



Electrical conductivity based algorithm for precise application of liquid nitrogenous fertilizers

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ABSTRACT

Precise application of nitrogenous fertilizers mainly urea ammonium nitrate (UAN) and granular urea (both pure and neem-coated) in aqueous form, is critically important for basal and foliar applications. The physicochemical properties of aqueous solution of these nitrogenous fertilizers plays important role in design of any liquid fertilizer application system. The study was carried out during 2019–20 at ICAR-Indian Agricultural Research Institute, New Delhi with an aim to develop algorithms for use in sensors-based systems for real time monitoring of available N concentration in the fertilizer solution before its application. The physicochemical properties like pH, electrical conductivity (EC), specific gravity (SG), dynamic viscosity (DV), surface tension (ST) and percentage light absorbance (LA) of urea ammonium nitrate (UAN-28%), pure urea, and neem coated urea in diluted form (pre-selected N-concentrations i.e. 0.78, 0.9, 1.08, 1.33, 1.75, 2.54 and 4.67% corresponding to the dilution ratios of 1:35, 1:30, 1:25, 1:20, 1:15, 1:10 and 1:05) were measured and analyzed for their significance with N-concentration. Electrical conductivity (EC) alone showed a significant relationship with N-concentrations. Prediction models were developed for diluted UAN and granular urea fertilizers based on the EC and N-concentrations. The regression models in terms of EC to predict N-concentration had coefficients of determination (R^2) of 0.998, 0.998, and 0.999 for diluted UAN, pure urea, and neem coated urea with water, respectively showed a great potential for their sensor based precise application. The controlled application of diluted liquid fertilizers with water can be achieved through sensing relevant physicochemical property.

Keywords: Electrical conductivity, Liquid nitrogenous fertilizers, Regression model

A nitrogenous fertilizer plays a significant role in agricultural production and productivity. It serves as the most essential input to satisfy nutrient requirements during various crop growth stages (Zhai 2006, Zhao and Yu 2006). Since, response of plant depends on the fertilizer rate, form, concentration and frequency of application (Fernández *et al.* 2013). Nitrogenous fertilizer diluted with suitable dilution ratio with water makes nutrient readily available for the plant intake and have higher nitrogen use efficiency and efficacy than solid fertilizers (Walsh *et al.* 2016). In hydroponically-grown plants, the nutrient solution with extremely low concentrations leads to growth inhibition. On the other hand, extremely high concentration causes osmotic stress, ionic toxicity, and growth restriction (Savvas *et al.* 1999). Additionally, in case of foliar application, higher concentration leads to leaf burning due to scorching (Castro

et al. 2022). Therefore, both rate and form of application of nitrogenous fertilizer are equally important for any sustainable crop production system.

The physicochemical properties have many applications in precision agriculture-based technologies (Othaman *et al.* 2019, Darmawan *et al.* 2023). Also, most of the sensor-based flow control systems rely on physicochemical properties, have proven their usefulness in sensing, monitoring, and controlling different chemical application systems (Sowmiya *et al.* 2017, Xu *et al.* 2019). Therefore, the relation between physicochemical properties with concentration and assessment of the feasibility of nitrogenous fertilizers such as urea ammonium nitrate (UAN), pure urea and neem-coated urea, for their basal/foliar application particularly with precision agro-machines is of prime importance.

This study aims to address the existing gap by analyzing the physicochemical properties of liquid nitrogenous fertilizers (UAN, pure urea, and neem-coated urea) at varying nitrogen concentrations, and develop algorithm based on the observed relationships between electrical conductivity and N-concentration to be use in the sensor-based metering systems. Although, the volumetric calibration of nutrient application relies on the relationship between

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concentration levels and their corresponding electrical conductivity. This research will provide valuable insights into optimizing different nutrients management practices. Also, it has the potential to significantly benefit small and marginal farmers, allowing them to optimize inputs and contribute to sustainable crop production.

MATERIALS AND METHODS

The study was carried out during 2019–20 at ICAR-Indian Agricultural Research Institute, New Delhi. Three liquid fertilizers i.e. UAN, pure urea and neem-coated urea were selected for the study. The composition of the selected liquid fertilizers with their physicochemical properties is listed in (Supplementary Table 1). Initially, the urea fertilizers were in solid form containing 46% N, diluted and converted into aqueous solutions (28% N) equivalent to the UAN (28% N). It helped in reducing the salt problems and maintaining the same level of N concentration in all three liquid fertilizers.

Preparation of samples for lab study: According to previous research findings and agronomic practices, the nitrogen concentration for basal and foliar application should not exceed 3% (Walsh *et al.* 2016, Sundaram *et al.* 2018). Keeping the above fact in view, the liquid fertilizers i.e. UAN, pure urea and neem coated urea, were diluted with distilled water in the ratios (fertilizer: water) of 1:05, 1:10, 1:15, 1:20, 1:25, 1:30, 1:35, to prepare the sample solutions having different N concentrations, viz. 4.67, 2.54, 1.75, 1.33, 1.08, 0.90 0.78%, respectively. Thereafter, physicochemical properties i.e. specific gravity (SG), dynamic viscosity (DV), surface tension (ST), pH, electrical conductivity (EC), and percentage light absorbance (LA), of all three liquid fertilizers were determined at each N concentration level. The main aim of the study was to determine the effect of nitrogen concentration on physicochemical properties, their feasibility in design of metering systems and select the most significant one for development of physicochemical properties-based N prediction model.

Determination of physical properties

Specific gravity (SG): SG of liquid fertilizer solutions was determined by density bottle method and calculated as:

$$\text{Specific gravity} = \frac{W_3 - W_1}{W_2 - W_1}$$

where W_1 , Weight of empty density bottle along with stopper (g); W_2 , Weight of water filled density bottle with stopper (g); W_3 , Weight of fertilizer solution filled density bottle with stopper (g).

Dynamic viscosity (DV): The viscosity refers to the resistance of fluid to flow. It was determined by Ostwald's viscometer method by determining the time required to flow for the liquid from upper mark A of the bulb of right limb to lower mark B through the capillary tube. The viscosity η_1 of fertilizer solution was determined as:

$$\eta_1 = \frac{\rho_1 t_1}{\rho_2 t_2} \eta_2$$

where η_1 and η_2 , Viscosity of test liquid (fertilizer solution) and reference liquid (distilled water), respectively; ρ_1 and ρ_2 , Density of test liquid (fertilizer solution) and reference liquid (distilled water), respectively; t_1 and t_2 , Time of flow of test liquid (fertilizer solution) and reference liquid (distilled water), respectively.

Surface tension (ST): ST of liquid fertilizer solutions having different N concentrations was found by drop weight method (Tate 1864) forming cylindrical drops at the tip of a stalagmometer nozzle by following standard procedure. Surface tension (σ) was calculated as:

$$\sigma \text{ (N/m)} = \frac{W}{2\pi r}$$

where r , Radius of the tip of the stalagmometer i.e. 0.75×10^{-3} m; W (kg), Mean weight of the single drop of the liquid = $\frac{W_2 - W_1}{150}$

Determination of chemical properties

pH and electrical conductivity (EC): pH and EC of fertilizer solution were determined by potentiometric and electrometric methods using digital pH and EC meter, respectively. The calibration of pH meter was done by the standard buffer solutions of pH=4 and pH=7 while EC meter was calibrated by using KCl (0.01 M) solution.

Light absorbance (LA): The instrument used for the measurement of percentage LA was digital spectrophotometer. The distilled water having 0% LA was used as a reference liquid. Sample to be measured was inserted between the spectrometer and photometer and the light of wavelengths 470 nm was passed through the solution. The percentage absorbance of the emitted light displayed by the spectrophotometer was recorded. All the experiments were conducted by following standard procedures and replicated thrice to reduce the error in the measurements.

Statistical analysis: Statistical analysis was carried out in two stages. In first, one-way ANOVA performed for completely randomized block design (CRBD) using Minitab software to interpretate the treatment main effects on physicochemical properties of all three liquid fertilizers. Tukey's test was used to study the significance among different response combinations. In the later stage, polynomial regression models were developed for all three fertilizers by using the programming language Python in Google Collaboratory.

RESULTS AND DISCUSSION

Urea (NH_2CONH_2), when dissolved in water converted into ammonium (NH_4^+) and cyanate (CNO^-) ions (Alexandrova and Jorgensen 2007), while urea ammonium nitrate [$(\text{NH}_2)_2\text{CO} \cdot \text{NH}_4\text{NO}_3$] in aqueous form yields ammonium (NH_4^+) and nitrate (NO_3^-) ions (Wahab and Mahiuddin 2001). These NH_4^+ and NO_3^- ions serve as important sources of nitrogen for plants. The ionic concentration when varied with dilution of liquid fertilizers in water, affect the physicochemical properties of the aqueous solution. The change in physiochemical properties with N concentration is of critically important for design

of any basal and foliar application systems as well as in green/poly house protected crops. Although, macro and micro-nutrients applied in hydroponic cultivation practices through different fertilizer products, became available for the plant in ionic form i.e. NO_3^- , NH_4^+ , SO_4^{2-} , H_2PO_4^- , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} etc. (Sanchez *et al.* 2021). The level of ionic concentration of plant nutrients affects the physical as well chemical properties like pH and EC of liquid and aqueous solution of fertilizer (Shawon *et al.* 2023). Keeping this fact in mind, the algorithm based on physicochemical properties and concentration level is practically viable to developed for multiple nutrients application system.

Effect of N concentration on physical properties of liquid fertilizers: Specific gravity measures the density of a substance in comparison to the density of water. The SG of aqueous solution of all three liquid fertilizers increased with increasing the N concentration. It was in the range of 0.99–1.056 for UAN, 0.983–1.018 for pure urea, and 0.980–1.029 for neem coated urea, respectively (Table 1). Results of the present study are in agreement with Makarov and Egorov (2018) who found that density/specific gravity of aqueous solution of UAN and urea fertilizers increased with increasing N concentration. It was also found that, variation of SG was not significant for each N concentration in case of UAN and pure urea, while overall effect of N concentration on SG was significant for all three fertilizers at 5% level of significance (Table 2). Also, SG was in closer proximity at each N concentration level, and within close range as that of water for all three liquid fertilizers.

Viscosity is a measure of fluid's resistance to flow. The dynamic viscosity was increasing with increase in

N concentration and vice versa. The maximum dynamic viscosity of 1.203 mPa-sec was found for UAN at 4.67% N concentration while the minimum dynamic viscosity of 0.850 mPa-sec was found for pure urea at 0.78% N concentration (Table 1). Like specific gravity, variations in dynamic viscosity measured at different N concentrations were not significant (Table 1), but the overall effect was significant at 5% level of significance (Table 2). Kawahara and Tanford (1966) reported same variation in density and viscosity of urea solution with different concentration.

Similarly, the significant increments in surface tension of neem coated urea solution were observed with increase in N concentration from 0.78–4.67% at 5% level of significance (Table 1). While in other two, ST values were non-significant in some N concentration levels but the overall effect was significant in case of all three liquid fertilizers (Table 2). At lower concentration (<1.33% N), the surface tension of liquid fertilizer was found close to that of pure water. Helonen *et al.* (2017) found the similar variation while studying urea-water solution properties (density, viscosity and surface tension) in an undersaturated solution. Kapusta *et al.* (2019) reported the same physical properties of urea water solution in their study.

Effect of N concentration on chemical properties of liquid fertilizers: pH, EC and LA indicate the ionic concentration (NH_4^+ , CNO^- , NO_3^-) in the aqueous solutions of the liquid fertilizers. The results revealed that, pH of aqueous solution of UAN decreased with increasing N concentration due to acidic nature of NH_4^+ ions. On the other hand, slight increase in pH of aqueous solution fertilizer was observed with increased N concentration in case of both urea

Table 1 Specific gravity, dynamic viscosity and surface tension of the liquid fertilizers at different N-concentrations

N-concentration (%)	Specific gravity (SG)			Dynamic viscosity (DV) (mPa-sec)			Surface tension (ST) (mN/m)		
	UAN	Pure urea	Neem coated urea	UAN	Pure urea	Neem coated urea	UAN	Pure urea	Neem coated urea
0.78	0.996 ^a	0.983 ^a	0.980 ^a	0.903 ^a	0.850 ^a	0.877 ^a	72.334 ^a	72.220 ^a	72.150 ^a
0.9	1.007 ^{ab}	0.984 ^a	0.987 ^b	0.913 ^a	0.853 ^a	0.883 ^a	72.385 ^a	72.262 ^{ab}	72.224 ^a
1.08	1.014 ^{bc}	0.987 ^b	0.993 ^c	0.952 ^a	0.873 ^b	0.916 ^b	72.459 ^a	72.323 ^b	72.373 ^b
1.33	1.027 ^{bc}	0.996 ^c	0.999 ^d	1.031 ^b	0.944 ^c	1.003 ^c	72.613 ^a	72.502 ^c	72.667 ^c
1.75	1.022 ^{cd}	1.006 ^d	1.009 ^e	1.073 ^b	1.043 ^d	1.041 ^d	74.011 ^b	72.970 ^d	73.551 ^d
2.54	1.032 ^d	1.012 ^e	1.017 ^f	1.124 ^c	1.072 ^e	1.082 ^e	76.712 ^c	73.810 ^e	74.469 ^e
4.67	1.056 ^e	1.018 ^f	1.029 ^g	1.203 ^d	1.141 ^f	1.119 ^f	80.352 ^d	75.126 ^f	75.807 ^f

*Mean follows the same letter(s) within N-concentration are not significantly different at 5% level of significance. UAN, Urea ammonium nitrate.

Table 2 ANOVA for physicochemical properties of selected liquid fertilizers at different N-concentrations

Liquid fertilizer	SG		DV		ST		pH		EC		LA	
	F value	P value	F value	P value	F value	P value	F value	P value	F value	P value	F value	P value
UAN	77.87	<.05	113.50	<.05	604.39	<.05	619.11	<.05	136165.26	<.05	4370.00	<.05
Pure urea	1566.83	<.05	1069.03	<.05	3877.01	<.05	3989.30	<.05	4911.45	<.05	32741.75	<.05
Neem coated urea	494.42	<.05	1537.38	<.05	5688.16	<.05	372.59	<.05	5599.38	<.05	227836.72	<.05

SG, Specific gravity; DV, Dynamic viscosity (mPa-sec); ST, Surface tension (mN/m); pH, Potential of hydrogen; EC, Electrical conductivity; LA, Light adsorbance (%).

Table 3 The potential of hydrogen, electrical conductivity and light absorbance of the liquid fertilizers at different N-concentrations

N-concentration (%)	Potential of hydrogen (pH)			Electrical conductivity (EC) ($\mu\text{S}/\text{cm}$)			Light absorbance (LA) (%)		
	UAN	Pure urea	Neem coated urea	UAN	Pure urea	Neem coated urea	UAN	Pure urea	Neem coated urea
0.78	6.783 ^a	7.073 ^a	7.066 ^a	15.812 ^a	13.530 ^a	11.792 ^a	0.001 ^a	0.001 ^a	0.002 ^a
0.9	6.770 ^a	7.080 ^a	7.086 ^a	24.565 ^b	18.136 ^b	17.421 ^b	0.001 ^a	0.002 ^a	0.003 ^b
1.08	6.750 ^a	7.126 ^b	7.120 ^a	39.451 ^c	26.627 ^c	27.607 ^c	0.003 ^b	0.003 ^c	0.006 ^c
1.33	6.453 ^b	7.183 ^c	7.196 ^b	56.750 ^d	41.460 ^d	44.119 ^d	0.009 ^c	0.014 ^d	0.010 ^d
1.75	6.323 ^c	7.457 ^d	7.291 ^c	70.813 ^e	59.206 ^e	59.828 ^e	0.012 ^d	0.021 ^e	0.013 ^e
2.54	6.140 ^d	7.813 ^e	7.456 ^d	82.412 ^f	76.525 ^f	74.053 ^f	0.018 ^e	0.026 ^f	0.029 ^f
4.67	5.647 ^e	7.943 ^f	7.700 ^f	109.469 ^g	92.767 ^g	91.714 ^g	0.042 ^f	0.096 ^g	0.095 ^g

*Mean follows the same letter(s) within N-concentration are not significantly different at 5% level of significance. UAN, Urea ammonium nitrate.

(Table 3). It was due to basic nature of urea fertilizers. Bull *et al.* (1964) reported that urea increases the pH of aqueous solution but higher concentration reduces the activity of hydrogen ions. The overall results revealed that, pH was not much affected by lower N concentration while significant variation was observed at higher concentration in case of all three liquid fertilizers at 5% level of significance (Table 2).

The reduction in EC with increased dilution was observed for all three liquid fertilizers (Table 3). Krishnan *et al.* (2023) reported the direct correlation of EC with ionic concentration in aqueous urea solution. Similar variation in EC with concentration of aqueous solution of ammonium nitrate was reported by Wahab and Mahiuddin (2001). The variation in EC of liquid fertilizers i.e. UAN, pure urea and aqueous neem coated urea with N concentration was clearer than any other physicochemical properties. It is significantly affected by N concentration (Table 2) and overall effect of concentration was also significant in case of all three liquid fertilizers at 5% level of significance (Table 2).

The percentage light absorbance was found in the range of 0.001–0.042%, 0.001–0.096% and 0.002–0.095% for UAN, pure urea and neem coated urea fertilizer, respectively (Table 3). Like specific gravity, the variations in percentage light absorbance (LA) measured at different N concentrations were non-significant at 5% level of significance (Table 2).

Results indicate that physical properties of the fertilizer solution are not much affected within the selected range of nitrogen concentration. These were found close to that of water, making it feasible to design a flow control system. On the other hand, EC is one of property that significantly affected by N concentration in case of three fertilizers. Because of its clear and greater change with N concentration (F value = 136165.26), it was most appropriate to select EC for the development of the algorithms for accurate prediction of N concentration in the solution. This will offer opportunity of more precise application of liquid fertilizer in any precision-based application system

The algorithms were developed for all three selected liquid fertilizers using a polynomial relationship between EC and different level of N concentrations. A significant

correlation was observed between EC and N concentration. The equations of this algorithm are as follows:

For the selected liquid fertilizers (Polynomial Regression Model)

Urea ammonium nitrate (UAN):

$$Y = 3.996 \times 10^{-6}X^2 - 0.0002X^2 + 0.0109X + 0.6703$$

$$[R^2 = 0.998, \text{Adjusted } R^2 = 0.995]$$

Aqueous urea:

$$Y = 1.786 \times 10^{-5}X^3 - 0.0021X^2 + 0.0917X - 0.1641$$

$$[R^2 = 0.998, \text{Adjusted } R^2 = 0.996]$$

Neem coated urea:

$$Y = 1.481 \times 10^{-5}X^3 - 0.0015X^2 + 0.0634X + 0.1983$$

$$[R^2 = 0.999, \text{Adjusted } R^2 = 0.999]$$

where Y, Percentage N concentration; X, Electrical conductivity (EC) value of the solution ($\mu\text{S}/\text{cm}$); R, Regression coefficient. The coefficients of determination for N concentration were 0.998, 0.998, and 1.00 for UAN, pure urea and neem coated urea. The data showed that when EC value input into the equation that resulted from the correlation between EC and N concentration, it provided reliable information about N availability in the fertilizer solution. Khlaif *et al.* (2021) developed the linear regression models between chemical properties of water and EC for its quality assessment based on the constitute concentration, found 0.834–0.979 prediction accuracy. Wu *et al.* (2019) reported EC algorithm-based fertigation system provide an optimal way of water and fertilizer management, contributed to water and fertilizer saving.

Nitrogen is one of the macro-nutrients that stimulates the plant growth and overall productivity. Application of nitrogenous fertilizer in liquid form is beneficial compared of solid application in terms of its efficacy and NUE. However, complete knowledge of available N concentration in solution prior to application is most important in case of liquid N fertilizer. Since, physicochemical properties of liquid fertilizers i.e. UAN, pure urea and neem coated urea significantly affected by N concentration level ranging from

1–5%. The physical properties like SG, DV and ST of the liquid fertilizers are considered most important properties in design of any flow control system, were found close to that of pure water. On the other hand, chemical properties like pH, EC and LA were used as an indicator in the development of algorithms to real time monitor the N concentration in automatic and precise liquid fertilizer application system. In this study, data revealed that the values of EC showed the close relation with N concentration. Therefore, the relationship between EC and N concentration was best described using a third-degree polynomial equation. The developed prediction models for all three liquid fertilizers: UAN, aqueous urea and aqueous neem coated urea, paved the way to use the EC as an indicator in any automatic monitoring and controlled application system of liquid nitrogenous fertilizers.

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