



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

CODEN: IJRSFP (USA)

*International Journal of Recent Scientific Research*  
Vol. 9, Issue, 4(D), pp. 25753-25757, April, 2018

**International Journal of  
Recent Scientific  
Research**

DOI: 10.24327/IJRSR

## Research Article

# ACCELERATED SOLVENT EXTRACTION OF COPPER USING CYANEX 301 AND ITS SPECTROPHOTOMETRIC DETERMINATION

**Bhanu Raman\*, Anita Madhu and Manisha Sawant**

Department of Chemistry, K.J.Somaiya College of Science and Commerce,  
University of Mumbai, India

DOI: <http://dx.doi.org/10.24327/ijrsr.2018.0904.1923>

### ARTICLE INFO

#### Article History:

Received 8<sup>th</sup> January, 2018  
Received in revised form 21<sup>st</sup>  
February, 2018  
Accepted 05<sup>th</sup> March, 2018  
Published online 28<sup>th</sup> April, 2018

#### Key Words:

Accelerated Solvent Extraction, Cyanex 301, Copper

### ABSTRACT

In spite of substantial time and solvent required, traditional extraction techniques in analytical laboratory shows the biggest bottlenecks and source of errors that occur during sample preparation. Difficulties encountered includes long duration per sample, large amount of solvent, maximum exposure of expensive hazardous solvents in the environment and difficult labor intensive. To bring this change stage of laboratory workflow the technique of Accelerated Solvent Extraction (ASE) is used to par with the powerful analytical techniques that exist today. ASE is an automated technique specialized in extraction of solid and semi-solid samples using liquid solvents at temperature above their normal boiling points. This technique is designed to reduce time and solvent required to achieve faster extraction. The proposed work is to extract copper using organodithiophosphinic acid reagent 2,4,4-bis trimethylpentylidithiophosphinic acid (Cyanex 301) in acidic medium using ASE. Copper mixed with Ottawa adsorbent were transferred to 33ml Zirconium extraction cell. Cyanex 301 in toluene used as an extracting agent were passed into extraction cell. It formed a complex with copper in acidic medium. During the extraction process ASE operational variables such as temperature, pressure, static time, purge time and extraction cycle were optimised to achieve efficient extractions. Extracts were collected and quantitatively evaluated in UV-Visible Spectrophotometer. ASE method has significantly reduced both sample preparation time and the amount of organic solvent used as compared to other traditional methods. The proposed method has been successfully applied to recover metal in real samples.

**Copyright © Bhanu Raman., Anita Madhu and Manisha Sawant, 2018**, this is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

## INTRODUCTION

Copper, atomic number (29), is a noble metal belonging to group 11 in the periodic table and is found in free metallic state in nature. It has two oxidation states +1 and +2 as cuprous and cupric form respectively. It is widely used in electricity, welding, wood preservatives and architecture construction. In humans, copper is found mainly in the liver, muscle and bone. Copper as trace minerals found in foods and dietary minerals helps to form haemoglobin and collagen in the body. Deficiency of copper leads to anemia, liver damage and can be treated with proper dietary copper supplements<sup>1</sup>.

Literature survey revealed numerous techniques, such as solvent extraction<sup>2</sup>, direct titration<sup>2</sup>, Colorimetric determination<sup>2</sup> and spectrophotometric titration<sup>2</sup>, have been used for determination of copper. Estimation of copper have been extracted by various extraction methods. Solvent extraction of copper with various chelating agents like Schiff

base derived from terephthalaldehyde and 5-amino-2-methoxy-phenol<sup>3</sup>, Trifluoroacetylacetone<sup>4</sup>, equimolar mixtures of N,N,N',N'-tetrahexylpyridine-3,5-dicarboxamide (L) with 2-hydroxy-5-t-octylbenzophenone oxime or 1-phenyldecane-1,3-dione (HB)<sup>5</sup>, dithiocarbamate<sup>6</sup>, Cyanex 272, Cyanex 302 and Cyanex 301<sup>7,8,9</sup> have been studied. Solid phase extraction of copper in water samples using surfactant coated alumina modified with indane-1,2,3-trione 1,2-dioxime have been studied<sup>10</sup>, diethyldithiocarbamate (DDTC) complex by polyurethane foam<sup>11</sup> have been studied. Organophosphorous acid Cyanex 301 were used for selective removal of transition metal by transport through polymer inclusion membrane<sup>12</sup> and also in preparation of extraction resin for radioactive waste determination<sup>13</sup>.

The above methods are laborious, time consuming, and large amount of solvents are used for extraction technique. These problems are easily solved by a newly automated extraction technique Thermo Fisher 350 Accelerated Solvent Extraction

\*Corresponding author: **Bhanu Raman**

Department of Chemistry, K.J.Somaiya College of Science and Commerce, University of Mumbai, India

(ASE 350). ASE 350 is a simple sample preparation technique where the samples are in either solid or semi solid form mixed with suitable adsorbent. Extraction takes place in the presence of pressure and temperature which are faster and efficient as compared to other traditional methods<sup>14</sup>. Direct extraction of lead, manganese, nickel, iron, copper, gold and cadmium with water EDTA mixtures using ASE were reported<sup>15,16</sup>. The present study highlights ASE of copper using Cyanex 301 and its estimation in spectrophotometer.

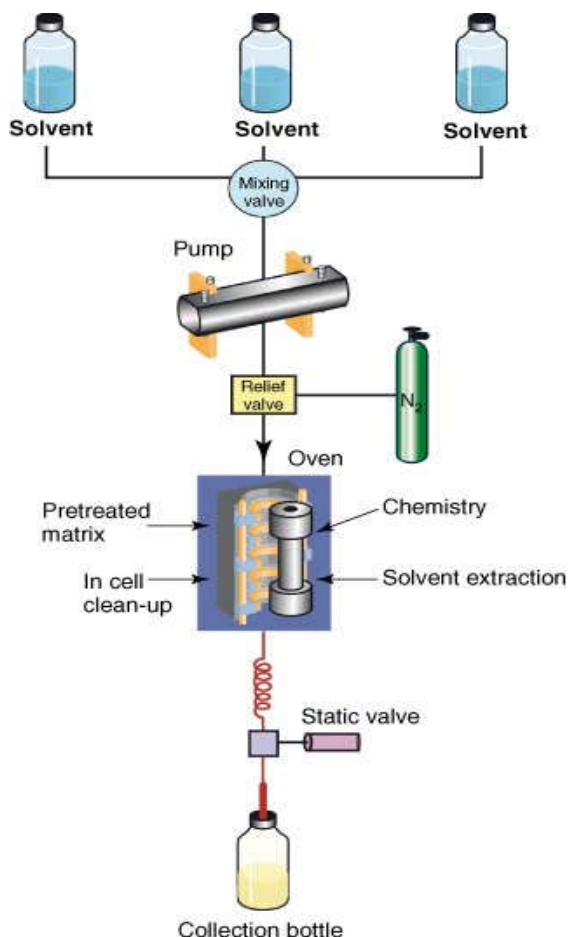
## MATERIALS AND METHODOLOGY

### Materials

**Stock solution:** Analytical grade E. Merck chemicals were used for experimental purpose. The extractant Cyanex 301 used was supplied from Cytec Inc. Canada.

**Instrumentation:** Thermo Fisher ASE 350 with pH hardened pathway from Thermo Fisher Pvt Ltd were used for extraction purpose. Spectronic Genesys 8 UV-VIS Spectrophotometer with 10mm path length cuvettes were used for absorbance measurement.

## METHODOLOGY



**Extraction Procedure:** Weighed 5.0 g of standard Copper sulfate pentahydrate in hand and mortar pestle to attain particle size smaller than 1.0 mm. Copper were dispersed with inert material containing 5 g of Ottawa sand adsorbent. This mixture was filled in 33 ml Zirconium Extraction Cell, covered with cellulose lid. Extraction cell then loaded into the carousel with pre-programmed temperature and pressure. Two solvent

bottles kept above the carousel containing extractant Cyanex 301 in toluene and acid solution HCl in each were passed into the carousel to attain static extraction for a certain period of time. Repeat cycles were performed to complete extraction. The complex formed was collected from the collection vessel section and were diluted to tenfold times to evaluate copper in spectrophotometer. Various optical parameters for optimum conditions were studied in spectrophotometer.

### ASE Parameter

#### Solvent

Solvent is required to solubilize the desired analyte. With various solvents like methanol, ethanol, benzene, toluene, alcohol, it was found that toluene was used as suitable solvents for extraction of copper with Cyanex 301. The solvent is kept in glass container of 1 litres capacity. HCl of desired concentration were passed in another glass bottle of 1liter capacity. Initially the entire ASE instrument was rinsed thoroughly with toluene to remove unwanted impurities and for the extraction purpose 30 ml volume of toluene were utilized.

#### Temperature

Temperature is required to increase the rate of extraction process thereby enhancing the extraction efficiency. Since the boiling point of toluene was  $110.6^{\circ}C$ , temperature was pre-set and maintained at  $120^{\circ}C$  throughout.

#### Pressure

Pressure was required to maintain solvents in liquid state and to move the fluid through the ASE system swiftly. Within the available range of 1000 - 3000 psi, it was found that extraction were effectively performed at 1500 psi. Hence 1500 psi pressure were used throughout the study.

#### Extraction Cell

Since present extraction requires acidic medium, pH hardened pathways 33 ml of Zirconium extraction cell permits the use of samples that require pretreatment with acid.

#### Cycles

In order to facilitate favorable extraction equilibrium, static cycles were studied. It was found that 2 cycles for 5 minutes were required to attain static equilibrium. After complete extraction, nitrogen gas was purged to remove the last trace of extracts. It was found that nitrogen gas was purged in 90 seconds.

#### Time

On the basis of the static extraction, cycle, the total extraction time for copper per extraction were completed in fifteen minutes.

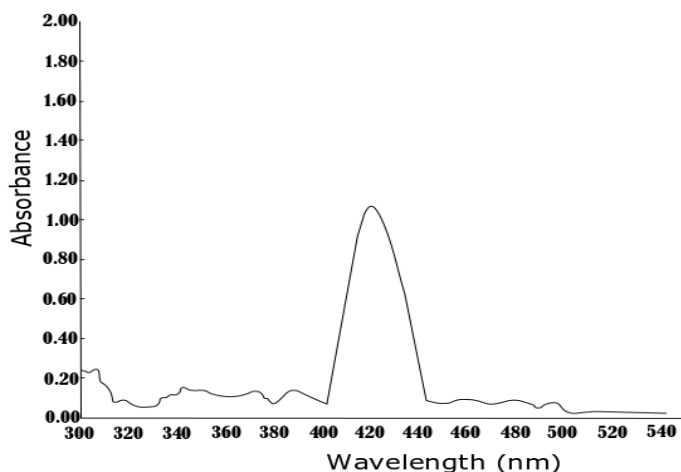
Parameter	ASE Optimum Condition
Extraction Cell	33 ml Zirconium Extraction Cell
Solvent	Toluene
Temperature	$120^{\circ}C$
Pressure	1500 psi
Static Extraction Time	5 minutes
Number of cycles	2
Purge Time	90s
Total Extraction Time	15 minutes

## RESULTS AND DISCUSSION

The complex Cu-Cyanex 301 after extraction were determined spectrophotometrically.

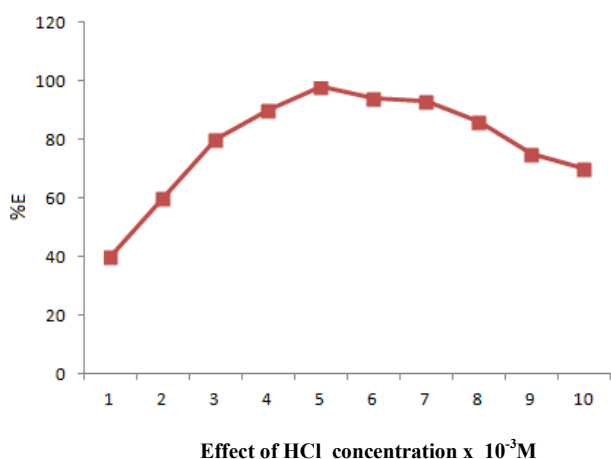
### Absorption Spectrum

The absorption of Copper- Cyanex 301 complex was studied over a wavelength range of 200-500 nm. The complex exhibited absorption maxima at 440nm. For all the further measurements, the wavelength of 440nm was chosen.



### Effect of HCl concentration

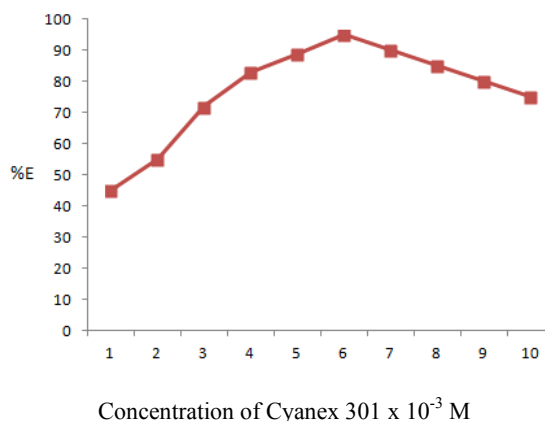
Since acidic conditions are required to carry out extraction hence various concentration of HCl were studied from 0.001M to 0.01M HCl. From the plot of percentage extraction with concentration of HCl it was found that extraction efficiency increased upto 0.005M HCl and beyond this the value decreases. Hence throughout experiment 0.005M HCl were used as the optimum concentration of HCl.



Effect of HCl concentration x 10<sup>-3</sup>M  
**Fig 2** Plot of Percentage Extraction against Concentration of HCl

### Effect of reagent concentration

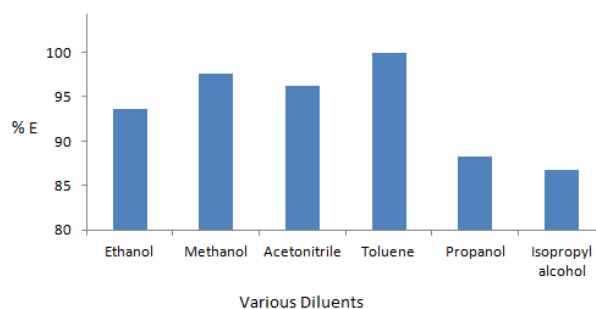
The optimum concentration of Cyanex 301 for quantitative extraction of Cu (II) was ascertained by extraction with varying concentrations of Cyanex 301 from 0.005 M-0.05M in toluene. The extraction was quantitative with 0.01M Cyanex 301 (Fig 3). Hence 0.01M Cyanex 301 in toluene was used throughout the study.



**Fig 3** Plot of Percentage Extraction against Concentration of Cyanex 301

### Effect of various diluents

In order to study the effect of diluents on extraction, 5g of copper sulfate pentahydrate with adsorbent Ottawas sand mixture, 0.005M HCl and 0.01M Cyanex reagent in different diluents were studied. The absorbance and % extraction of copper decreased in the order: Toluene (99.99%), Methanol (97.56%), Acetonitrile (96.23%), Ethanol (93.62%), Propanol (88.32%), Isopropyl alcohol (86.80%) (Fig.4). Toluene gave quantitative extraction and hence for all further studies toluene was chosen as diluents.



**Fig 4** Plot of Percentage Extraction against Various Diluents

### Effect of Stability of complex

The copper Cyanex 301 complex was found to be 8 hours stable.

### Nature of the Copper-Cyanex 301 complex

While varying extractant concentration to ascertain the nature of the extracted species Distribution Ratio "D" was evaluated. A graph of log[D] versus log[Cyanex 301] at fixed molarity of 0.005M HCl was plotted. The slope was 2.08 indicating the probable composition of the extracted species as 1:2 or Cu: (Cyanex 301)<sub>2</sub>.

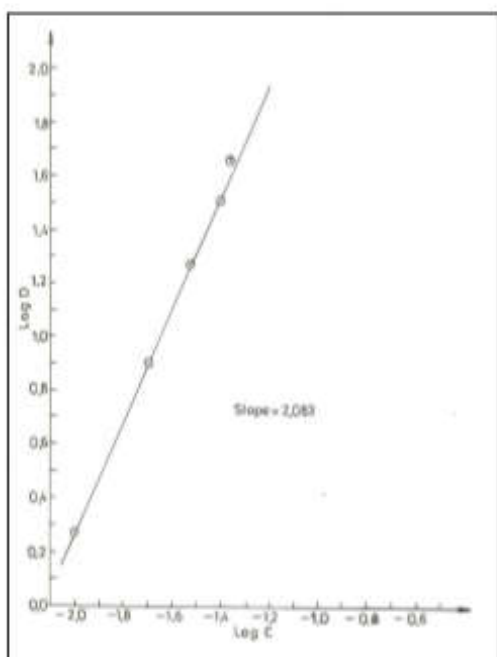


Fig 5 Plot of Log D against Log Cyanex 301

#### Validity of Beer-Lambert law

A calibration graph for determination of copper was prepared under optimum experimental conditions. Beer's law was found to obey in the range of 0.1 ppm to 5 ppm of copper at 440 nm. (Fig.5)

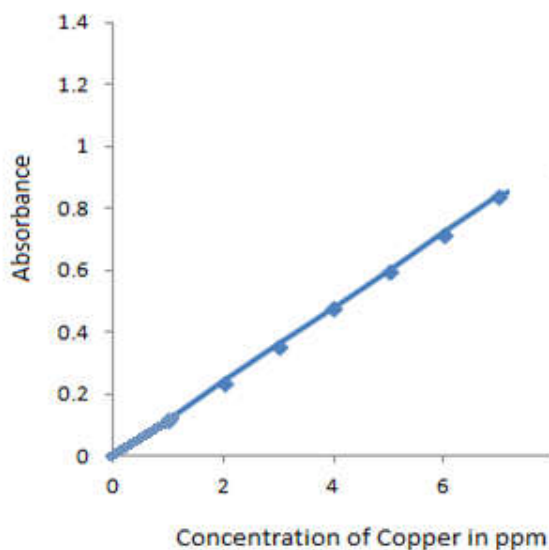


Fig 6 Plot of Absorbance against Concentration of Copper

**Spectrophotometric data for the determination of copper after extraction with Cyanex 301:** From the above observation indicates that complex copper with Cyanex 301 shows an intense peak at 440 nm ( $\lambda_{max}$ ). Beer's law is obeyed over the copper concentration range of 0.1 to 5.0 ppm. The composition of extracted species is found to be 1:2. [Cu: Cyanex 301] by Job's continuous variation and mole ratio method thus confirming the oxidation state of Copper as +2. The molar absorptivity is found to be  $5894.74 \text{ mole}^{-1}\text{cm}^{-1}\text{dm}^3$ . The Sandell's sensitivity is  $10.0 \times 10^{-3} \mu\text{gml}^{-1}\text{cm}^2$ . The value of standard deviation was  $2.12 \times 10^{-3}$  with coefficient of variation as 0.76.

#### Analysis of Cu (II) in real samples

##### From Pharmaceutical samples

The Pharmaceutical tablet samples were powdered and mixed with Ottawa adsorbent. These samples were tested with proposed method and also by ICP.

Results are tabulated in Table 4

Sample	Concentration of Copper ppm <sup>a</sup> (by present method)	Concentration of Copper ppm (by ICP)	Recovery (%) <sup>a</sup>
CopperSebacate	3.8 mg	4.0 mg	95.00
Supradyn	3.32 mg	3.39 mg	97.93
Zinc copper	1.9 mg	2.0 mg	95.00

<sup>a</sup> Average of five determinations analysis.

##### From food stuffs

Foodstuffs like lentils, almonds, mushrooms were analysed for its copper content.

Sample	Concentration of Copper ppm* (by present method)	Concentration of Copper ppm (by ICP)	Recovery (%) <sup>*</sup>
Lentils	0.48 ppm	0.5 ppm	96.00
Almonds	0.37 ppm	0.4 ppm	92.50
Mushrooms	0.40 ppm	0.43 ppm	93.02

\*Average of five determinations analysis.

#### CONCLUSION

The data presented strongly indicate that, by using elevated temperatures and pressures with organic solvent, efficient extraction of analytes can be achieved from solid samples. ASE was found to be less time consuming. Less volume of solvent have been used thereby reducing the cost for solvent purchase and waste disposal. The organic extracts being colored, afforded to determine copper metal directly in spectrophotometer. ASE systems offers a level of automation and precision that greatly exceeds traditional sample preparation techniques. This method proves to be more reliable, fastest, simple and novel method extraction.

#### Acknowledgements

The author would like to thank: Sincere thanks to Cytec Canada for providing free sample of Cyanex 301 Sincere thanks to Cytec Canada for providing free sample of Cyanex 301 1) Principal Dr. Vijay Joshi, K.J. Somaiya College, Vidyavihar, Mumbai. 2) Mr. Chetan Chavan, Mr. T. Vishnuvardhanrao, Mr. Chanakya Thaker and Mr. Chetan Chaudhari for permitting to work on ASE 350 in Thermo Fisher Scientific Pvt Ltd, Powai, Mumbai. 3) Cytec Canada Co. for supplying sample of Cyanex 301.

#### References

1. C. F. Poole, *Encyclopedia of Separation Science*, vol. 3, Academic Press, 2000.
2. Vogel, 1989, *Textbook of Quantitative Chemical Analysis*, 5<sup>th</sup> edition, pg 177, 184, 379, 455, 517, 583, 619, 689 and 724.
3. Wail AlZoubi, Mohamad Khaled Chebani "Solvent extraction of chromium and copper using Schiff base derived from terephthalaldehyde and 5-amino-2-methoxy-phenol," *Arabian Journal of Chemistry*, Volume 9, Issue 4, July 2016, Pages 526-531.

4. W. G. Scribner, W. J. Treat, J. D. Weis, and R. W. Moshier "Solvent Extraction of Metal Ions with Trifluoroacetylacetone" *Anal. Chem.*, 1965, 37 (9), pp 1136–1142
5. Aleksandra Borowiak-Resterna & Jan Szymanowski "Copper Extraction From Chloride Solutions With Mixtures Of Solvating And Chelating Reagents" *Journal Solvent Extraction And Ion Exchange* Volume 18, 2000 - Issue 1, page 77 – 91.
6. Vedula S. Sastri, Keijo I. Aspila, And Chuni L. Chakrabarti. " Studies on the solvent extraction of metal dithiocarbamate" *Canadian Journal Of Chemistry*. Vol. 47, 1969, pp 2320 – 2323.
7. Kathryn C.Sole, J.BrentHiskey, " Solvent extraction of copper by Cyanex 272, Cyanex 302 and Cyanex 301" *Hydrometallurgy* Volume 37, Issue 2, February 1995, Pages 129-147.
8. Priyadarshini Shinde and P M Dhadke, "Solvent extraction separation of Cu (II) and Ni (II) ith Cyanex 301, *Indian Journal of Chemical Technology*, Vol. 3, November 1996, pp 367 – 370.
9. Anant P. Argekar, Ashok K. Shetty, " Extraction and Spectrophotometric Determination of Copper (II) with bis(2,4,4-trimethylpentyl)dithiophosphinic acid", *Analytical Sciences*, Vol.12, (1996) No 2, page 255 – 258.
10. Mahdi Hossein, Nasser Dalali, Ali Karimi, Kourosh Dastanra "Solid Phase Extraction Of copper, nickel, and cobalt in water samples using surfactant coated alumina modified with indane-1,2,3-trione 1,2-dioxime and determination by flame atomic absorption spectrometry ", *Turk J Chem J Chem* 34 (2010) , pp 805 – 814.
11. Otoniel D. Sant'Ana<sup>I</sup>; Luciene S. Jesuino<sup>I</sup>; Ricardo J. Cassella<sup>II</sup>; Marcelo S. Carvalho; Ricardo E. Santelli, "Solid phase extraction of Cu(II) as diethyldithiocarbamate (DDTC) complex by polyurethane foam", ISSN 1678-4790.
12. Andras Koris, Darko Krstic, Xianguo Hu, Gyula Vatai, 2005, *Environment Protection Engineering*, Vol 31, no.3-4.
13. Glary Clark, 2001, "Integrated Project Management Planning For The Deactivation Of The Savannah River Site F-Cyanon Complex", WM'01 Conference, February 25-March 1, 2001, Tucson, AZ
14. John L. Ezell, " Accelerated Solvent Extraction of Organometallic and Inorganic compounds ", *Comprehensive Analytical Chemistry XLI*, Mester and Sturgeon (Eds.) @ 2003 Elsevier
15. O. Sadik, A. Wanekaya and S.Myung, 2002, "Pressure assisted chelating extraction : a novel technique for digesting metals in solid matrices", *Analyst*, 127, 3 – 7.
16. Bruce E. Ritcher, Brian A. Jones, John L. Ezzell and Nathan L. Porter, "Accelerated Solvent Extraction :A Technique for Sample Preparation ", *Analytical Chemistry* , Vol. 68, No.6, March 15, 1996.
17. M. Ghaedi, F. Ahmadi, and M. Soylak, "Simultaneous preconcentration of copper, nickel, cobalt and lead ions prior to their flame atomic absorption spectrometric determination," *Annali di Chimica*, vol. 97, no. 5-6, pp. 277–285, 2007.
18. N. Jalbani, T. G. Kazi, M. K. Jamali, B. M. Arain, H. I. Afridi, and A. Baloch, "Evaluation of aluminum contents in different bakery foods by electrothermal atomic absorption spectrometer." *Journal of Food Composition and Analysis*, vol. 20, no. 3-4, pp. 226–231, 2007.
19. M. B. Arain, T. G. Kazi, M. K. Jamali, N. Jalbani, H. I. Afridi, and J. A. Baig, "Speciation of heavy metals in sediment by conventional, ultrasound and microwave assisted single extraction methods: a comparison with modified sequential extraction procedure," *Journal of Hazardous Materials*, vol. 154, no. 1–3, pp. 998–1006, 2008.
20. R. Ansari, T. G. Kazi, M. K. Jamali et al., "Improved extraction method for the determination of iron, copper, and nickel in new varieties of sunflower oil by atomic absorption spectroscopy," *Journal of AOAC International*, vol. 91, no. 2, pp. 400–407, 2008.
21. M. Ghaedi, M. R. Fathi, A. Shokrollahi, and F. Shajarat, "Highly selective and sensitive preconcentration of mercury ion and determination by cold vapor atomic absorption spectroscopy," *Analytical Letters*, vol. 39, no. 6, pp. 1171–1185, 2006
22. V. Camel, "Solid phase extraction of trace elements," *Spectrochimica Acta—Part B*, vol. 58, no. 7, pp. 1177–1233, 2003. View at Publisher · View at Google Scholar · View at Scopus.

**How to cite this article:**

Bhanu Raman *et al.* 2018, Accelerated Solvent Extraction of Copper Using Cyanex 301 and its Spectrophotometric Determination. *Int J Recent Sci Res.* 9(4), pp. 25753-25757. DOI: <http://dx.doi.org/10.24327/ijrsr.2018.0904.1923>

\*\*\*\*\*