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Utility Of 3-Hydroxy-3-M-Tolyl-1-P-Methoxyphenyltriazene As Chromogenic Reagent For Spectrophotometric Determination Of Nickel (II) In Environmental Samples

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Abstract:*A selective and sensitive spectrophotometric method for Nickel (II) determination using 3-Hydroxy-3m-tolyl-1-p-methoxyphenyltriazene is described. The physical characteristic of the reagent was light yellow shinning needles with the melting point of 112^{0}C. The elemental analysis results agreed very well with those of theoretical for C, H and N. Nickel (II) reacts with the reagent in pH range of 8.0-8.3 to give a yellow colored complex with a composition of 1:2 at a working wavelength of 412nm. The molar absorptivity coefficient, Lambert-Beer's Law range and stability constant (Log$_{10}\beta$) were 20800dm^3 mol^{-1}cm^{-1}, 0.25-1.25x10^{-5}M and 10.4091 respectively. The complex with a composition of 1:2 (Ni:L) is more stable and more sensitive in comparison with some other hydroxytriazenes previously studied for Nickel(II) determination. Many cations and anions do not interfere with Nickel (II) determination. However, Sn^{2+} and Cu^{2+} if present interfere seriously with the Nickel (II) determination. The interference of Cu^{2+} can be avoided by masking it with oxalate solution. The proposed method was used for determination of Nickel (II) in soil and plant samples from Meru dumpsite. The t-test and F-test values showed that there is no statistical difference in the results of flame atomic spectrophotometric and the proposed method. Hence, the method can be employed for Nickel (II) determination in the environmental samples.*

Key Words:*hydroxytriazene, Nickel (II), environmental sample, spectrophotometric, interferences, elemental analysis.*

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I. Introduction

Nickel (II) is uniformly distributed in soil profile and occurs in nature mainly in five isotopic forms: 58 (67.8%), 60 (26.2%), 61 (1.2%), 62 (3.7%), 64 (1.2%)[10].It exists at a very low level in the environment[22]. It is used in ceramics, surgical and dental prostheses, magnetic tapes, computer components, stainless steel, nonferrous alloys, super alloys, Nickel-Cadmium batteries, coinage manufacture, certain pigments, electronic products, welding products, electroplating and as catalysts[30,31]. Nickel alloys and nickel plated materials are used in the production of bathroom fittings, food processing, consumer white goods, kitchen and tableware, manufacture of cables and wires, fasteners, motor vehicles, jet turbines, shipbuilding and textiles[10]. The increasing Nickel levels in soil, air and water due to human activities of recent years have attracted the considerable attention of various researchers in different parts of the world. The passive diffusion and transport system are the main mechanism which plants use for Nickel uptake[1].

The deficiencies of Nickel in plant reduce urease activity, disturb nitrogen assimilation and contribute to reduction of scavenging of superoxide free radical. Excessive nickel in plants contributes to ultrastructural modifications, inhibits photosynthesis, produces iron deficiency which leads to chlorosis and foliar necrosis, affects nutrient absorption by roots, impairs plant metabolism, disturb mitotic root tips, induce leaf spotting, retard shoot and biomass production[1]. This reduces the growth and yield of agricultural crops[5]. This implies that Nickel is toxic to plants and agricultural crops when present in large amounts in soil. The contamination of the soil by this element can be influenced by continuous use of the modern agricultural practices like pesticides and synthetic fertilizers, presence of Nickel smelters, industrial waste materials, lime sewage sludge, and urban wastes[26]. The decrease in soil pH due to reduced use of soil liming in agricultural soils and increased acid rain in industrial areas results in Nickel (II) mobilization which in turnbecomes problematic. The use of contaminated

water for irrigation purposes will influence the levels of Nickel (II) in the soil. The contamination of surface water by Nickel could be due to dissolution of industrial processes, waste disposal, Nickel ore-bearing rocks and leaching from metals in contact with water, such as pipes and fitting[28]. Dusts from volcanic emissions, inorganic fertilizers particularly phosphate and atmospheric nickel originating from meteoric dusts, smoke particles from forest fires, volcanic ash, wind-blown soil dust, aerosols from oceanic dust and wastewater streams containing

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Nickel can also find their ways into surface water[20]. The toxicity of Nickel is a threat to environment and public health because of increasing contamination and accumulation in soil and atmosphere which transfer it through the food-chain to crops, fruits and vegetables[24].

Nickel(II) is mobile in plants and accumulates in plant leaves and seeds. The amount of Nickel in particular food will vary with the place, seasons, the part of the plants and the age. Leaves have more Nickel than stem and roots and old leave has high amount of Nickel than young leaves. Some of foods with high amount of Nickel include red kidney beans, legumes: lentils, peanut, peas, soya beans and chickpeas, whole wheat, rye, whole grain, oat, millet, cocoa, buckwheat, chocolate, tea, gelatin, baking powder, soya products, dried fruits, canned foods, beverages, certain vitamin supplements and strong licorice. The uptake of the Nickel by plants has a relationship with its toxicity, which may have certain threats with respect to humans and animals through food chain. The general population can be exposed to Nickel through taking water and food which is contaminated with this metal[2]. An uptake of high quantities of Nickel causes lung cancer, nose cancer, larynx cancer, prostate cancer, dizziness and sickness, lung embolism, respiratory failure, birth defects, asthma and chronic bronchitis, allergic reactions, dermatitis,pneumonitis, vesicular eczema and damage of liver, kidney, spleen, brain and tissue[20]. Furthermore, an increasing awareness pertaining food quality to human diet and water quality requires a continuous monitoring of the contaminants in water, food, and soil using easily affordable, simple, effective, sensitive, selective and less time consuming equipment. This will aid in decision making on ways of reducing contamination and human exposure hence making the entire population free from the risks associated with Nickel (II) contamination. This endeavour can be achieved by reducing the levels of heavy metals such as Nickel in contaminated soils to make land resources safe for agricultural production thus enhancing food security and reducing land tenure problems which are due to changes in the land use patterns. This will assist in establishing the time at which various techniques such as chemical methods (immobilization, encapsulation,and soil washing), biological methods/ phytoremediation (phytoextraction, phytostabilization and phytovolatilization) and physical methods (soil replacement, soil isolation, electrokinetic remediation and vitrification) for cleaning up heavy metal contaminated soil can be used[12,16]. In view of the above, it is crucial to develop techniques which can be used at micro levels for the determination of Nickel (II). A number of analytical techniques are currently being used for quantitatively determining Nickel (II) in various samples[8,11,30]. Among these methods UV-Visible spectrophotometric technique is the most commonly used because it is cheaper, easier to handle, hasexcellent sensitivity and rapid in generating results. This method relies on the stability of the coloured complex formed between the analyte metal ions and the organic complexing agent (chromogenic reagent). The chromogenic reagent used should possess functional analytical group which can interact with the element in question leading tosubsequent observation of analytical signal[27]. A number of organic reagents in spectrophotometric techniques for Nickel determination have been used by various researchers[22,27]. Some of these reagents suffer from low sensitivity, poor selectivity, and employing surfactants to increase the sensitivity[25]. Therefore, there is need to continue searching for new analytical reagents with increased sensitivity and selectivity which do not require the use of the surfactants or extraction when determining Nickel at micro levels spectrophotometrically in environmental samples.

Hydorxytriazenes are chelating agents of great utility in areas of analytical chemistry such as spectrophotometric and complexometric techniques[19]. They form colored chelates with many transition metals[19] which qualify them to be sensitive and selective reagents in spectrophotometric techniques for metal ions determination[6]. However, the effectiveness of the chelating agent is influenced by the basic strength of the functional groups, the number of the chelate ring formed, size and the electronegativity of the bonding atom[15].This implies that, a new chelating agent which is more sensitive, selective or specific for a particular metal ion, displaces strongly matrix in the sample from metal ion, forms a very stable chelates with metal ions without side reactions and does not require the use of masking agents or surfactants can be synthesized while taking into account factors relating to analytical behavior.

Therefore, in the present investigation, a sensitive, selective, and rapid spectrophotometric method has been developed using the chromogenic reagent which forms a very stable complex with Nickel (II) ion to determine trace amount of Nickel (II) ion in the environmental samples.

II. Materials And Methods

Apparatus

PG-990 Atomic absorption spectrophotometer, melting point (model MRC MPA 12), PH-meter (HI 2211 PH/OR P meter), HANNA Instruments, Elemental Analyzer (Vario EL III), ultra-pure water equipment (model MLLI-Q equipped with Q-POD), ultra violet/visible spectrophotometer (UV 1800 Shimadzu)

Chemicals and Solutions

In the present study, all the chemicals used were of analytical grade. Ultra-pure water and pure ethanol were used for solution preparation. A stock standard solution of 0.01M Ni^{2+}containing a few drops of concentrated hydrochloric acid was prepared using Nickel Chloride hexahydrate (BDH, AR grade). The solution was standardized using 0.001M EDTA solution and murexide as an indicator. Working standard solutions were prepared by diluting stock solutions using appropriate dilution factor. 0.01M hydroxytriazene solution was prepared using ethanol.

Sampling Techniques Soil sampling

Soil samples were collected using a stainless steel trowel at the same locations as the plant from the top 10cm rooting zone which reflected the metallic burden[3]. Soil and plant samples of the same species were also collected from a location which was about 5 km from the study site. Twenty-five samples were collected randomly, and each of five group bulking consisted of five composite replicates. This ensured estimation of the dumpsite Nickel variability with reasonable precision. Fresh soils were then transferred upon collection into polythene bags and thereafter taken into ice-cold box for transportation to the laboratory for analysis. In the laboratory, all matter which were not soiled in nature were removed. 100g of a fresh sample was placed into an evaporating basin with constant weight and then taken into an air circulation oven at 60^{o}C for 24 hours. This was followed by cooling in a desiccator.

The comminution of the dried soil samples was done using motor and pestles until samples passed through a 2mm sieve. The sieved soil sample was heaped into a cone and quartered on a smooth, impervious base. Two different quarters were kept, and the process continued, retaining other pairs of quarters each time until the required analyte sample was obtained.

Plant sampling

Plant samples were collected at the beginning of dry weather in order to avoid the accumulation of wind -blown soil and dust from surrounding environment using purposive type of sampling technique. Five replicate samples which were collected from each location within the area of 9.0m^2 was carried out at the beginning of the plants reproductive stage whereby mature leaves exposed to sunlightjust below the growing tip on stems and branches which were not damaged or covered with dust /soil were taken while those of past full maturity stage were disregarded. 100g of fresh sample were loosely packed in the polythene bag and transferred into ice cold box in order to minimize any deterioration of the samples before transportation to the laboratory. All the samples were sponged with cotton wool wetted in a 0.1% detergent solution which was phosphate free and rinsed quickly with water to remove the surface dust, soil particles, and spray residues such as pesticides. The rinsing was done quickly to avoid leaching of some of the chemical components. The samples were dried at 60^{o}C for 24hours in an oven in the presence of air circulation immediately after maceration using blender to minimize biochemical changes. The grinding using mortar and pestles was done until the samples passed through a mesh of 0.5mm sieve. The mixing using conning and quartering followed in order to obtain a representative analytical sample. The dried samples were packed in a well-sealed plastic container to reduce any uptake of the water vapour.

Digestion procedures Soil samples

30ml of aqua regia was added to 10g of ground dry samples in 250ml digestion flask while swirling and then heated for 50 minutes at 95^{o}C after which the temperature was raised to 150^{o}C at which sample was boiled until the volume was reduced to about 5ml. The interior of the digestion flask wall was washed down with a small amount of ultra-pure water. The swirling of the digestion flask was done throughout during digestion in order to keep the wall clean and prevent the loss of the sample. The mixture was cooled and 7.5ml of hydrogen peroxide (30%) was added, and then heated at 150^{o}C while swirling until the volume of the solution decreased to 5ml. The mixture was cooled, filtered with Whatman No. 42 filter paper and < 0.45µm Millipore filter paper into a 25ml volumetric flask. The residue was washed and filtrate directed into the flask, then topped to the mark.

Plant sample

1.0g of plant sample was placed in a 250ml digestion tube and 20ml of concentrated HNO_3 was added. The sample was heated for about 45 minutes at 90 ^{o}C and then temperature increased to 100 ^{o}C at which it was boiled until the brown gas/vapour disappeared. The sample was then allowed to cool and 1ml of H_2O_2 was added to dissolve the remaining HNO_3. The sample was then heated for 20minutes until a lightly clear solution was

obtained. It was then allowed to cool and 100ml of ultra-pure water added, then heated for about 15 minutes until the volume decreased to about 5ml. The interior walls of the tube were washed down with a little ultra-pure water and the tube then swirled throughout the digestion to keep the wall clean and prevent the loss of the sample. After cooling, 5ml of 1% HNO_3 was added to the sample. The solution was filtered with Whatmann No. 42 filter paper and <0.45µm Millipore filter paper. It was then transferred quantitatively to a 25ml volumetric flask by adding distilled water.

III. Results And Discussions

The physical characteristics and elemental analysis results are summarized in Table no1.

Table no 1: Physical characteristics and elemental analysis of Hydroxytriazenes

S/NO	Hydroxytriazenes	Colour and shape of crystal	Crystalized from	M. P ^{0}C	%C %H %N	Molecular Formula
L_I	3-Hydroxy-3-m-Tolyl-1-0-carboxyphenyltriazene	Light yellow shining needles	Ethanol	178	Th 61.96 4.83 15.49 Exp 61.44 4.69 14.66	$C_{14}H_{13}N_3O_3$
L_{II}	3-Hydroxy-3-m-Tolyl-1-P-Methoxyphenyltriazene	Light yellow shining needles	Ethanol	112	Th 65.33 5.88 16.34 Exp 64.56 5.77 16.87	$C_{14}H_{15}N_3O_2$
L_{III}	3-Hydroxy-3-m-Tolyl-1-1-phenyltriazene	Light yellow shining needles	Ethanol	124	Th 68.68 5.76 18.50 Exp 69.91 5.57 18.23	$C_{13}H_{13}N_3O$
L_{IV}	3-Hydroxy-3-0-Tolyl-1-0-carboxyphenyltriazene	Light yellow shining needles	Ethanol	138	Th 61.96 4.83 15.49 Exp 60.48 4.63 14.69	$C_{14}H_{13}N_3O_3$

The reagent L_I, L_{II}, L_{III} and L_{IV} were light yellow shinning needles with the melting point of 178^{0}C, 112^{0}C, 124^{0}C and 138^{0}C respectively. The crystallization was performed using ethanol in all the cases. The elemental analysis data are in good agreement with the theoretical values for C, H and N.

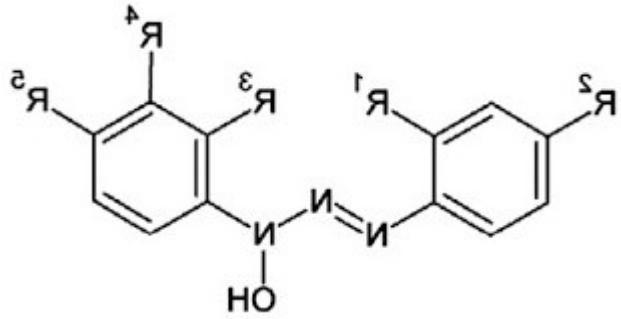
Table no 2consists of the results of spectrophotometric determination of Nickel (II) with hydroxytriazenes.

Table no 2: Spectrophotometric determination of Nickel (II) with Hydroxytriazene

S/No	Name of the reagent	Composition of the complex	Colour of the complex	Working wavelength in nm	Optimum pH range	Beer's Law range x10^{-5}m Ni:L	Molar absorptivity dm^{3}mol^{-1}cm^{-1}	Sandell's sensitivity ng/cm^2	Standard deviation for determination	Log β_{10}
i.	3-Hydroxy-3-m-Tolyl-1-0-carboxy-	1:1	Greenish	412	8.35-9.20	0.15-0.9(1:6)	25,333	2.318	0.007	6.1103
ii.	phenyltriazene3-Hydroxy-3-m -Tolyl-1-p-Methoxyphenyltriazene	1:2	yellow Yellow	412	8.0-8.3	0.25-1.5(1:6)	20,800	2.823	0.011	10.4091
ii.	3-Hydroxy-3-m-Tolyl-1-1-phenyltriazene	1:2	Yellow	415	7.2-7.55	0.4-2.0(1:6)	13,250	4.431	0.018	10.5144
v.	3-Hydroxy-3-0-Tolyl-1-0-carboxyphenyltriazene	1:1	Greenish yellow	405	7.0-8.7	0.4-2.4 (1:6)	11,000	5.337	0.032	6.1580

The spectrum of the complex against reagent blank ((M) :(L) = 1:5) was carried out in the wavelength region of 371nm to 560nm. Nickel (II) reacts with reagent (L_I, L_{IV}) and (L_{III}, L_{II}) in alkali medium to give greenish-yellow and yellow colored complex with composition of 1:1 and 1:2 respectively. The working wavelength in nm for reagent L_I, L_{II}, L_{III} and L_{IV} were found to be 412, 412, 415, 405nm while the optimum pH range were 8.35-9.20, 8.0-8.3, 7.2-7.55 and 7.0-8.7 respectively. The molar absorptivity coefficient for reagent L_I, L_{II}, L_{III} and L_{IV} were

25333, 20800, 13520 and 11000 and Lambert – Beer's Law range $x10^{-5}$M were 0.15-0.9, 0.25-1.25, 0.4-2.0 and 0.4-2.4 respectively. These results revealed that, the method using reagent L_I is more sensitive followed by the one employing reagent L_{II}. The stability constant ($Log_{10}\beta$) for Ni (II)-Hydroxytriazene using reagent L_I, L_{II}, L_{III} and L_{IV} were 6.1103, 10.4091, 10.5144 and 6.1580 respectively. These values indicated that reagent L_{III} and L_{II} forms more stable complexes with Nickel (II) in comparison with reagent L_I, and L_{IV}. These can be accounted for by considering the substitution attached to the parent hydroxytriazene which may alter the pka value of the reagent or enhance or interfere with the resonance of the chelate ring or can be explained in terms of a steric interference which is responsible for preventing favorable metal-reagent orientation[21].The stability of metallichydroxytriazene complex can be lowered with substituent which lowers the pka value of the parent hyrdoxytriazene. Hence the stability of metal ion with hydroxytriazene which have intra-molecular hydrogen bonded stricture (chelate structure) can be lowered by any factor that breaks hydrogen bonding of the chelate stucture.



A B

Substitution of COOH at ortho position on ring B for reagent L_I and L_{IV} contribute to strong acid character of the hydroxytriazenes which makes the Nickel (II)-hydroxytriazenes less stable compared to reagent L_{III}. This can be as a result of –M effect of COOH groups. The methyl group at ortho position on ring A for reagent L_{IV} forms slightly stale Nickel (II) complex compared to methyl group at Meta position. This is due to the +I effect (electron pushing) or methyl group is more dominant on the –OH bearing Nitrogen atom or reagent L_{IV} than reagent L_I due to the distance factor. This accounts for slightly higher values of stability constant for reagent L_{IV} in comparison to reagent L_I. The hydroxytriazenes with methoxy (OCH_3) at Para position on ring B for reagent L_{II} should have been a weaker acid and slightly more stable complex with Nickel (II) than that formed by reagent (L_{III}) due to the +M effect of $–OCH_3$ groups. This can be attributed to the +M effect of the methoxy not being operative due to the strong +M effect of –N=N- group and only the –I effect of methoxy group is affecting the acidity of the hydroxytriazenes and the stability of its Nickel (II) complexes. Otherwise if +M effect of methoxy group could have been operational, the acidity of the Hydroxytriazenes could have been less and could have formed more stable complex than that of reagent L_{III}. Further, these results revealed that reagents forming 1:2 composition with Nickel (II) forms more stable complexes than those forming 1:1 which implies that the number of chelate rings formed relates to the stability of Nickel (II) – hydroxytriazenes complexes. The data of standard deviation shows that the proposed method has high precision.

The study of the effect of foreign ions (cations and anions) on the determination of Nickel (II) under optimum condition was carried out in order to establish their tolerance levels hence the selectivity of the method under investigation. These results are summarized in Table no 3.

Table no 3: Effect of diverse ions in Nickel (Ii) determination

Diverse Ions	**REAGENT (I) Mole Ratio Ni:L=1:6**		**REAGENT (II) Mole Ratio Ni:L=1:6**		**REAGENT (III) Mole Ratio Ni:L=1:6**		**REAGENT (IV) Mole Ratio Ni:L=1:6**	
	Mole ratio diverse ions: Nickel (II)	Recovery %	Mole ratio diverse ions: Nickel (II)	Recovery %	Mole ratio diverse ions: Nickel (II)	Recovery %	Mole ratio diverse ions: Nickel (II)	Recovery %
Cl^-	10.0	99.0± 0.004	10.0	100.2± 0.009	10.0	101.3± 0.02	10.0	101.8± 0.04
Br^-	10.0	99.0± 0.001	10.0	98.0± 0.009	10.0	100.0± 0.02	10.0	99.1± 0.04
CH_3COO^-	10.0	100.2± 0.001	10.0	97.6± 0.02	10.0	101.8± 0.02	10.0	102.2± 0.03
CO_{32}^-	5.0	100.6± 0.005	10.0	98.3± 0.02	10.0	100.8± 0.01	10.0	101.3± 0.04

PO_{43-}	1.0	93.9± 0.008	10.0	97.6± 0.02	5.0	96.4± 0.02	1.0	99.1± 0.04
SO_{42-}	1.0	98.2± 0.006	1.0	98.3± 0.008	5.0	100.0± 0.02	10.0	97.8± 0.04
C_20_{42-}	1.0	99.6± 0.008	10.0	98.3± 0.03	5.0	96.7± 0.01	1.0	101.3± 0.05
I^-	5.0	98.0± 0.004	10.0	101.2± 0.03	5.0	100.8± 0.01	5.0	100.0± 0.03
S_20_{32-}	5.0	98.4± 0.008	1.0	101.5± 0.03	1.0	97.5± 0.03	1.0	102.2± 0.03
NO_{2-}	10.0	103.1± 0.008	5.0	104.6± 0.01	10.0	95.7± 0.04	10.0	100.7 0.03
SO_{32-}	1.0	98.0± 0.005	1.0	99.5± 0.03	1.0	98.7± 0.02	1.0	100.4± 0.05
S_{2-}	1.0	100.0± 0.004	1.0	99.3± 0.03	5.0	96.4± 0.02	1.0	102.2± 0.05
HPO_{42--}	1.0	98.2± 0.004	10.0	98.3± 0.03	10.0	95.9± 0.02	5.0	103.1± 0.03
F_-	10.0	103.7± 0.004	5.0	102.4± 0.02	10.0	97.2± 0.01	10.0	102.7± 0.03
NO_{3-}	10.0	99.4± 0.006	10.0	100.0± 0.02	10.0	99.2± 0.02	10.0	104.5± 0.03
WO_{42-}	10.0	102.5± 0.005	1.0	100.5± 0.02	10.0	97.2± 0.04	5.0	101.8± 0.05
MO_70_{246}	5.0	98.0± 0.008	10.0	100.7± 0.009	10.0	97.0± 0.04	1.0	102.7± 0.04
NH_{4+}	10.0	99.8± 0.006	10.0	101.5± 0.009	10.0	102.5± 0.04	10.0	101.3± 0.04
Na_+	10.0	98.6± 0.004	10.0	100.5± 0.01	10.0	100.5± 0.02	10.0	100.0± 0.03
K_+	10.0	98.4± 0.004	10.0	98.3± 0.01	10.0	101.5± 0.02	10.0	101.8± 0.03
UO_{2}^{2+}	1.0	94.5± 0.008	5.0	97.8± 0.03	10.0	102.8± 0.04	1.0	109.4± 0.05
Mn_{2+}	1.0	98.4± 0.006	5.0	95.1± 0.02	10.0	100.0± 0.03	1.0	109.4± 0.05
Ba_{2+}	10.0	97.9± 0.006	10.0	97.6± 0.02	10.0	98.7± 0.03	10.0	118.8± 0.03
Pb_{2+}	1.0	99.6± 0.004	10.0	95.1± 0.03	10.0	96.4± 0.03	1.0	104.5± 0.04
Hg_{2+}	1.0	889. ± 0.004	1.0	99.0± 0.03	10.0	102.8± 0.03	10.0	103.6± 0.04
Sn_{2+}	1.0	71.5± 0.004	1.0	80.5± 0.02	1.0	100.5± 0.03	5.0	100.0± 0.05
Th_{4+}	1.0	109.4± 0.008	1.0	100.2± 0.02	10.0	102.5± 0.02	1.0	112.6± 0.03
Cd_{2+}	1.0	98.0± 0.008	5.0	100.5± 0.02	5.0	101.5± 0.02	5.0	103.1± 0.03
Mg_{2+}	5.0	98.0± 0.005	10.0	100.0± 0.009	10.0	100.3± 0.01	10.0	104.5± 0.02
Ca_{2+}	5.0	98.4± 0.005	10.0	100.5± 0.009	10.0	104.6± 0.04	10.0	102.2± 0.05
ZrO_{2+}	1.0	110.7±	5.0	99.5± 0.03	1.0	103.6± 0.04	1.0	126.5± 0.04
CO_{2+}	1.0	103.7± 0.006	5.0	99.0± 0.03	1.0	153.6± 0.02	1.0	157.0± 0.06
Cu_{2+}	1.0	130.8± 0.008	1.0	92.4± 0.02	1.0	101.5± 0.02	1.0	134.1± 0.04
Zn_{2+}	1.0	138.9± 0.008	1.0	100.0± 0.02	1.0	106.6± 0.04	1.0	130.0± 0.04

The variation of greater than ±5% in the absorbance of the sample upon adding foreign ion was considered to have interfered. A close examination of this table revealed that quite a number of cations and anions did not interfere with the determination of Nickel (II) spectrophotometrically using various hydroxytriazenes even when present in tenfold excess over the analyte. However, (UO_2^{2+}, Hg^{2+}, Sn^{2+}, Th^{4+}, Zro^{2+}, Cu^{2+}, Zn^{2+}, PO_4^{3+}), (Sn^{2+}, Cu^{2+}), (Co^{2+}, Zn^{2+}), (UO_2^{2+}, Th^{4+}, Zro^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}) interfered seriously with reagent L_I, L_{II}, L_{III} and L_{IV} at one fold excess. The present study revealed that reagent L_{II} and L_{III} are more

selective than the other two reagents studied. Despite the fact that reagent L_{III} is more stable and have high selectivity, it cannot be used in the determination of Nickel (II) spectrophotometric in the environmental samples which Nickel (II) exists in trace amounts due to its low sensitivity.

This leaves reagent L_{II} to be more appropriate to be employed in the spectrophotometric determination of Nickel (II) in the environmental samples. The interference of Cu^{2+}can be prevented by masking it with oxalate ion solution which does not interfere even at tenfold excess[26].The sensitivity of the spectrophotometric determination of Nickel (II) utilizing reagent L_{II} was compared with some other spectrophotometric methods in the literature and the results are given in table no 4.

Table no 4: Comparison of characteristic performance of proposed techniques with other similar techniques reported in literature

S/No.	Reagent	Beer's Law range mg/Hg	Molar absorptivity $mol^{-1}cm^{-1}x10_4$	Stability constant $x10^9$	References
1.	3-Hydroxy-3-phenyl-1-0trifluorophenyl-triazene-1	0.11738 - 0.46952	1.8	_	Ghiasvand*et al.* (2006)
2.	3-hydroxy-3-methyl-1-(4sulphonami-dophenyl)-triazene	0.5869 - 3.5214	0.943	2.239	Khan&Khanam (2010)
3.	3-hydroxy-3-phenyl-1-(4trifluoromethylphenyl) triazene	0.35214 - 2.9345	0.970554	_	Regar *et al.*(2016)
4.	3-hydroxy-3-n-propyl-1-(4sulphonamido-phenyl) triazene	0.5869 - 3.5214	0.6743	_	Khanam*etal.* (2014)
5.	3-hydro-3-isopropyl-1-(4sulphonamidophenyl) triazene	0.5869 - 3.5214	0.7076	_	Khanam*etal.* (2013)
6.	3-hydroxy-3-m-tolyl-1-p-methoxyphenyltriazene	0.146725 - 0.733625	2.08	32.6888769	Used in present study

This table reveals that the present proposed spectrophotometric method employing reagent L_{II} is the most sensitive spectrophotometric method for Nickel (II) determination.

Table no 5 summarizes Nickel (II) concentration values in soil and *Amaranthus vividis* samples which were obtained with objective of checking the reliabilityof the proposed method when applied to determine Nickel (II) in the environmental samples.

Table no 5: Levels of Nickel (II) in environmental sample from Meru dumpsite in Buuri Sub-County Kenya

	Amount of Nickel (II) in soil sample (mg/Kg)		Amount of Nickel (II) in *Amaranthus vividis* sample (mg/Kg)	
S/No.	AAS	Present method	AAS	Present method
1.	2.51	2.47	2.12	2.03
2.	2.26	2.23	1.40	1.38
3.	1.89	1.85	1.19	1.15
4.	2.22	2.09	1.96	1.86
5.	2.33	2.30	2.03	1.96
6.	0.96	0.91	0.13	0.11
	$F_{calculated}$=1.002 $F_{tabulated}$=5.05 $T_{calculated}$=0.1544 $t_{tabulated}$=2.228		$F_{calculated}$=1.038 $F_{tabulated}$=5.05 $T_{calculated}$=0.4773 $t_{tabulated}$=2.228	

Flames atomic absorption spectrophotometric technique was used as a standard reference method for checking the accuracy of the proposed method. Results shows that levels of Nickel (II) in the soil and plant samples obtained from the dumpsite were higher than their corresponding levels in their respective control. This can be attributed to anthropogenic nature of the dumpsite[3]. Recycling and sorting out or converting these dumpsite wastes to other useful products can lead to a friendly environment free from health hazards. The values obtained were within the normal range for both soil (2-7.5mg/Kg) and plant (0.02-5.0mg/Kg). However, they were below critical soil concentration (100mg/Kg) and critical plant concentration (10-100mg/Kg) (table no 6).

Table no 6: Concentration of Heavy Metals in plants and soils, and critical concentrations in plants and soils

Metal	Normal range in plants($mgkg^{-1}$)	Critical plant conc ($mg\ kg^{-1}$) A	Critical plant conc ($mg\ kg^{-1}$) B	Normal range in soils ($mg\ kg^{-1}$)	Critical soil conc ($mg\ kg^{-1}$)
As	0.02-7	5-20	1-20	0.1-40	20-50
Cd	0.1-2.4	5-30	4-200	0.01-2.0	3-8
Co	0.02-1	15-50	4-40	0.5-65	25-50
Cr	0.03-14	5-30	2-18	5-1500	75-100
Cu	5-20	20-100	5-64	2-250	60-125

Hg	0.005-0.17	1-3	1-8	0.01-0.5	0.3-5
Mn	20-1000	300-500	100-7000	20-10000	1500-3000
Mo	0.03-5	10-50	-	0.1-40	2-10
Ni	0.02-5	10-100	8-220	2-750	100
Pb	0.2-20	30-300	-	2-300	100-400
Sb	0.00001-0.2	-	1-2	0.2-10	5-10
Sc	0.001-2	5-30	3-40	0.1-5	5-10
Sn	0.2-6.8	60	63	1-200	50
V	0.001-1.5	5-10	5-13	3.500	50-100
Zn	1-400	100-400	100-900	1-900	70-400

Source: Radojevic & Bashkin (2006).

A: concentrations above which toxicity is likely
B: concentrations likely to cause a 10% reduction

The low values obtained were associated with the seasonal variation.The samples were collected during rainy season; the time during which leaching of the metals underground is high. This approach is supported by the works which were carried out by Isola*et al*. (2015), Olatunji *et al*. (2016) which revealed that during dry season the levels of Nickel (II) in the soil is high compared to rainy season. The low concentration of Nickel (II) in the soil samples was attributed to the tendency of the plants to continuous removal of heavy metals from the soil. The low value of Nickel (II) obtained from the plant samples compared to its critical value can be attributed to possibility of having the metal ions which inhibit its uptake like Cu^{2+} and Zn^{2+}. The other factors which could have contributed to low uptake of Nickel (II) by plants include; Nickel (II) concentration, plant metabolism, the acidity of soil and organic matter composition[4]. The t and f values calculated at 95% confidence level indicated that, there is no statistical difference in the results of flame atomic absorption spectrophotometric and the proposed method. Hence the proposed method can be used to determine Nickel (II) in the environmental sample.

IV. Conclusion

A spectrophotometric technique for the determination of Nickel (II) using 3-Hydroxy-3-m-tolyl-1-pmethoxyphenyltriazene has been proposed. The strengths of the proposed method are freedom from interferences, high selectivity, high sensitivity and stability in comparison with some of the hydroxytriazene which havebeen reported for the determination of the Nickel (II). The selectivity of the reagent could be improved further by use of an appropriate masking reagent to suppress the interference of diverse metal ions. The results of the proposed methodare comparable with those obtained using flame atomic absorption spectrophotometric forNickel (II) determination in soil and plant samples from the dumpsite as revealed by t-test and F-test. The values of Nickel (II) in soil and plant samples from the dumpsite were below critical values hence there is no need for serious concern about pollution of the environment by Nickel (II) due to the presence of the dumpsite.

V. Recommendation

The studies on the same site and other siteswithin Meru County should be carried out for the determination of other toxic elements.

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