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Colorimeter Portable to Determine Ammonium Using to Manure Tetector

Yohan, Fifit Astuti, and Adimas Wicaksana

Program Studi Teknik Mesin, Universitas Pamulang, Jl. Surya Kencana No.1, Pamulang 15417, Tangerang Selatan, Indonesia.

E-mail: dosen01358@unpam.ac.id

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Abstract: Contruction of colorimeter and calibration are presented in this paper. In this investigation involves design, detection system, and measurement. Colorimeter was fabricated in dimension (10 x 10 x 6) cm³ consist of light source, modular data, and transducer. The light sources were LEDs which responds of wavelength peak at 467 nm on 0,141 W/m². Arduino Uno R3 is used to data tabulation in calculate absorbance system with 1.8.5 software. Then transducer was used a LDR which useful for consider the light in sample and reference. The calibration curve of ammonium consentration shows linierity range at 0.1 to 2 ppm with y = 0.0234x + 0.0905, R= 0.9716. The portable colorimeter was found accuration and precision about 88,7 % and 99,8%. the portable colorimeter gives the best result in this investigation and use to fake manure detector in Agricultural application for domestic farmer.

Keywords: Colorimeter, ammonioum, manure, wavelenght, absorbance

Abstract: Konstruksi kolorimeter dan kalibrasi disajikan dalam makalah ini. Dalam penelitian ini melibatkan perancangan, sistem deteksi, dan pengukuran. Colorimeter dibuat dalam dimensi (10 x 10 x 6) cm³ yang terdiri dari sumber cahaya, data modular, dan transduser. Sumber cahayanya adalah LED yang merespon puncak panjang gelombang 467 nm pada 0,141 W / m^2 . Arduino Uno R3 digunakan untuk tabulasi data dalam menghitung absorbansi sistem dengan software 1.8.5. Kemudian transduser digunakan LDR yang berguna untuk mempertimbangkan cahaya dalam sampel dan referensi. Kurva kalibrasi konsentrasi amonium menunjukkan rentang linieritas 0,1 hingga 2 ppm dengan y = 0,0234x + 0,0905, R = 0,9716. Colorimeter portabel didapatkan akurasi dan presisi sebesar 88,7% dan 99,8%. Colorimeter portabel memberikan hasil terbaik dalam penyelidikan ini dan digunakan untuk detektor kotoran palsu dalam aplikasi pertanian untuk petani domestik.

Kata kunci: Colorimeter, ammonioum, pupuk kandang, panjang gelombang, absorbansi

INTRODUCTION

The effort to protect the domestic farmer need to implemented through take care fertilizer formulation. This activity need the farmer to avoid the counterfeiting the fertilizer. The Indonesia government has regulation to protect farmer in the circulation fake manure, the government issues PP No.8 in 2001, about plant cultivation fertilizers. Although the government efforts has done, indeed not enough without farmer's utilities. Colorimeter technique is a useful analytical tool for determining concentration of coloured materials in the solution [1]. Such as Fatimah, S., et. al. has used low cost colorimeter to determine paracetamol [2] and Marie, H., et al. colour analysis use colorimetric methods [3]. The colorimetric method was supported through colored reagents. Otherwise the colored reagent may read by visual manner, it is only to qualitative determination. Ammonium in environment water has determinated by Heosang, J., et all using Nessler method [4]. The simple and low cost colorimetry efforts a userfriendly to farmer, hope the colorimetry can useful the in increase harvest. Ammonium is a one of nutrient for plants which abundant in nature. Urea, NPK, and compost widely used in the Indonesia Agriculture. In Indonesia Compost is made as home industri major in wate management unit (WMU) Sukmajaya Depok West Java, processes the organic waste in to compost fertilizer, Balikpapan government continues to reduce volume of waste entering the Manggar Final Disposal. One of them is by processing organic

waste into compost fertilizer as intermediate treatment fscilities operates in Daksa Housing, East Balikpapan, in the Sicanang Main Waste bank, Medan belawan has processes the waste such as vegetables scraps, fruit, food scraps, in to fertilizer. This scarcity leads farmers look for other fertilizer alternatives such as making their own compost, but the compost fertilizer content is nonstandard. Colorimetry is needed to solve this problem to help farmer include increase harvest, environment controlling, and advance Agricultural techniques. In 2017, yohan and fifit have fabricated a simple spectrophotometry with range wavelength 460-630 nm [5]. Aqueous sample which in contain Ammonium then drops with Neesler reagent leads the yellowed aqueous. This yellowed aqueous will give maximum absorb the light at 420-470 nm. The yellowed aqueous measures in colorimetry which refer to concentrate of ammonium in numbers scale. The colometry was completed with evaporator apparatus to separation prosess the ammonium from manure or fertilizer. The evaporator apparatus were the kit of determination ammonium tools. They were have low cost, usefriendly, and good acuration, presicion.

METHODS

Modeling

A colorimetry has dimension (10x10x6)cm³, completed with two photodiodes, beam sources (467 nm), 4bit digital tube TM1637, two cuveet size 8 mL, battery 6 volt, and power control. Colorimetry system shown in figure 1 is sheme on Portable colorimetry is operated at 6 volt. There are two stages is powered the scheme, consist of LED unit and Arduino unit. The Light Emitting Diode (LED) produces wavelength at 467 nm through two samples and refferences in the box sources lattices. The double beam system describes in figure 2, the light beam is divided in two direction, one direction strive to sample and other to reference which can be measures in same condition. Doble beam system is designed to overcome the drift effect, the basic principle is the same as single beam only different at amounts of beams. It has an advantages such as measuring together between sample and blanko in the same times and condition indirect. The distant of beams source to photodiodes at 2,5 cm shown in the figure 3 repectively. The casing of colorimetry is made from polyester resin colored black with MEKP hardener. It is colored black has purpose to avoid an interference light leads instability measurement. In the right side, there are two covets holder which have size 1,5 x 0,5 cm respectively and socket of beam source, each other in the left side containes a arduino uno R3 and supporting component, power supply DC12 V, battery 6 volt. The colorimetry kit is needed evaporator apparatus. It is consists of evaporator tube, heater, and paper sheet. Evaporator tube and heater have dimension and area surface at $(7.5 \times 1.5 \times 2.5)$ cm³ and (3.5×2) cm². The evaporator is operated at 3 watt.



Figure 1. Scheme on Portable Colorimetry



Figure 2. Colorimetry double beam system



Figure 3. Casing of colorimetry portable



Figure 4. Evaporator apparatus

Testing

There was two preparation in this investigation. The first, the colorimetry testing preparation, the glow LED set up at fit condition with rotate the potensiometer. Arduino Programming was written base on the lambert-beer formula. Then colorimetry was charged before to use for 3 hours. The second, calibration curve of ammonium aqueous preparation. The ammonium solution is prepared at 0.1 to 2 ppm respectively. The light of LEDs is observed through the sampel and refference cuvets. The covet holder is placed at 1 cm at source beam. The photodiodes cubes made from aluminium metal to avoid the outer light penetrating. The LEDs wavelengt was calibrated in Metrology LIPI-Serpong, South Tangerang. The testing procedure is explained briefly below.

- 1) Setting up the programm of colorimetry at zero number condition.
- 2) Turn on the led at 0.018 watt then checked the interference light is not penetrates a photodiode cubes. The colorimetry and support apparatus shown in figure 6. The colorimetry has the option "ON" or "OFF:" and the potentiometer has function as power regulator.
- 3) Prepare the standard calibration solution from 0.1 to 2 ppm ammoium concentration. The solution calibration will lead yellowed solution after is given a reagent solution as shown in Figure 5.
- 4) Record the data, absorbance value on ammonium measurement respectively.
- 5) Sample Pretreatment of manure (NPK, Urea, or compost) use volumetric flask then drop the sampel at 0.5 mL on a paper sheet. The evaporator turn on for 30 minutes.
- 6) Measure the samples then plot the result to comparing on ammonium scale indikator.



Figure 5. colored aqueous (yellow) contain ammounium in range 0.1 to 2 ppm using Nessler method.



Figure 6. Colorimetry kit equipments

CALCULATION

Absorbance in 467 nm spectral region base on beam references and samples were related on the beer-lambert-Bouguer expression, commonly known as Beer's Law , so the absorbance in the aqueous can be determined

$$A = -\log T = \frac{P}{P_o}$$

where A is the aqueous absorbance, P and Po are radiant beams on samples and refferences respectively [6]. Then, the concentration ammonium from distillation expression as follows

$$M_p = \frac{4.V_{a1.}B_{a2}}{B_{a1}}$$

where Mp is manure concentration, V is volume of Sample , B is weight of sample, then to determine RSD given by

$$RSD = \sqrt{\frac{RSS}{(n-2)}}$$

Where RSD is Residual Standard Deviation, RSS is Residual Sum of Square [7]. Limit of Detection (LOD) of a colorimetry may be defined as

$$LOD = \gamma bl + 3S$$

where LOD is Limit of detection, y bl is a yield blank and S is a standard deviation [8]. For the presicion and accuration, they can be known as

Precision = (100 - RSD) %

Accuration = (100 - Er) %

where Er is an Error in measurement consider with standart concentration.

RESULT AND DISCUSSION

The colorimetry portable has designed and fabricated using arduino R3 based on has been worked by Yohan, et al in 2018 [5]. software 1.8.5, wavelenght 467 nm, dimension specification (10 x 10 x 6) cm³, completed with the display using 4-Bit Digital tube module, The colorimetry was designed in double beam system (references and samples) to reduce interference in the samples measurement. The fabricated colorimetry portable was tested within measure 5 ammonia concentration, 0.1, 0.5, 1.0, 1.5, and 2.0 ppm using colored nessler reagent. The nessler reagent were droped 0.25 mL respectively ammonia aqueous and there was an increase observed signal gradually in linier to increase ammonia aqueous concentration. The colorimetry uses double beam spectrophotometer approach with single light source and two photodetectors, one for refference and another for detection as design by Gong, W in 2009 [9]. Differential or ratio measurement in a double beam system can reduce the common noise, detector, and relevant electronic and in addition, reduce the effects of variable intrinsic optical properties of the environmental sample [10]. LED properties is measured in LIPI Metrologi results the waveleght and irradiant energy at 467 and 0.141 W/m². The irradiant of LED needs a monocromator as lambert-beer law in spectrophotometer UV-Vis, polychromatic radiation from outer sxystem cause deviation and linierity [11]. The deviation can be caused by polychoromatic and higher or lower concentration of ammonium in the nessler reagent. The recommeded usage for Nessler reagent at range 0.02 to 2.5 mg/L.

For the main results, figure 7 shows a good linierity at 0.1 to 2 ppm gradually result a correlation coefisien 0.9716. At table 1 present some fixed and relative bias for calibration curve, continuing the calculation in table 1 obtain the total bias error. The calculation have been carried out for each of five concentration, the fixed bias gives a constant error +0.09 ppm regardless of the true concentration, then the relative bias average results +0.0023 ppm. The measurements of low concentration of ammonium lead a detection limit as LOD value. The LOD results at 0.05 A, with ESD 0.0035 and yield 0.004 A therefore a not conduct in lower 0.1 ppm.

In Figure 8 shows scale indicator to determine manure or fertilizer fake through fabricated colorimetry portable measurement. In range 0.1 A to upper gives information that the manure in standart condition to using in Agricultural then in range 0.095 to 0 A shows a non standar fertilizer (fake manure). The problems in ammonium measurement are a lost of ammonium concentration in solution is caused evaporation at open condition although the measurement have to did immediatelly. Additionally, in figure 9 and 10 present NPK and Urea measurement which result for commerce NPK has scale value at 0.112 A, its means the NPK in manure standart range then urea have absorbance value at 0.107 till in manure standart range.

Additionally, the accuration and presicion have conducted with considering samples and standard. The concetration 1 ppm for determine a accuration consider a upper LOQ value and lower LOL. The portable colorimeter was found accuration and precision about 88,7 % and 99,8%.



Figure 7. Graph of ammonium curve calibration curve in range 0.1 to 2 ppm using nessler method.

True Concentration (ppm)	Estimated error due to fixed bias (ppm)	Estimated error due to relative bias (ppm)	Estimated total error due to bias (ppm)	Predicted determination (ppm)	Absorbance (A)
0.1	0.090	0.0023	0.0923	0.1923	0.095
0.5	0.090	0.0115	0.1015	0.6015	0.103
1	0.090	0.0230	0.1130	1.1130	0.109
1.5	0.090	0.0345	0.1245	1.6245	0.125
2	0.090	0.0460	0.1360	2.1360	0.140

Table 1. Fixed and relative bias in ammonia calibration curve.



Figure 8. Absorbance Scale indicator uses colorimeter in determination of fake manure.



Figure 9. NPK Measurements use Colorimetry portable



Figure 10. Urea Measurements use Colorimetry portable

CONCLUSION

The colorimetry has fabricated from arduino, LED, and other devices. Colorimetry for ammonium determination results LOD 0.05 A, ESD 0.0035, and accuration and precision at 88,7 % and 99,8%. This datas prove that the ammonia measurements of manure can be conducted in range 0.1 to 2 ppm. The fake manure have absorbance in range 0.095 to 0 A. NPK and Urea mesurements result 0.112 and 0.107 A therefore that colorimetry can use for fake manure detector.

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