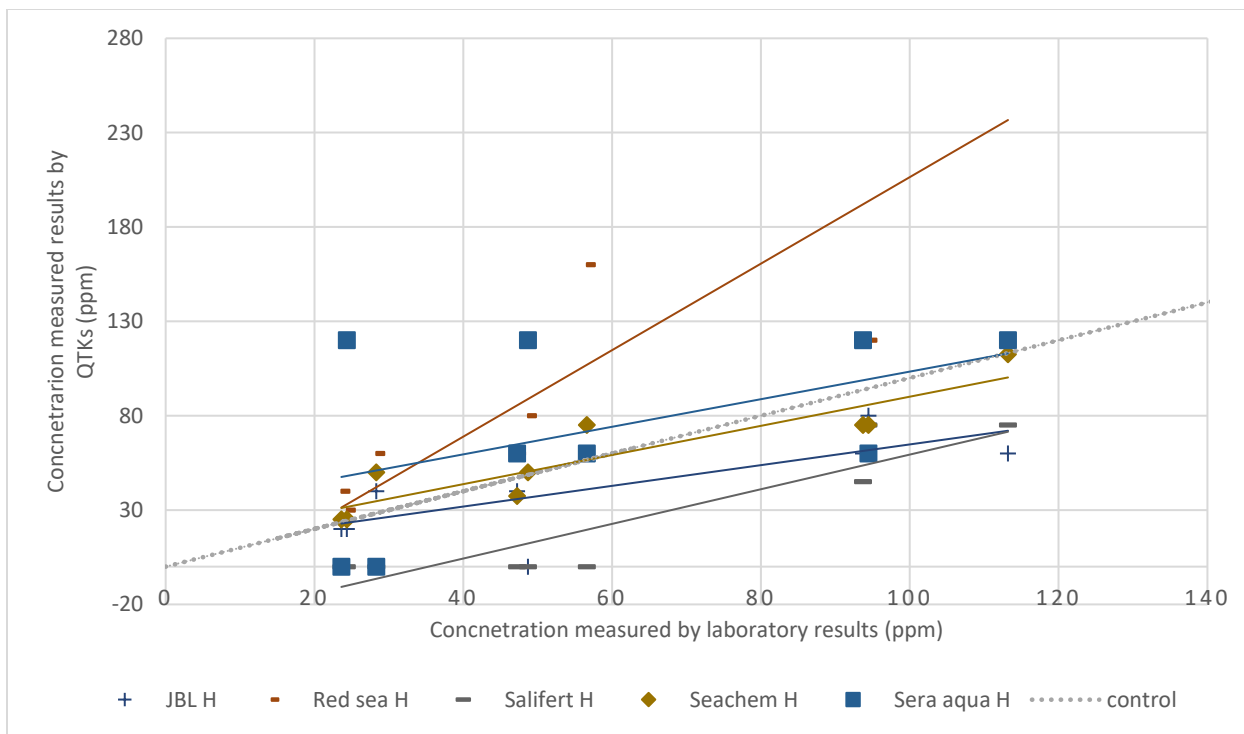


Figure A 37. Regression fits between laboratory analysis and the results of the **magnesium** test kits for **Hoagland** solution.

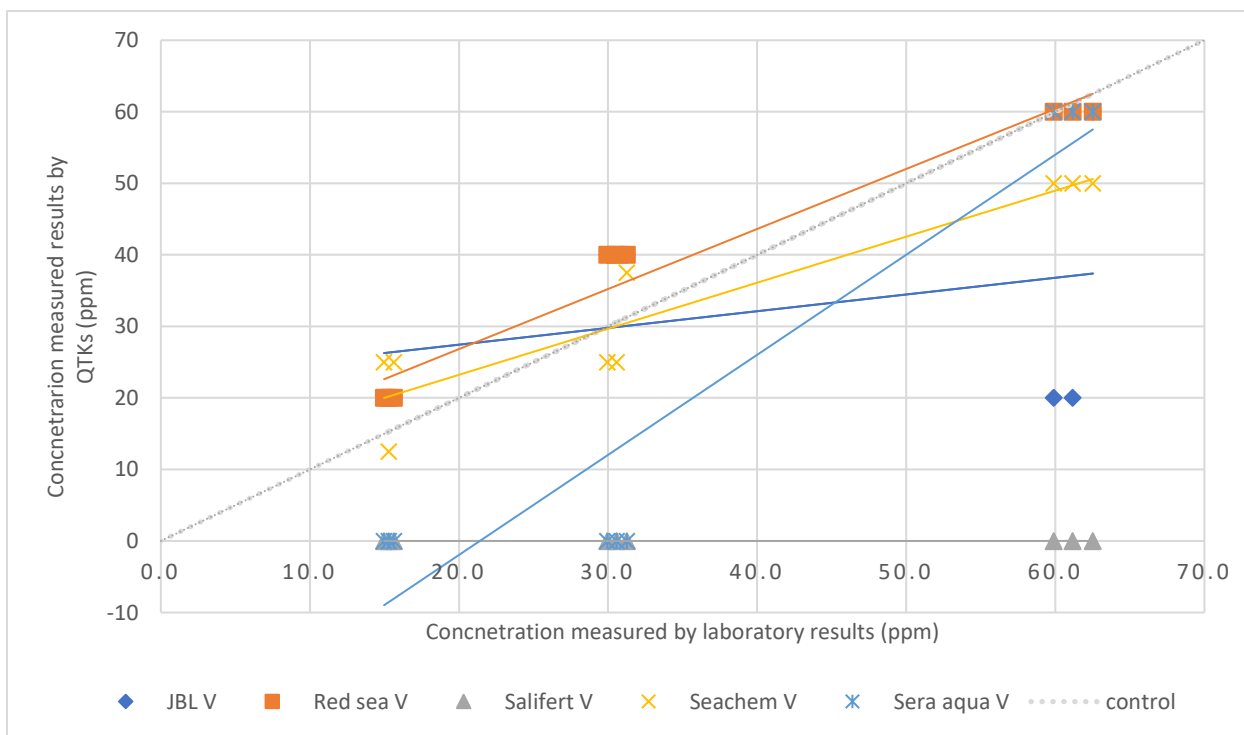


Figure A 38. Regression fits between laboratory analysis and the results of the **magnesium** test kits for **Vegbloom** solution.

## 7.8. Copper (Cu<sup>+</sup>, Cu<sup>2+</sup>) Tests

### Calibration

Table A 16. Linear regression parameters and R<sup>2</sup> values of calibration for Cu<sup>+</sup>, Cu<sup>2+</sup> test kits

	Identified wavelength	R <sup>2</sup>	Slope	Intercept
<b>Standard solution</b>				
API	450	0.99	0.21	-0.0001
JBL	602	1.00	0.33	0.002
Salifert	622	0.97	0.03	0.0004
Seachem	602	0.97	0.31	0.01
Sera Aqua	596	1.00	0.26	0.01

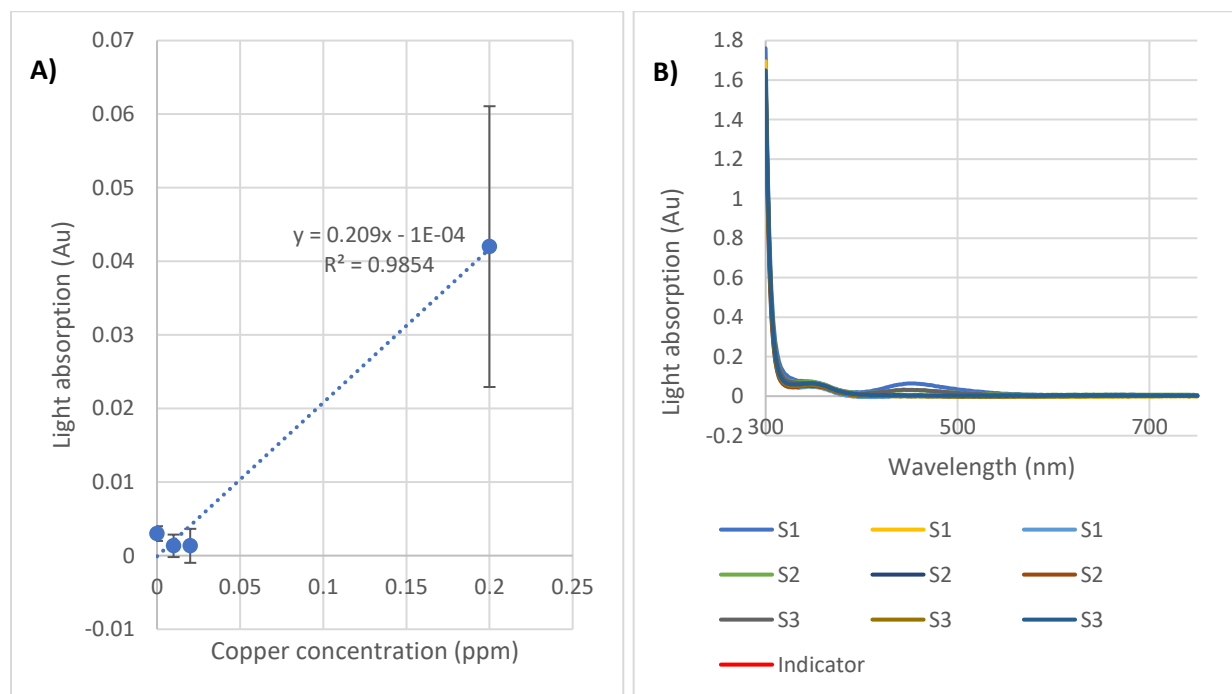


Figure A 39. Light absorption graph (A) and calibration curve (B) of copper API test kit.

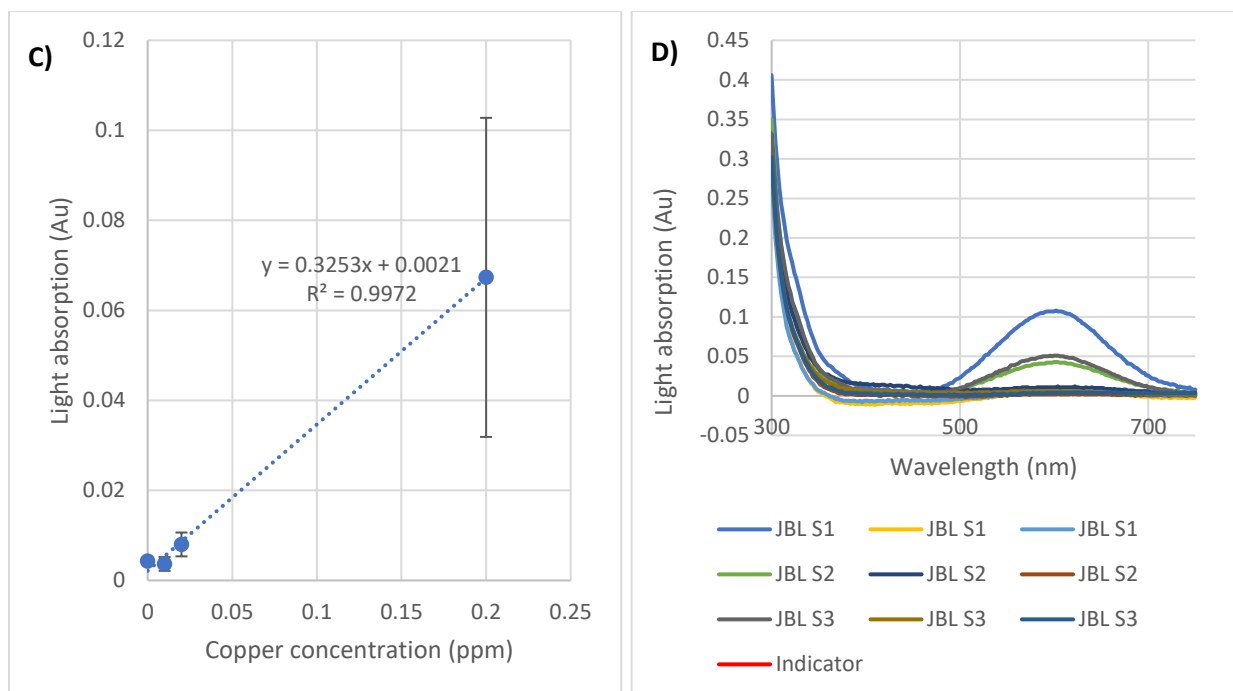


Figure A 40. Light absorption graph (C) and calibration curve (D) of copper JBL test kit

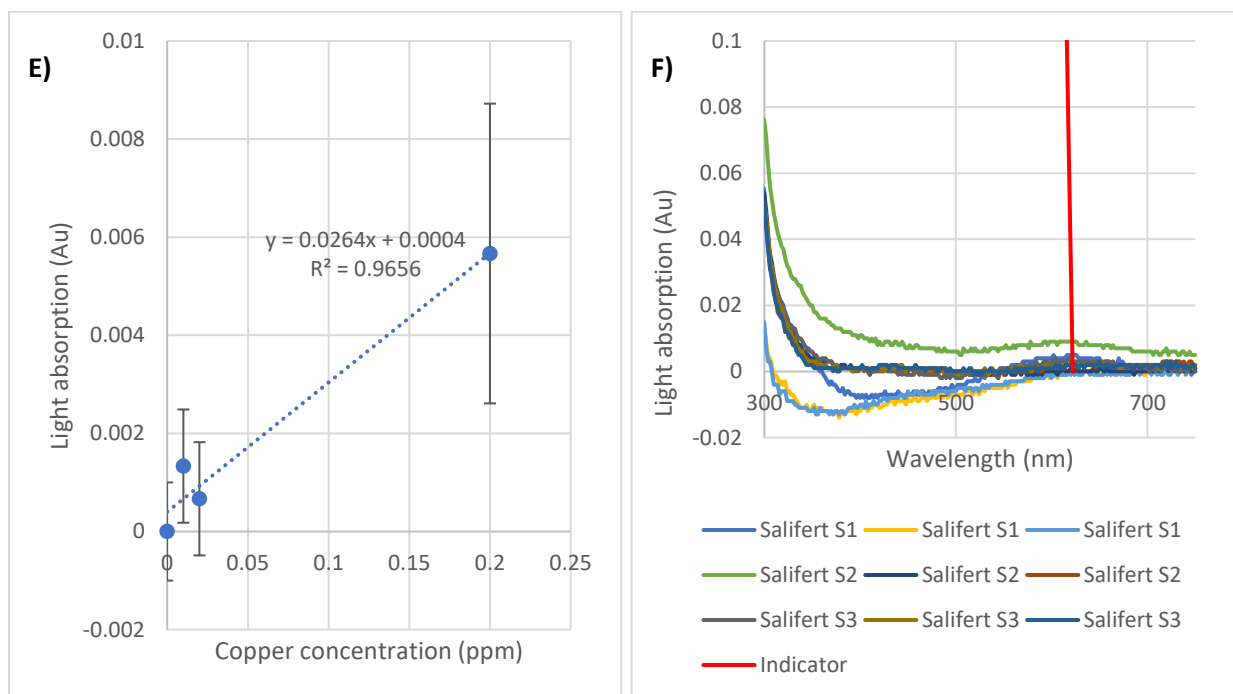


Figure A 41. Light absorption graph (E) and calibration curve (F) of copper Salifert test kit

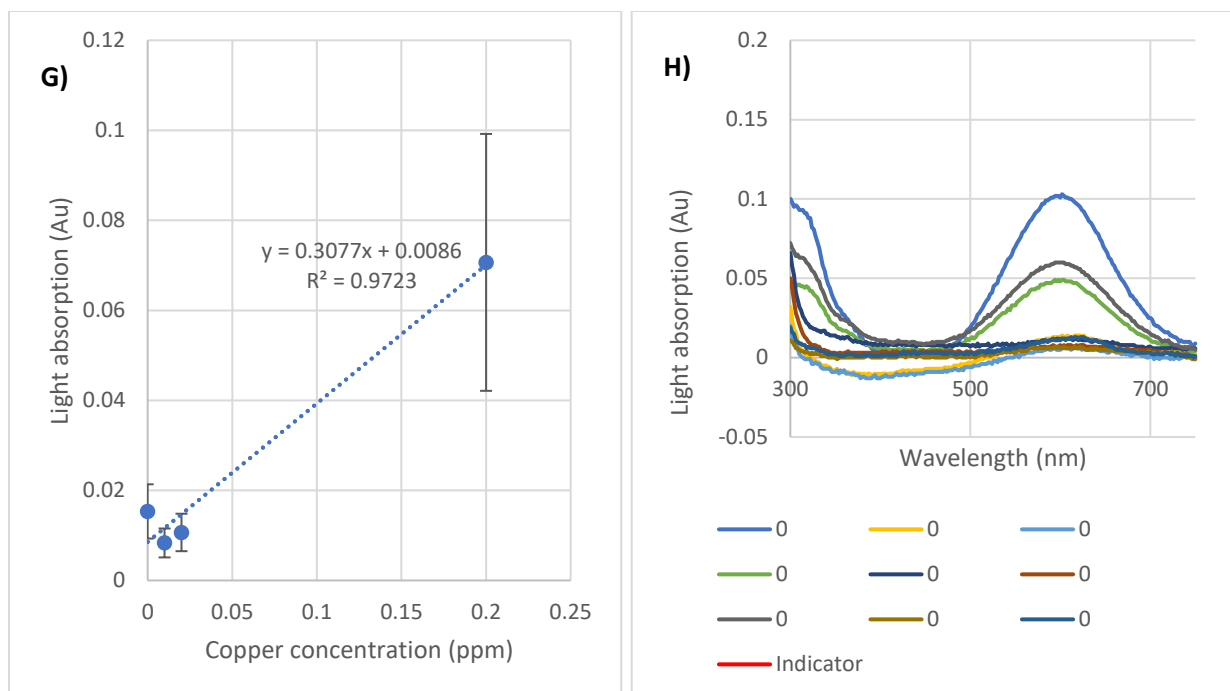


Figure A 42. Light absorption graph (G) and calibration curve (H) of copper Seachem test

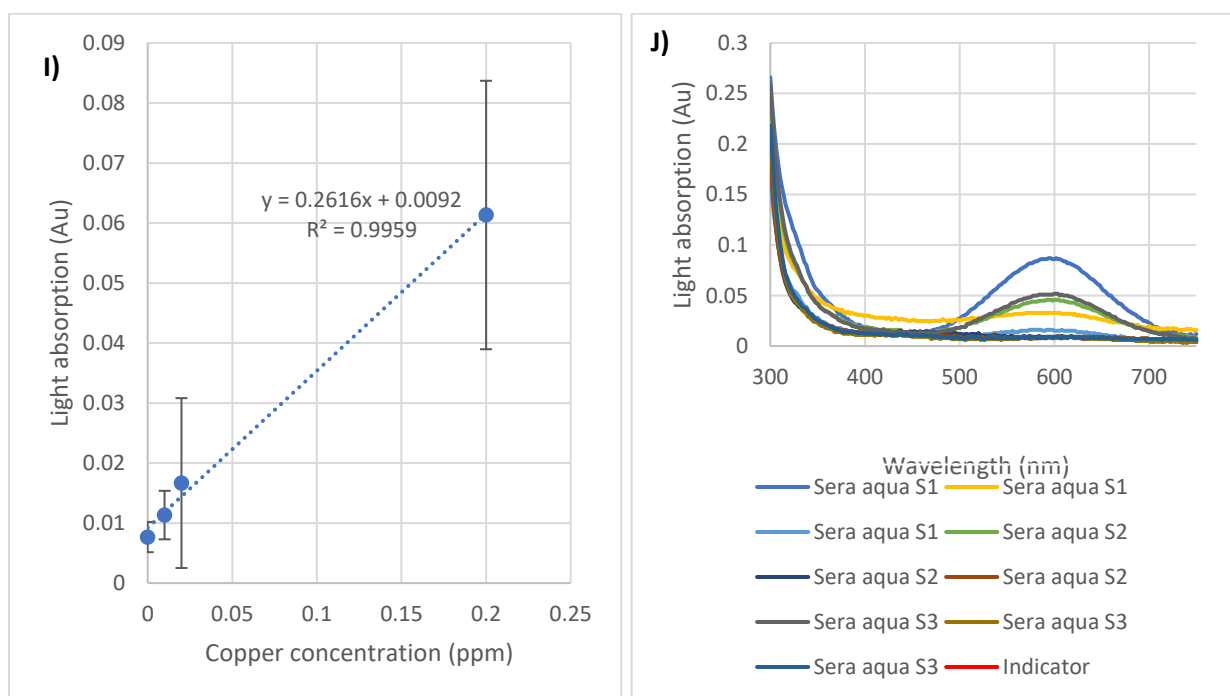


Figure A 43. Light absorption graph (I) and calibration curve (J) of copper Sera Aqua test kit.

Table A 17. Results aquarium test kits for **copper** measurements of **Vegbloom** and **Hoagland** solutions at different concentrations followed by the percent error. Darker color indicates higher error.

Solution	Target value	Dilution	Laboratory results	API		JBL		Salifert		Seachem		Sera Aqua	
				Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
Hoagland	0.04	2:01	0.04	0.10	162.0	0.03	24.1	0.17	336.1	0.67	1577.3	1.60	3911.4
		2:01	0.05	0.11	128.8	0.11	114.4	0.25	400.6	0.91	1716.3	1.15	2207.1
		2:01	0.05	0.11	128.8	0.16	218.9	0.33	552.3	0.92	1735.8	1.17	2230.0
	0.02	1:01	0.02	0.02	17.3	0.02	21.0	-0.05	365.6	0.30	1418.4	0.01	27.5
		1:01	0.025	0.05	89.6	0.09	279.6	0.25	901.2	0.47	1764.7	0.00	87.9
		1:01	0.025	0.06	147.0	0.09	255.0	0.40	1508.0	0.40	1517.7	0.03	34.4
	0.01	1:02	0.01	0.02	134.6	0.01	11.8	-0.02	251.9	0.00	85.6	0.02	121.4
		1:02	0.0125	0.11	815.1	0.07	437.9	0.17	1295.5	0.07	457.5	-0.01	198.1
		1:02	0.0125	0.09	623.7	0.10	683.8	0.06	385.3	0.07	457.5	-0.01	167.5
Vegbloom	0.1	2:01	0.08	0.21	156.6	0.03	62.1	0.52	544.7	0.75	836.2	0.03	67.5
		2:01	0.08	0.24	198.5	0.04	46.7	0.44	449.9	0.97	1112.4	0.03	58.0
		2:01	0.08	0.23	192.5	0.04	46.7	0.33	307.7	0.89	1010.8	0.04	48.4
	0.05	1:01	0.04	0.13	221.9	0.02	39.5	0.17	336.1	0.00	88.3	0.00	92.4
		1:01	0.04	0.13	221.9	0.02	54.9	0.17	336.1	-0.01	112.7	0.01	82.9
		1:01	0.04	0.13	233.8	0.02	54.9	0.29	620.5	0.00	104.5	0.02	44.6
	0.025	1:02	0.02	0.08	280.5	0.01	40.5	0.10	392.9	0.02	20.9	-0.01	142.2
		1:02	0.02	0.08	304.4	0.01	55.9	0.10	392.9	0.02	20.9	0.01	65.7
		1:02	0.02	0.09	328.4	0.01	55.9	0.21	961.8	0.01	27.8	0.00	103.9

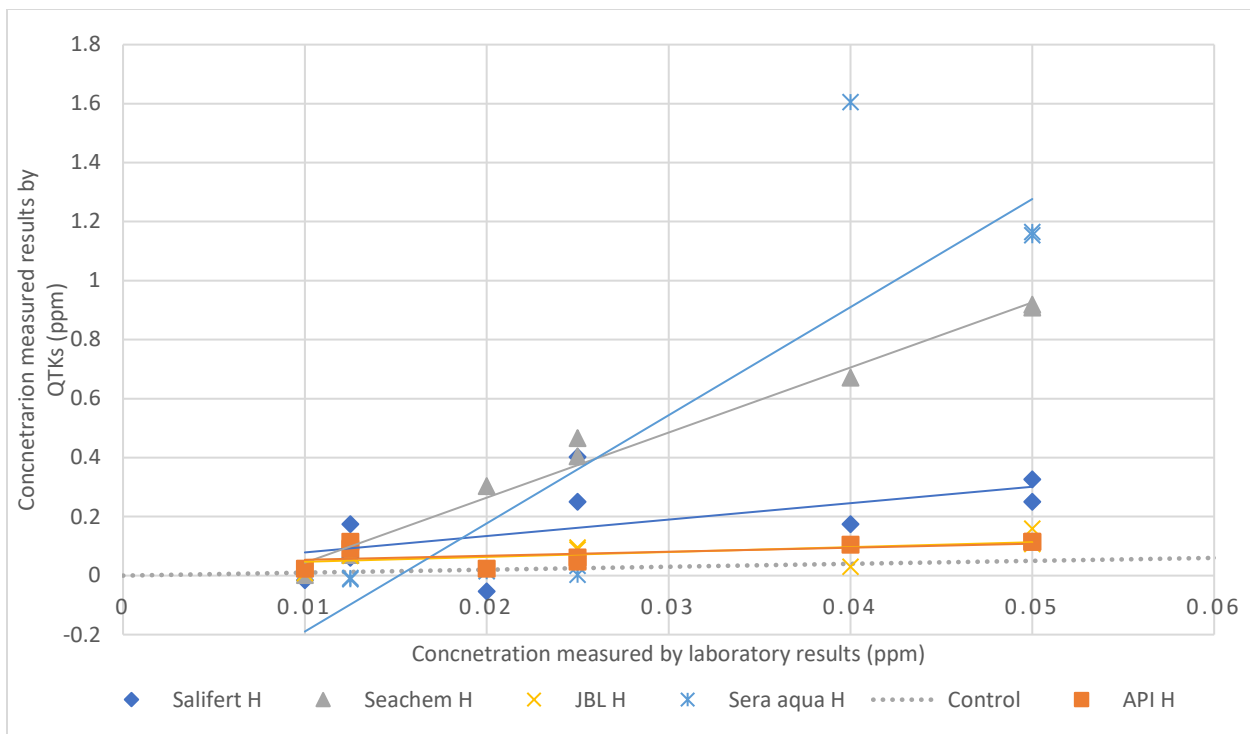


Figure A 44. Regression fits between laboratory analysis and the results of the **copper** test kits for **Hoagland** solution.

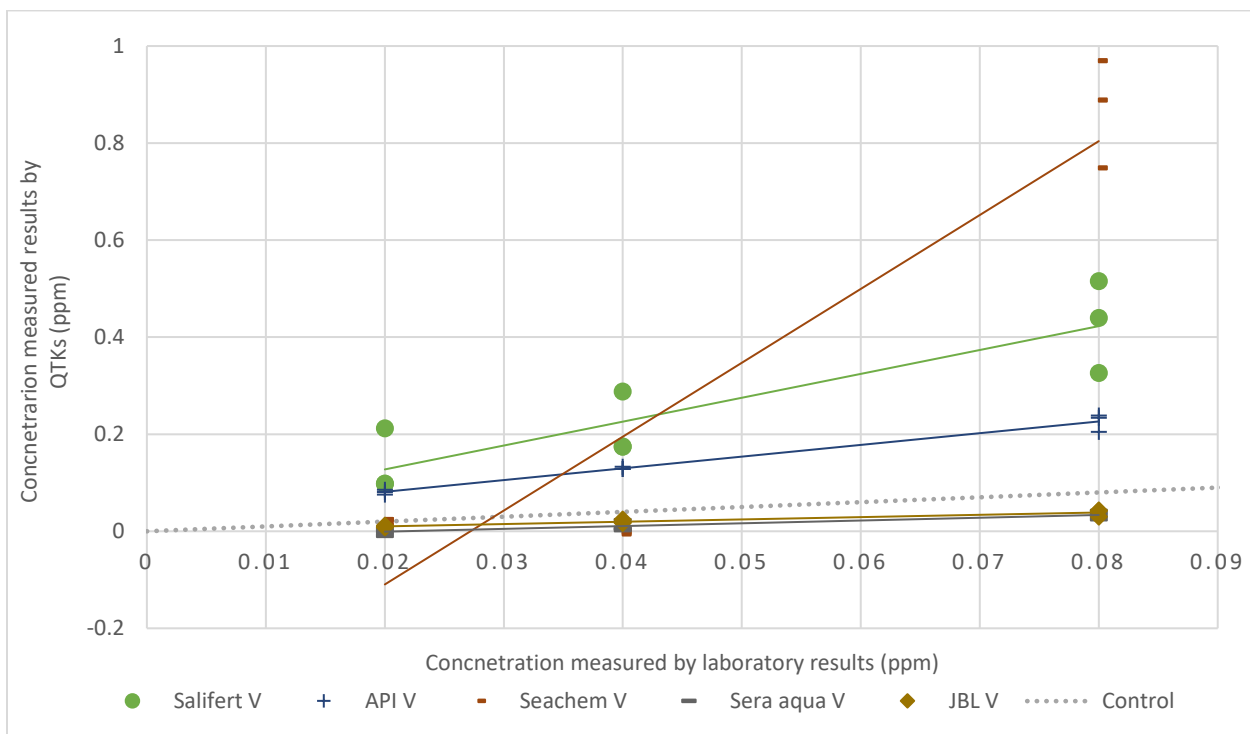


Figure A 45 Regression fits between laboratory analysis and the results of the **copper** test kits for **Vegbloom** solution.



## 7.9.Iron (Fe<sup>2+</sup>, Fe<sup>3+</sup>) Tests

### Calibration

Table A 18. Linear regression parameters and R<sup>2</sup> values of calibration for Fe<sup>2+</sup>, Fe<sup>3+</sup> test kits.

	Identified wavelength	R <sup>2</sup>	Slope	Intercept
<b>Standard solution</b>				
Fluval	596	0.960437	0.380676	0.013606
JBL	560	0.977347	0.446285	0.013498
Red Sea	524	0.958548	0.154244	0.00989
Seachem	560	0.983354	0.190602	0.040664
Sera Aqua	564	0.983021	0.489574	0.004132

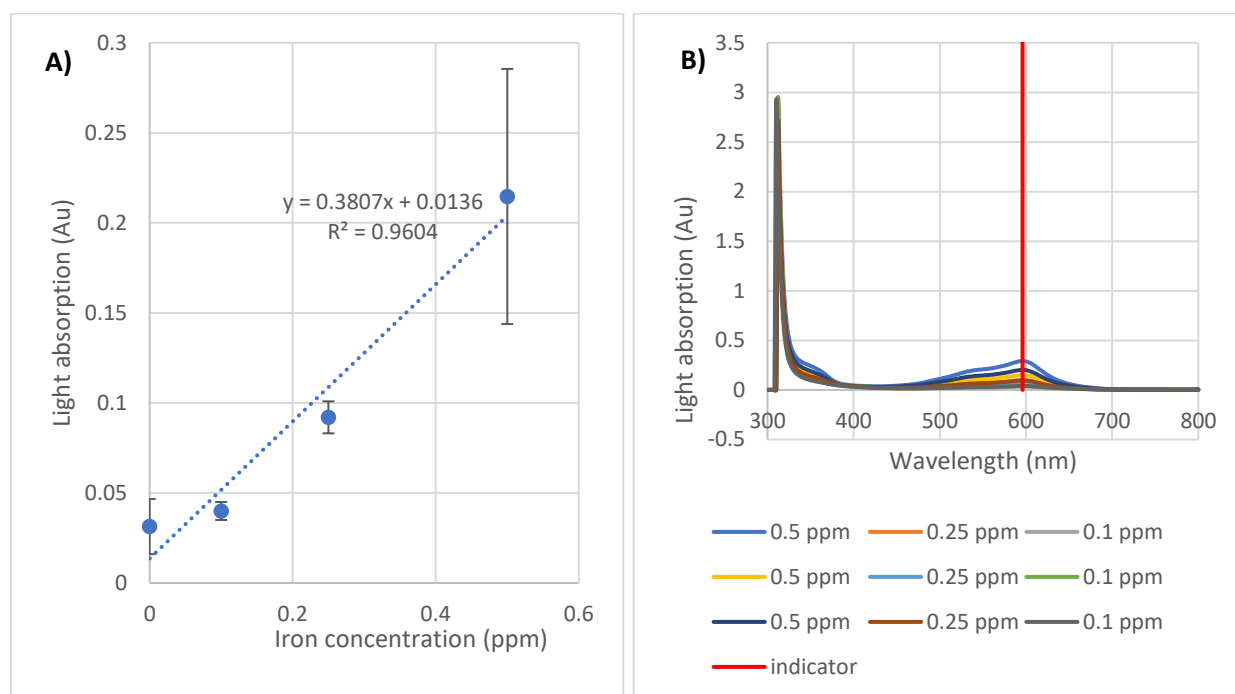


Figure A 46. Light absorption graph (A) and calibration curve (B) of iron Fluval test kit.

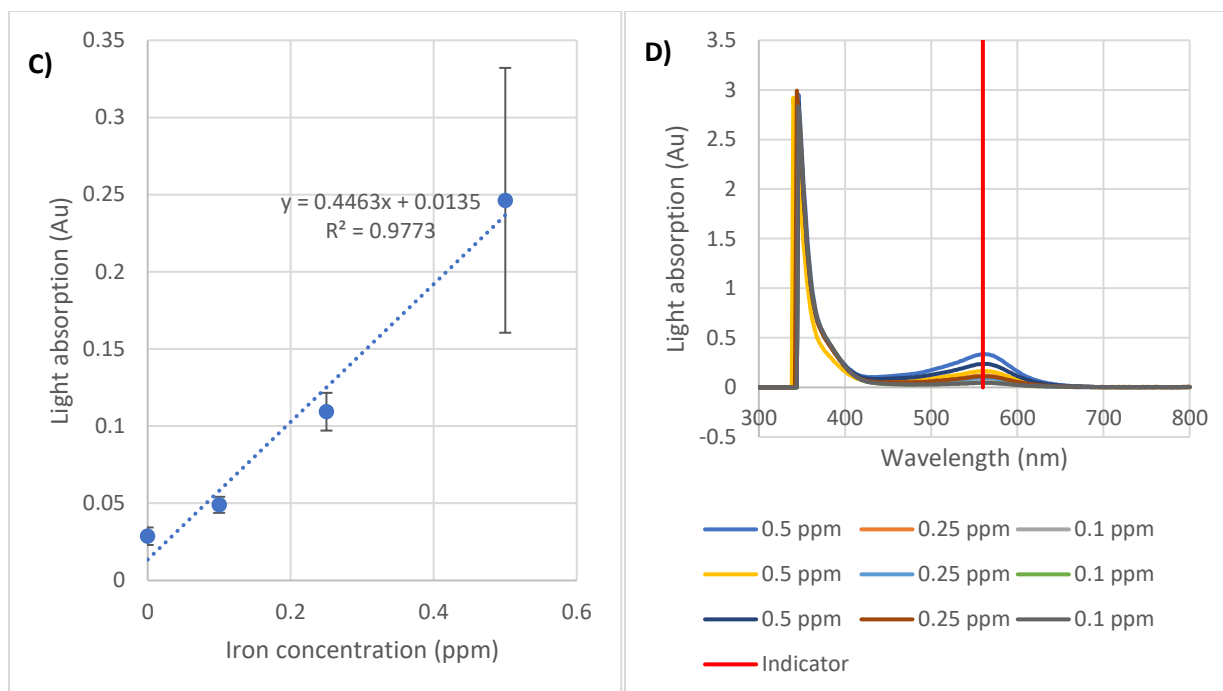


Figure A 47. Light absorption graph (C) and calibration curve (D) of iron JBL test kit.

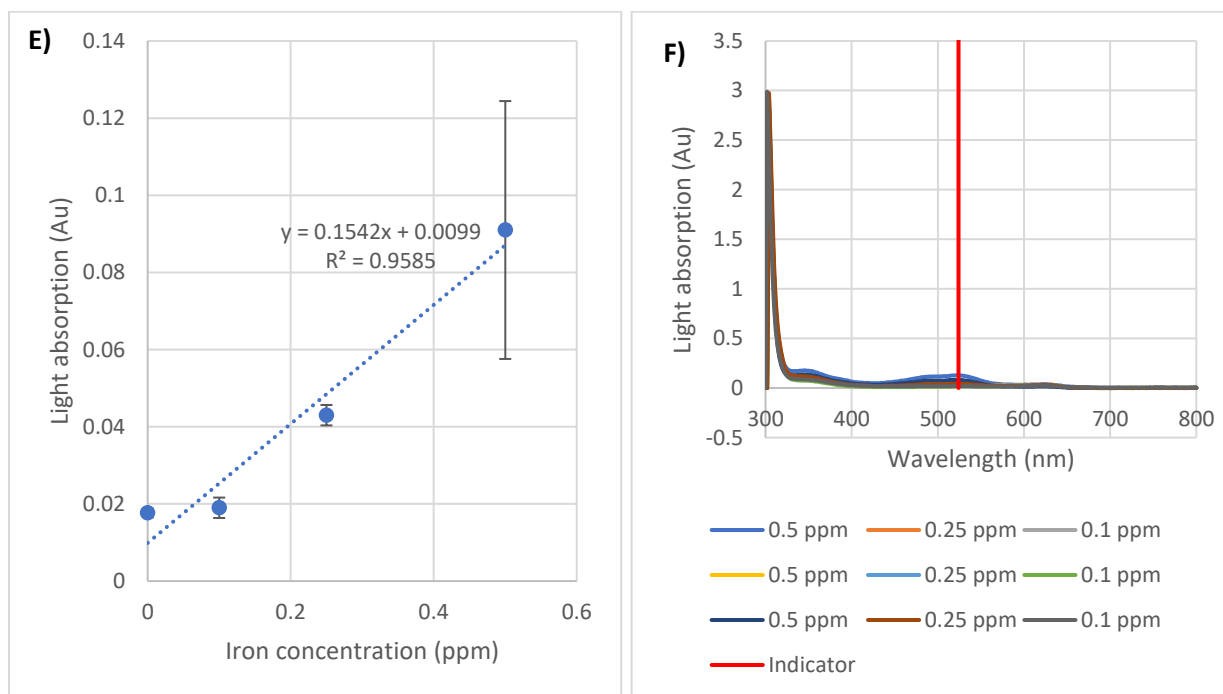


Figure A 48. Light absorption graph (E) and calibration curve (F) of iron Red Sea test kit.

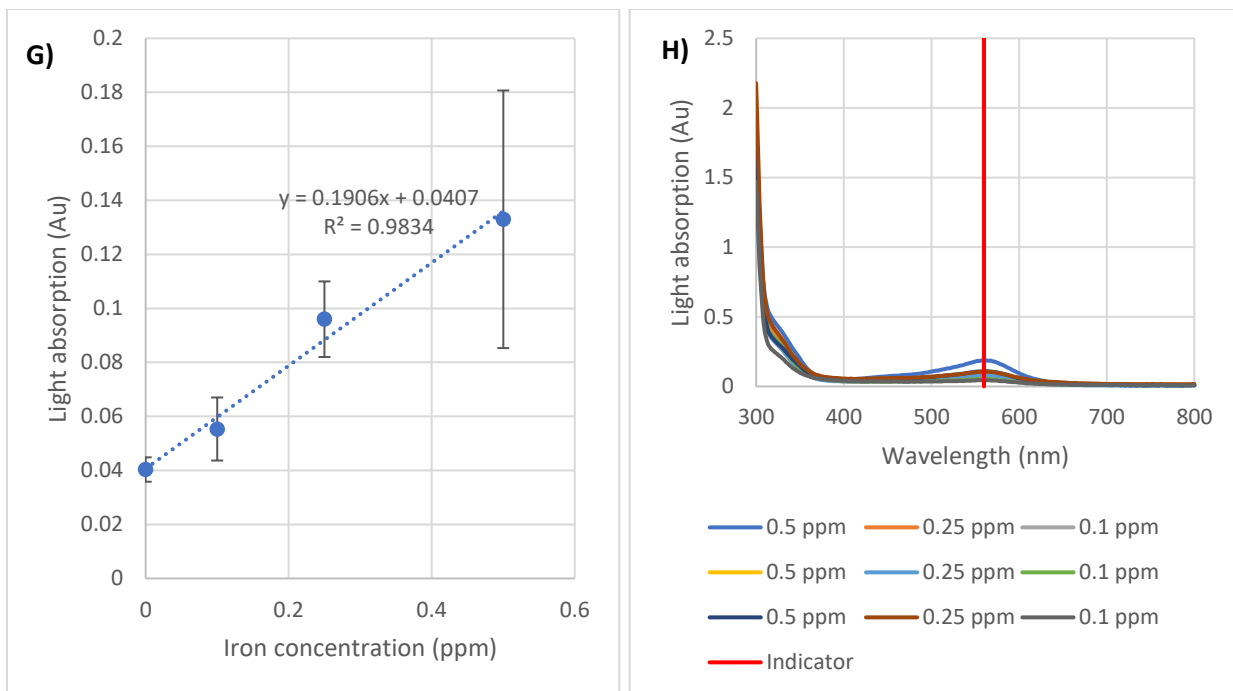


Figure A 49. Light absorption graph (G) and calibration curve (H) of iron Seachem test kit.

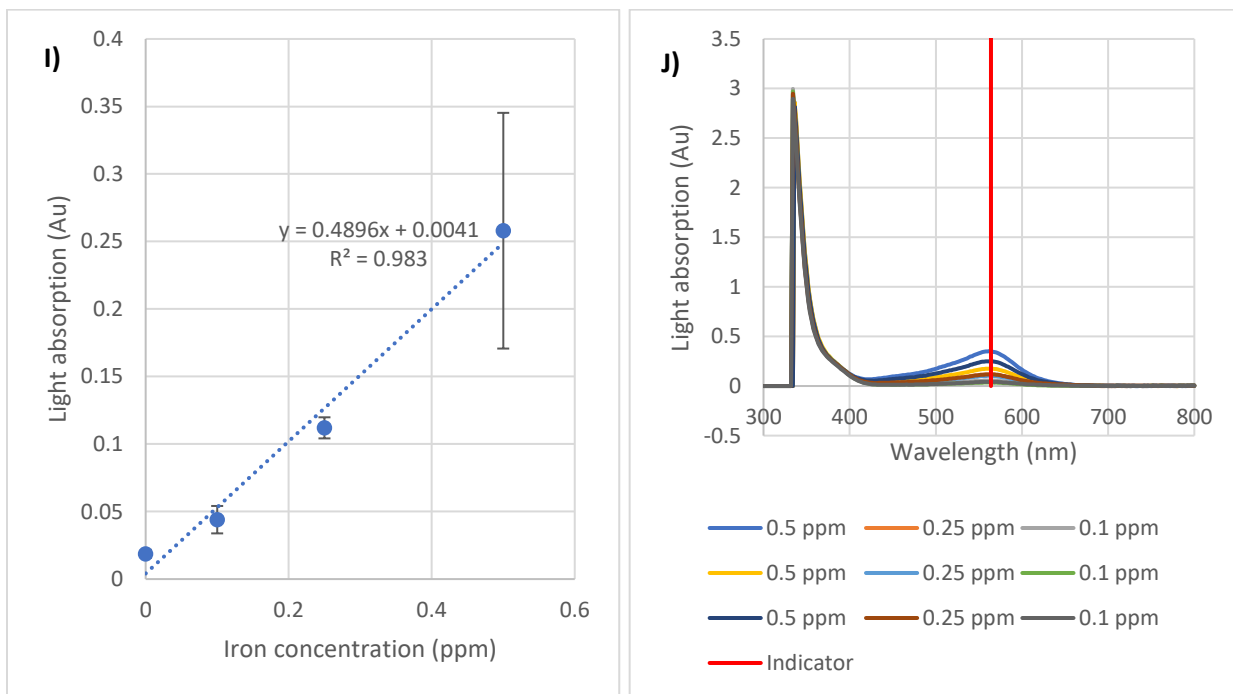


Figure A 50. Light absorption graph (I) and calibration curve (J) of iron Sera Aqua test kit.

Table A 19. Results of aquarium test kits for **iron** measurements of **Vegbloom** and **Hoagland** solution at different concentrations followed by the percent error. Darker color indicates higher error.

Solution	Target value	Dilution	Laboratory results	Fluval		JBL		Red Sea		Seachem		Sera Aqua	
				Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
Hoagland	1.25	1:2	0.42	0.395	5.9	0.523	24.6	0.448	6.7	0.154	63.4	0.484	15.2
		1:2	0.38	0.513	35.1	0.588	54.8	0.558	46.9	0.049	87.2	0.551	45.1
		1:2	0.42	0.508	21.0	0.577	37.4	0.571	36.0	0.101	75.9	0.535	27.4
	0.5	1:5	0.17	0.182	7.2	0.210	23.2	0.195	14.8	-0.082	148.5	0.206	21.2
		1:5	0.15	0.188	25.0	0.218	45.6	0.221	47.4	-0.035	123.4	0.204	36.0
		1:5	0.17	0.190	11.9	0.214	25.9	0.228	33.9	-0.004	102.2	0.218	28.4
	0.25	1:10	0.08	0.080	0.2	0.093	16.2	0.078	1.9	-0.077	196.4	0.106	32.5
		1:10	0.08	0.085	6.4	0.100	24.6	0.143	79.2	-0.098	222.6	0.100	24.8
		1:10	0.08	0.090	12.9	0.100	24.6	0.098	22.4	-0.072	189.8	0.104	30.0
Vegbloom	0.39	1:3	0.42	0.461	9.7	0.505	20.3	0.424	1.0	0.038	90.9	0.470	11.8
		1:3	0.44	0.466	5.5	0.514	16.4	0.455	3.0	0.075	83.0	0.478	8.2
		1:3	0.41	0.440	6.8	0.492	19.5	0.424	3.0	0.049	88.1	0.449	9.1
	0.24	1:5	0.25	0.282	11.9	0.319	26.7	0.301	19.5	-0.025	109.8	0.288	14.2
		1:5	0.27	0.282	6.5	0.324	22.2	0.306	15.6	-0.009	103.4	0.296	11.7
		1:5	0.25	0.261	5.7	0.301	22.0	0.286	15.7	0.007	97.2	0.280	13.2
	0.12	1:10	0.13	0.161	28.0	0.180	43.2	0.199	57.9	-0.025	119.6	0.106	15.9
		1:10	0.13	0.161	21.7	0.176	32.7	0.214	61.7	-0.025	118.6	0.169	27.8
		1:10	0.12	0.177	43.4	0.167	35.2	0.194	56.9	-0.025	120.0	0.149	20.6

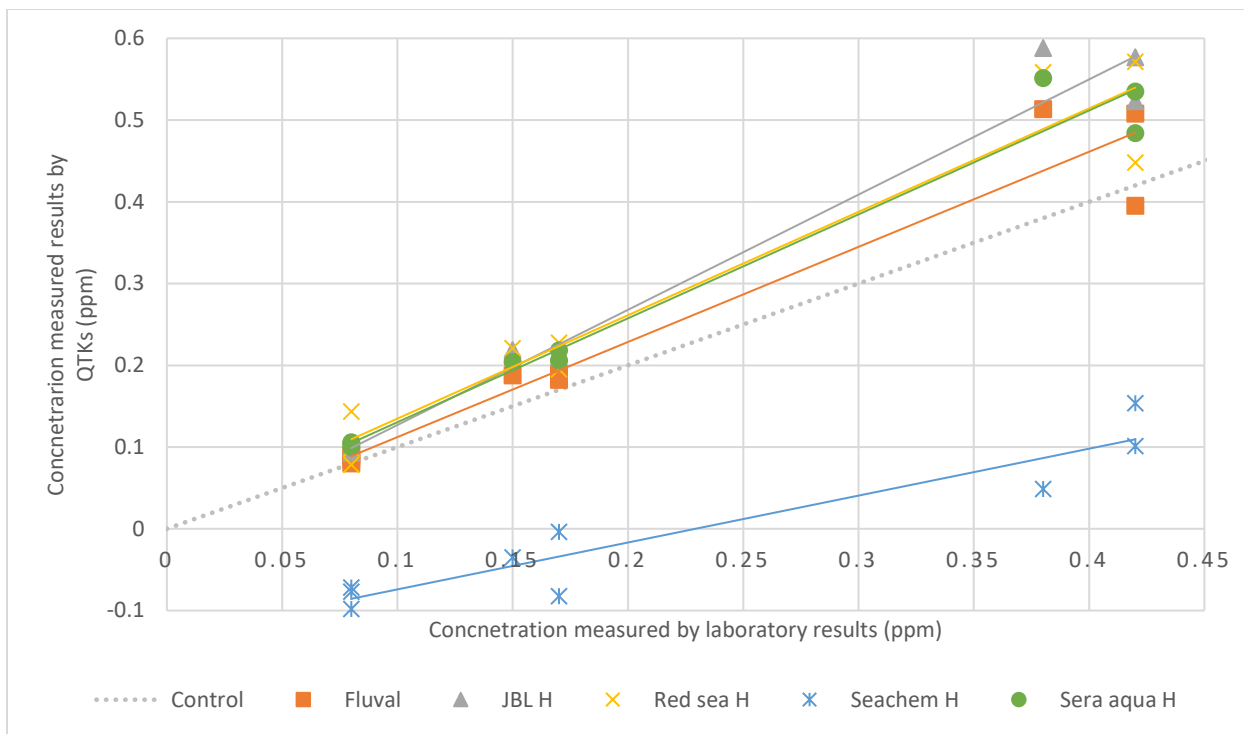


Figure A 51. Regression fits between laboratory analysis and the results of the **iron** test kits for **Hoagland** solution.

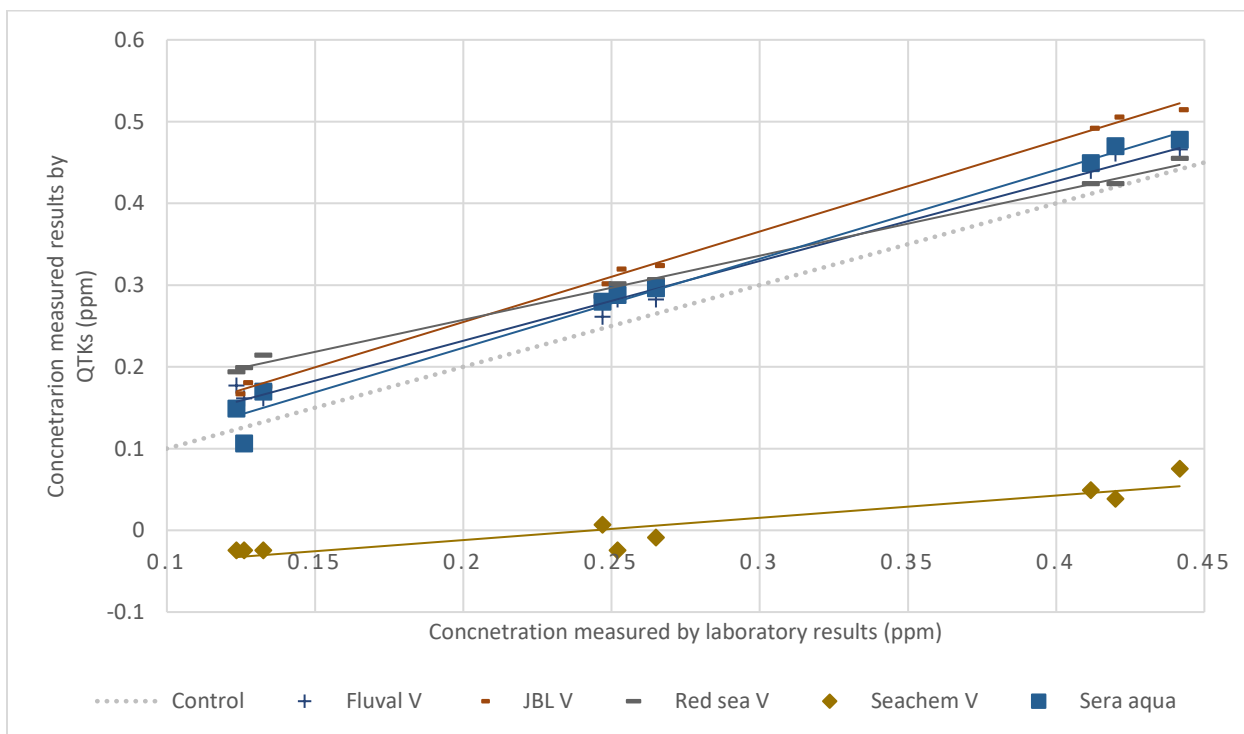


Figure A 52. Regression fits between laboratory analysis and the results of the **iron** test kits for **Vegbloom** solution.

## 7.10. pH Tests

### Calibration

Table A 20. Linear regression parameters and  $R^2$  values of calibration for pH test kits.

	Identified wavelength	$R^2$	Slope	Intercept
<b>Standard solution</b>				
API	616	0.903	0.428	-2.570
Fluval	616	0.900	0.522	-3.125
JBL	616	0.856	0.093	-0.533
Sera Aqua	616	0.866	0.140	-0.800

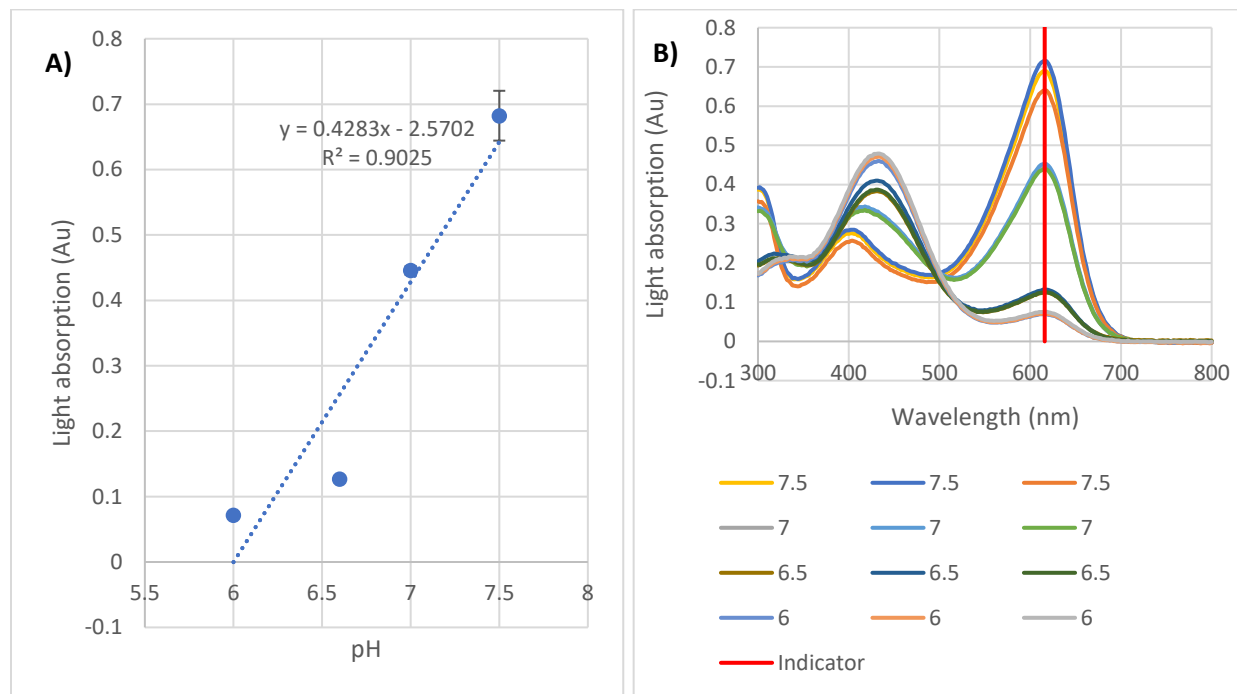


Figure A 53. Light absorption graph (A) and calibration curve (B) of pH API test kit

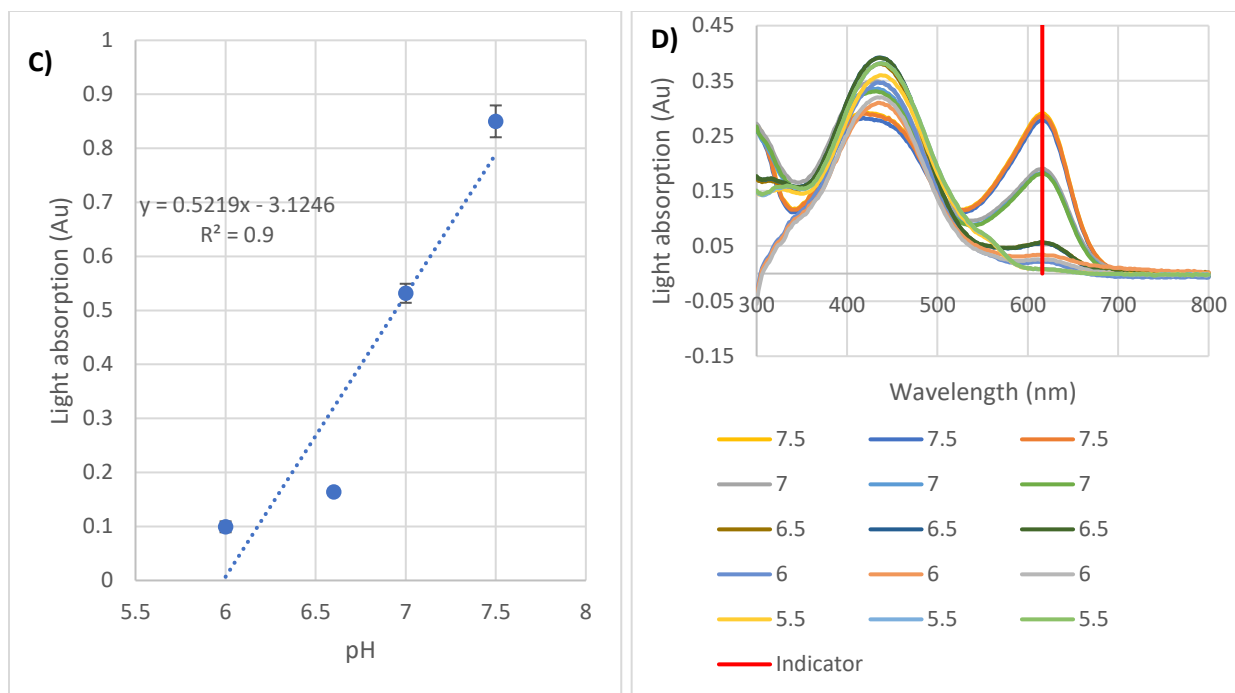


Figure A 54. Light absorption graph (C) and calibration curve (D) of pH Fluval test kit

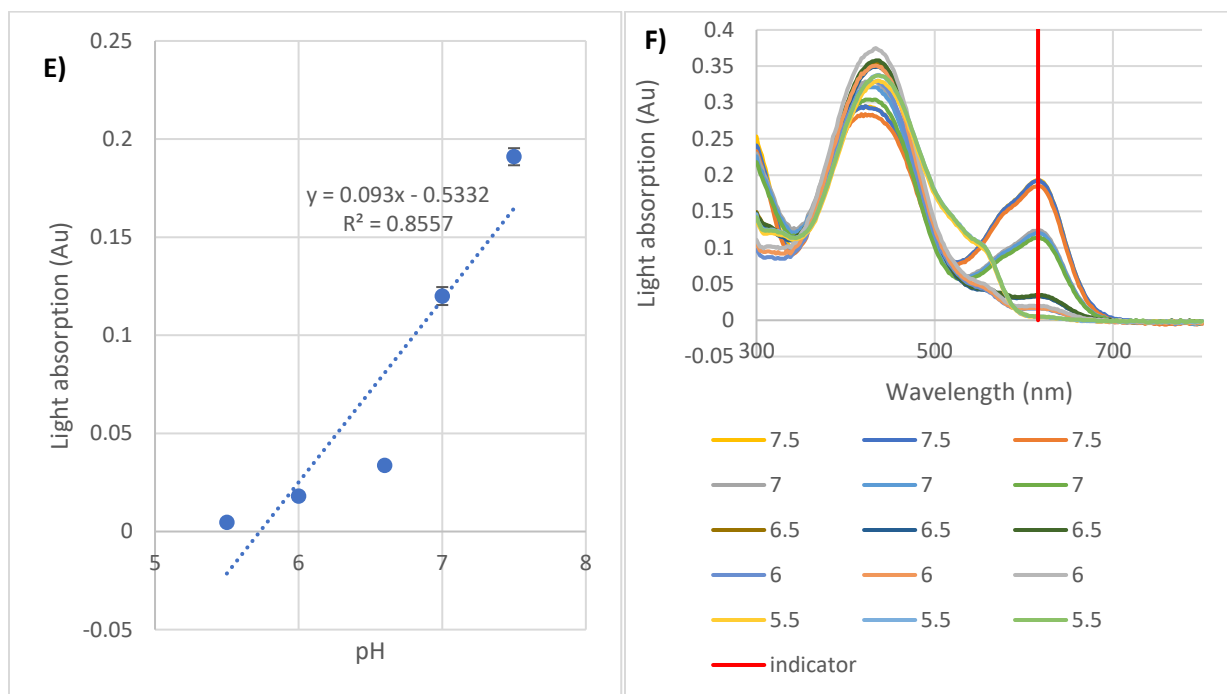


Figure A 55. Light absorption graph (E) and calibration curve (F) of pH JBL test kit

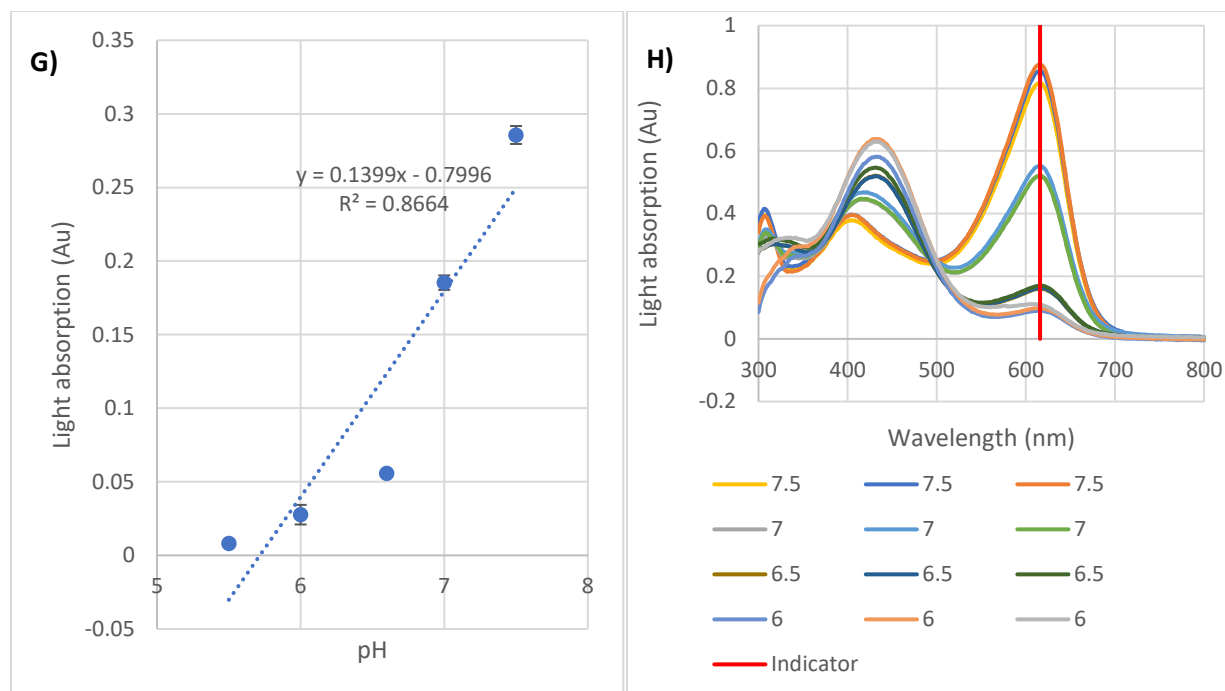


Figure A 56. Light absorption graph (G) and calibration curve (H) of pH Sera Aqua test kit.



Table A 21. Results of API, Fluval, JBL, Sera Aqua test kits and NT sensor ISE for **pH** measurements of **Vegbloom** and **Hoagland** solution at different concentrations followed by the percent error. Darker color indicates higher error.

Solution	Target value	API		Fluval		JBL		Sera Aqua		NT sensor	
		Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %	Measured value (ppm)	Percent error %
Hoagland	5.99	6.37	6.42	6.32	5.58	6.21	3.74	6.22	3.78	6.01	0.33
	6.04	6.32	4.69	6.31	4.55	6.12	1.28	6.14	1.74	6.03	0.17
	5.98	6.36	6.40	6.38	6.65	6.19	3.55	6.17	3.24	6.18	3.34
	6.48	6.74	4.06	6.71	3.51	6.74	4.02	6.77	4.43	6.52	0.62
	6.51	6.81	4.59	6.78	4.21	6.72	3.21	6.70	2.96	6.49	0.31
	6.5	6.81	4.71	6.85	5.46	6.81	4.69	6.85	5.32	6.51	0.15
	7	7.37	5.31	7.40	5.76	7.61	8.73	7.67	9.54	7.00	0.00
	6.98	7.39	5.84	7.32	4.93	7.47	7.04	7.49	7.29	6.94	0.57
	7.01	7.33	4.59	7.30	4.18	7.58	8.12	7.80	11.22	7.02	0.14
	7.5	7.74	3.14	7.82	4.33	8.19	9.22	8.34	11.20	7.34	2.13
	7.49	7.67	2.47	7.77	3.75	8.21	9.65	8.20	9.43	7.34	2.00
	7.51	7.75	3.19	7.94	5.77	8.35	11.22	8.45	12.48	7.11	5.33
Vegbloom	5.99	6.34	5.91	6.37	6.35	6.21	3.74	6.22	3.78	6.01	0.33
	5.99	6.40	6.93	6.42	7.24	6.30	5.18	6.34	5.81	5.91	1.34
	6.02	6.56	8.99	6.44	6.96	6.33	5.19	6.32	5.04	5.98	0.66
	6.51	6.79	4.34	6.85	5.24	6.75	3.71	6.80	4.39	6.40	1.69
	6.5	6.79	4.39	6.84	5.26	6.79	4.53	6.81	4.77	6.37	2.00
	6.52	6.89	5.61	6.90	5.76	6.99	7.18	7.05	8.17	6.44	1.23
	7.01	7.22	2.99	7.37	5.11	7.54	7.50	7.67	9.38	6.89	1.71
	7	7.36	5.14	7.40	5.73	7.57	8.12	7.70	10.05	6.92	1.14
	6.99	7.46	6.79	7.56	8.13	7.80	11.66	7.81	11.74	6.90	1.29
	7.49	7.67	2.41	7.82	4.47	8.23	9.94	8.18	9.24	7.36	1.74
	7.49	7.74	3.28	7.88	5.18	8.21	9.65	8.38	11.92	7.42	0.93
	7.5	7.72	2.99	7.96	6.12	8.56	14.09	8.05	7.38	7.46	0.53

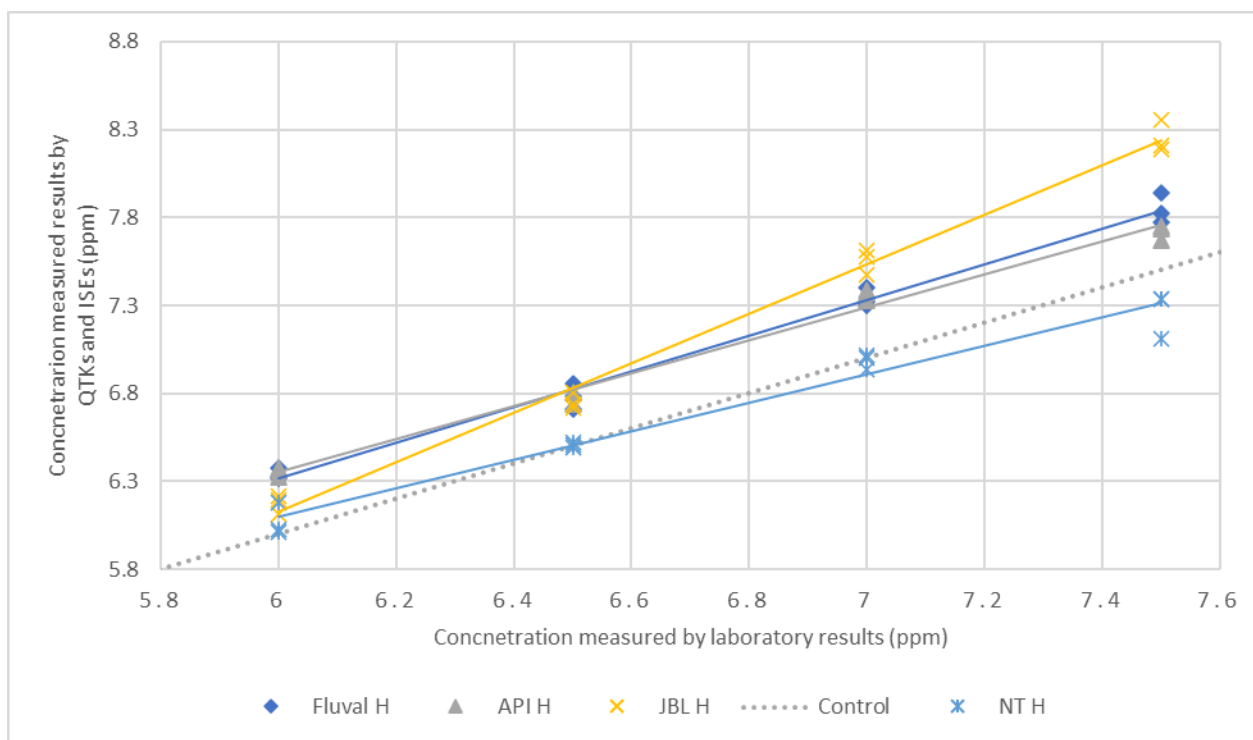


Figure A 57. Regression fits between laboratory analysis and the results of the **pH** test kits and ISE for **Hoagland** solution.

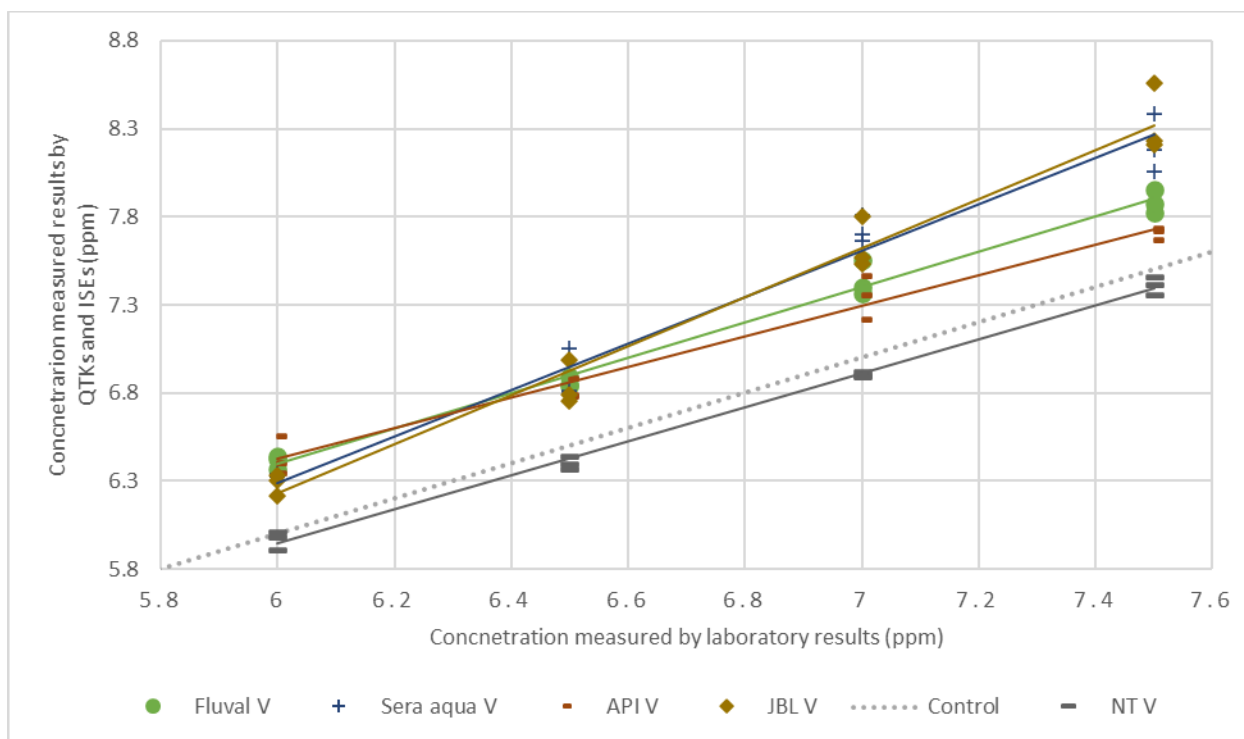


Figure A 58. Regression fits between laboratory analysis and the results of the **pH** test kits and ISE for **Vegbloom** solution.

Table A 22. The price paid for colorimetric tests. February 2022. Exchange rate history in January 2022 (www.exchange-rates.org)

<b>Ion</b>	<b>Brand</b>	<b>Test Kit Name</b>	<b>Number of tests</b>	<b>Cost</b>	<b>Price per measurement</b>	<b>Notes</b>
Ammonia	API	Ammonia test kit	130	CAD 19.99	CAD 0.15	
Ammonia	Fluval	Ammonia test kit	50	CAD 11.16	CAD 0.22	
Ammonia	JBL	PROAQUATEST NH <sub>4</sub> <sup>+</sup>	50	CAD 26.19	CAD 0.52	
Ammonia	Red Sea	Marine care multi test kit	50	CAD 53.20	CAD 0.15	Price for Marine care multi test kit including NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , pH and KH, with 355 tests in total
Ammonia	Salifert	NH <sub>4</sub> <sup>+</sup> Profi test	50	CAD 12.43	CAD 0.25	
Ammonia	Sera Aqua	Sera ammonium/ammonia-test	60	CAD 16.65	CAD 0.28	
Copper	API	Copper test kit	90	CAD 8.09	CAD 0.09	
Copper	JBL	PROAQUATEST Cu Copper	50	CAD 19.48	CAD 0.39	
Copper	Salifert	Cu Profi test	50	CAD 14.97	CAD 0.30	
Copper	Seachem	MultiTest™ Copper	75	CAD 16.50	CAD 0.22	
Copper	Sera Aqua	Sera copper-test (Cu)	50	CAD 15.59	CAD 0.31	
Iron	Fluval	Iron test kit	50	CAD 10.66	CAD 0.21	
Iron	JBL	PROAQUATEST Fe Iron	50	CAD 23.61	CAD 0.47	
Iron	Red Sea	Trace-Colors pro multi test kit	50	CAD 72.99	CAD 0.52	Price for Trace-Colors pro multi test kit including Fe, I <sub>2</sub> and K, with 140 tests in total
Iron	Seachem	MultiTest™ Iron	75	CAD 16.50	CAD 0.22	
Iron	Sera Aqua	Sera iron-test (Fe)	75	CAD 19.22	CAD 0.26	
Nitrate	API	Nitrate test kit	90	CAD 19.99	CAD 0.22	
Nitrate	Fluval	Nitrate test kit	80	CAD 18.99	CAD 0.24	
Nitrate	JBL	PROAQUATEST NO <sub>3</sub> <sup>-</sup> Nitrate	40	CAD 36.72	CAD 0.92	
Nitrate	Red Sea	Marine care multi test kit	50	CAD 53.20	CAD 0.15	Price for Marine care multi test kit including NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , pH and KH, with 355 tests in total
Nitrate	Salifert	NO <sub>3</sub> <sup>-</sup> Profi test	60	CAD 15.35	CAD 0.26	

<b>Ion</b>	<b>Brand</b>	<b>Test Kit Name</b>	<b>Number of tests</b>	<b>Cost</b>	<b>Price per measurement</b>	<b>Notes</b>
Nitrate	Seachem	MultiTest™ Nitrite/Nitrate	70	CAD 20.31	CAD 0.29	Price for MultiTest™ Nitrite/Nitrate test kit including NO <sub>3</sub> <sup>-</sup> and NO <sub>2</sub> <sup>-</sup>
Nitrate	Sera Aqua	Sera nitrate-test (NO <sub>3</sub> <sup>-</sup> )	60	CAD 14.51	CAD 0.24	
Nitrite	API	Nitrite test kit	180	CAD 19.99	CAD 0.11	
Nitrite	Fluval	Nitrite test kit	75	CAD 14.99	CAD 0.20	
Nitrite	Red Sea	Marine care multi test kit	50	CAD 53.20	CAD 0.15	Price for Marine care multi test kit including NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , pH and KH, with 355 tests in total
Nitrite	Seachem	MultiTest™ Nitrite/Nitrate	70	CAD 20.31	CAD 0.29	Price for MultiTest™ Nitrite/Nitrate test kit including NO <sub>3</sub> <sup>-</sup> and NO <sub>2</sub> <sup>-</sup>
Nitrite	Sera Aqua	Sera nitrite-Test (NO <sub>2</sub> <sup>-</sup> )	75	CAD 12.11	CAD 0.16	
pH	API	PH test kit	250	CAD 6.34	CAD 0.03	
pH	Fluval	pH Low Range Test	225	CAD 8.12	CAD 0.04	
pH	JBL	PROAQUATEST pH 3.10-10.0	50	CAD 14.76	CAD 0.30	
pH	Sera Aqua	Sera pH-Test	100	CAD 9.10	CAD 0.09	
Phosphate	API	PHOSPHATE test kit	150	CAD 24.99	CAD 0.17	
Phosphate	Fluval	Phosphate test kit	70	CAD 17.99	CAD 0.26	
Phosphate	JBL	PROAQUATEST PO <sub>4</sub> <sup>3-</sup> Sensitive	50	CAD 19.78	CAD 0.40	
Phosphate	Red Sea	Phosphate marine test kit	100	CAD 22.97	CAD 0.23	
Phosphate	Salifert	PO <sub>4</sub> <sup>3-</sup> Profi test	60	CAD 17.39	CAD 0.29	
Phosphate	Seachem	MultiTest™ Phosphate	75	CAD 16.50	CAD 0.22	
Phosphate	Sera Aqua	Sera phosphate test	60	CAD 18.03	CAD 0.30	

Table A 23. The price paid for titration test kits. Purchase date: January 2022. Exchange rate history in January 2022 (www.exchange-rates.org). The number of tests depend on the amount of titrant used

Ion	Brand	Test Kit Name	Price of test kit	Notes
Calcium	Sera Aqua	Sera Calcium-Test (Ca)	CAD 18.07	
Calcium	Red Sea	Calcium Pro Reef test kit	CAD 31.74	
Calcium	Salifert	Ca Profi Test	CAD 13.09	
Calcium	JBL	PROAQUATEST Mg-Ca	CAD 30.63	Price for PROAQUATEST Mg-Ca test kit including both Mg and Ca tests
Calcium	Seachem	Reef Status™ Calcium	CAD 38.09	
Calcium	API	CALCIUM TEST KIT	CAD 11.04	
Calcium	Fluval	Calcium Test Kit	CAD 11.04	
Magnesium	Seachem	Reef Status™ Magnesium	CAD 38.60	
Magnesium	Sera Aqua	Sera Magnesium-Test (Mg)	CAD 36.82	
Magnesium	Red Sea	Magnesium Pro Reef test kit	CAD 31.99	
Magnesium	Salifert	Mg Profi Test	CAD 17.39	
Magnesium	JBL	PROAQUATEST Mg-Ca	CAD 30.63	Price for PROAQUATEST Mg-Ca test kit including both Mg and Ca tests
Potassium	JBL	PROAQUATEST K Potassium	CAD 59.84	
Potassium	Salifert	Potassium Reef Test	CAD 16.62	
Potassium	Red Sea	Trace-Colors Pro Multi test kit	CAD 72.99	Price for Trace-Colors pro multi test kit including Fe, I <sub>2</sub> and K, with 140 tests in total

Table A24. The price paid for ISEs. Purchase date: January 2022. Exchange rate history in January 2022 ([www.exchange-rates.org](http://www.exchange-rates.org))

Ion	Brand	ISE Name	Number of tests	Cost	Price per measurement	Notes
Ammonium	NT Sensors	IMACIMUS ISE for (NH <sub>4</sub> <sup>+</sup> ) Ammonium	500	CAD 150	CAD 0.30	The life span of ISEs are approximately 6 months or 500 measures. If the probes are used every day, the minimum average number of samples is multiplied by a factor of 2 (NT Sensors, 2022). This price is for electrodes only and the total amount of the ISE, multi-ion probe, pH probe, calibration and conditioning solutions and multi-channel Ion meter was 3900CAD
Nitrate	NT Sensors	IMACIMUS ISE for (NO <sub>3</sub> <sup>-</sup> ) Nitrate	500	CAD 150	CAD 0.30	
Potassium	NT Sensors	IMACIMUS ISE for (K <sup>+</sup> ) Potassium	500	CAD 150	CAD 0.30	
Calcium	NT Sensors	IMACIMUS ISE for (Ca <sup>2+</sup> ) Calcium	500	CAD 150	CAD 0.30	