



## Estimation Free Cyanide on the Sites Exposed of Organisms Mortality in Sura River /November 2018

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### Abstract

Inductively coupled plasma mass spectrometry (ICP-MS) and high-performance liquid chromatography hyphenated were used cyanide determination. Samples preparation, digestion, and extraction efficiency. Analytical methods for the determination of total acute toxicity of cyanide at temperatures from 4- 24 and dissolved oxygen  $6.1 \pm 0.4$  mg/L on different stages of five basic sites of Euphrates rivers water were more sensitive at lower temperatures. Results have been obtained from analysis of water samples with recoveries of 88.1% to 100 % and Relative Standard Deviations (RSD) of <0.05 %. This study proves the potential application of the newly developed method for the analysis of free cyanide in river waters while the study time we could not get any kind of fish especially after the mortality in November 2018.

**Keywords:** Hydrogen Cyanide, Euphrates, River water.

### Introduction

Sura means low ground, a place in Iraq from the land of Babylon, close to the ancient city of Babylon, a river with much water, is the largest river that takes its water from the Euphrates River and runs between the Kafa and the village of Al- Qasim. This branch of the Euphrates is divided into two parts. The first direction is to the west this section is called Al-Alqmi. It passes through Kufa and the other branch is called Sura, it passes through the city of Sura to the Nile and Wasit, this city importance in the history of Iraq, as this bridge is the road between Kufa and cities and Baghdad. Water Rivers consider an essential for population survival and important to many of the economy.

Therefore, contamination in water resources should be a matter of concern to human health [1]. Fish farming is characterized by a wealth of local population is keen to feed, which is a portion of healthy food and an easy way to breed and live. *Cyprinus carpio* one of the most cultured species in breeding areas. Cyanide consider is one of the most toxic substances on earth and aquatic life even at low concentrations and used widely in metal mining operations as pesticides agents intermediates in agricultural chemical products.

Cyanide is not an element but a compound composed of only carbon and nitrogen and its chemical behavior in rivers and sediments is complex and toxicity is influenced by more factors, including alkalinity or acidity [2]. Free cyanide bioaccumulation in the food chain or persists like toxic metals but it once reacted, leaves a little residual trace [3].

In water, cyanide exists of form free state ( $\text{CN}^-$  and  $\text{HCN}$ ), simple cyanide ( $\text{NaCN}$ ), complex cyanide and total cyanide and persists in the dissociated form ( $\text{HCN}$ ) in pH below 7 and the degree of its toxicity depends on the solubility and the dissociation rate to form free cyanide [4], it has low persistence in the aquatic environment and does not accumulate in or store within the tissue of organism due to of its rapid detoxification at sub-lethal doses and death at lethal doses.

The toxicity of cyanide is attributed to presence of  $\text{HCN}$  derived from dissociation of the complexes that penetrate cell walls to cause mortality [5]. Environmental fate about forms of the cyanide in the aquatic ecosystem is affected by temperature, pH, dissolved oxygen, salinity and other ions, complexation agents and sunlight [6].

The cyanide complexes that are frequently accessible to aquatic ecosystems specifically in the waters river and some of its living organisms were the most cyanide sensitive aquatic organisms tested [7], so this study aimed to determine the acute toxicity (LC50) of hydrogen cyanide and the relative sensitivity of water followed by its impact on behavior factors surrounding it. The technique is inductively coupled plasma mass spectrometry (ICP-MS) [8]. Some authors have used other detection techniques, such as hydride generation atomic absorption spectrometry (HG-AAS) or electro thermal

atomic absorption spectrometry in order to minimize spectral interferences hampering arsenic cyanide determination, the dynamic reaction cell by introducing the reacting gas, usually ammonia, hydrogen, oxygen, or methane. Argon in plasma readily forms polyatomic ions, with the same mass to charge ( $m/z$ ) as the analyzed element, with matrix atoms in the sample. The reacting gas overcomes this by atom transfer or charge transfer reactions [9].

## Methodology

### Collection Samples and Study Area

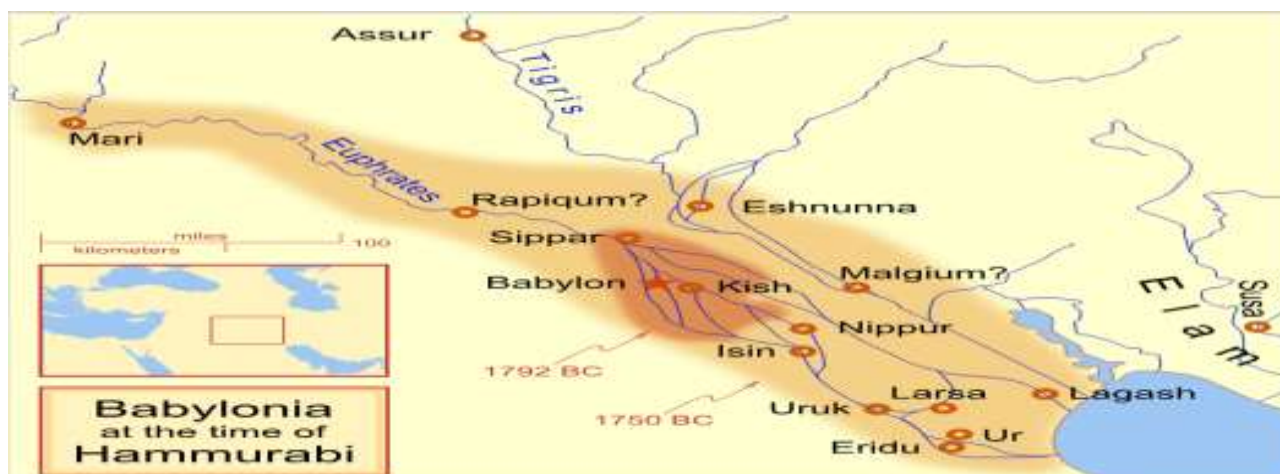


Fig. 1: Sura city (The Cambridge Ancient History: Prolegomena & Prehistory: Vol. 1, Part 1. Accessed 15 December 2010)

Water samples were collected during the fish mortality period in November 2018. Five water samples (sub-surface) were collected by means of a Van Dorn water sampler and then separated into two parts for analysis before and after filtration filtered through 0.45 $\mu$  Millipore. The filtrates were placed in glass containers and were divided into two parts for pre-treatment and post-treatment. Standard methods by [10]. (24 before and 24 after) one sample three replicate total water 48.

The standards and certified reference materials (CRM) with cyanide and complex data on Cyanide speciation in water must be gathered, Speciation analysis of Cyanide involves three steps: extraction, separation, and detection. A combination of analytical techniques must be used to obtain sufficient selectivity and sensitivity for speciation analysis.

### Laboratory Analysis

#### Mechanical Working of Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Depended a most critical step in water analysis is sample preparation. Many solvents and extraction methods for Cyanide from water samples have been tested. Methanol, water, a mixture of water-methanol in different ratios, and diluted acids are the most frequently used solvents. The most common extraction methods are mechanical stirring, Soxhlet extraction, ultrasound extraction [11]. Total cyanide Determination was determined parameters such as reaction gas flow rate and Rpa were optimized in order to obtain the highest intensity solution containing the lowest intensity in the blank.

Standard solutions and blank were prepared in three different ways: [1] with the use of distilled water and nitric acid [2]. With the use of water matrix after filtration. [3] With the use of water matrix after extraction. Reaction gas flow rate and Rpa were optimized thrice, as we had three pairs of blanks and standard solutions. The greatest difference in signal intensities between blank and standard solution was obtained at 0.55 ml in a minute, thus this flow rate was

selected as optimal (0.55 and 0), respectively. It was checked by the analysis of certified reference materials CRMs (BCR-627, MODAS-5) [12]. Depending on APHA, 2005 some physical and chemical properties of water samples were measured.

## Statistical Method

The analysis of variance (ANOVA) using a complete randomized design (CRD) was employed to test the differences between the eight date palm residues and A. tortillas in all the measured properties using the SAS statistical package. Least significant difference at 5% level of probability (LSD 0.05) used to detect the differences among the means of all the measured properties. Correlation analysis was carried out to find out the relationship between the heating value and each of the chemical constituents and ultimate and proximate analysis of the date palm residues [13].

## Results and Discussion

### Total Physical and Chemical Properties Determination

The Mean physical and chemical properties of the water samples were measured and the results were as follows and compared with the limited in WHO 2005 and were found as follows, temperature  $24 \pm 4$  °C, pH  $7.2 \pm 0.3$  at 24°C, dissolved oxygen  $6.1 \pm 0.4$  mg/L, carbon dioxide  $6.1 \pm 0.5$  mg/L, total hardness  $28.4 \pm 4.4$  mg as  $\text{CaCO}_3/\text{L}$ , phosphate  $0.59 \pm 0.02$   $\mu\text{g/L}$ , salinity 0.11ppm, specific gravity 1.00 and conductivity less than 10  $\mu\text{S/cm}$ . Water has checked the water for the next day renewed.

### Total Cyanide Determination

Result by inductively coupled plasma mass spectrometry (ICP-MS) showed medium for toxicity test cyanide 88 % purity were conducted with a total of 100 ml were selected from five each sample with three replicates and were exposed cyanide test

concentrations (0.58, 0.62, 0.70, 0.76, 0.86) ml these resulted in the mortality of the fish (It was synchronized with the time of mortality on November 2018) the range-finding test with The measured concentration of cyanide in the water samples are summarized in Tables (1) Cyanide levels were compared to maximum contaminant with the limit provided by the WHO criteria [14]. The measured concentration of cyanide in the Euphrates river water samples were compared to maximum contaminant limit Environmental Protection Agency provided by the WHO criteria [15]. Mean (0.72 mg/L) for cyanide distribution in water samples.

Since there was no study in the recent months and we were unable to obtain live fish in this period, the results were compared with the results of the limit Environmental Protection Agency provided by the WHO 2006 and the registration of cyanide concentrations for the period 2018 November as a reference for future comparison, the major source of chronic toxic chemical exposure is from surface water which irrigated with contaminated water, it is essential to determine toxic chemicals in the surface water. Such as cyanide among the toxic chemicals that may contaminate the drinking water and agricultural water.

Based on our clinical observation in Ministry of Environment and Health, high concentrations of cyanide was assumed to be a source for the health problems due to a fatal compound, and its acute poisoning usually readily diagnosed. It is a clear and early warning indicator of aquatic organisms especially fish and mollusks. Despite the result that caused only high toxicity most cyanide in surface water will form hydrogen cyanide and evaporate. However, the amount of hydrogen cyanide formed is generally not enough to be harmful to humans. Some cyanide in water will be transformed into less harmful chemicals by microorganisms [16].

Table 1: Total Cyanide concentration in ICP MASS (n = 5)

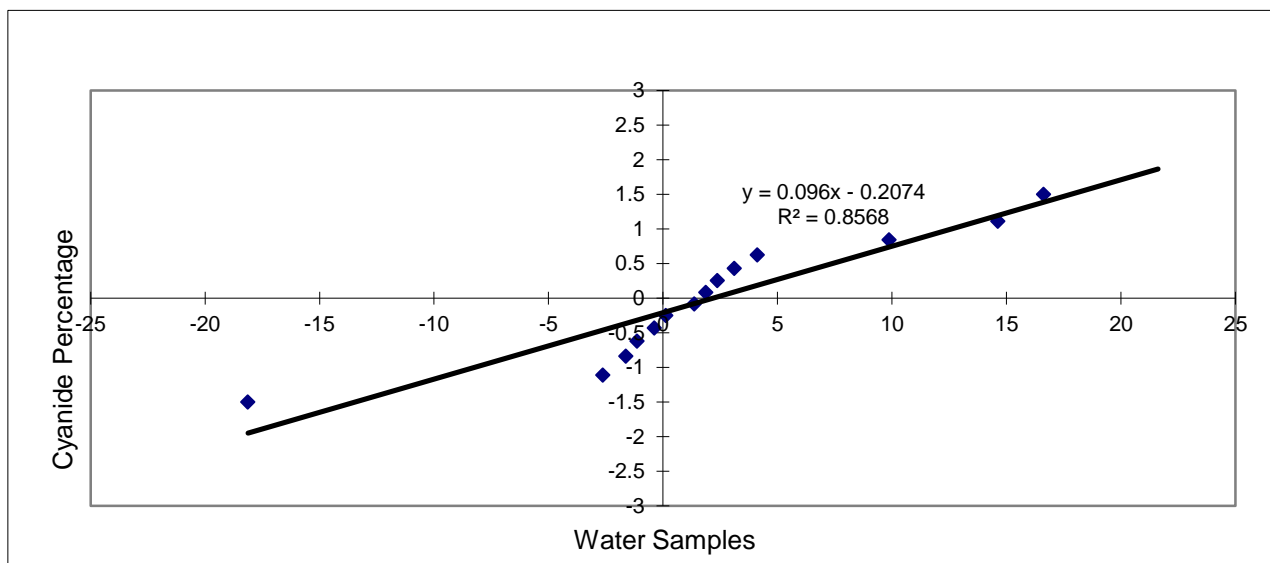
Station	Cyanide ml First reading	Standard Deviation	Mass Fraction Mg/l	Cyanide ml Second reading	Standard Deviation	Mass Fraction Mg/l	CR column recovery. %]
1	0.58	0.006	5.27	0.32	0.002	13.59	93
2	0.62	0.005	4.93	0.22	0.001	12.39	90
3	0.70	0.005	4.81	0.40	0.003	12.90	88
4	0.76	0.006	4.76	0.33	0.003	13.02	102
5	0.86	0.009	5.33	0.21	0.006	13.01	99
P value	0.02	-	-	0.03	-	-	-

Excessive cyanide exposure can result in acute acquired; however, chronic cyanide poisoning which comes from contaminated water or from contaminated air may well not be detected. In similar studies, several groundwater sites were examined in northern China where cyanide levels 41.34 mg/L exceeded the limits allowed for drinking water [17]. Another study in Tabriz, Iran found the maximum of 0.0069 mg/L cyanide concentration in industrial effluents [18].

Based on cyanide concentrations in our results water samples, it seems that the contamination effect this can make a health problem by contaminated waters, fruits, or vegetables in the future and high levels of cyanide in the rivers and its penetration to the soil may transfer and contaminated the water wells in the coming years. Distribution of cyanide concentrations in Euphrates water in Figure [1] simultaneous control group from other sites. The results did not differ significantly.

**Table 2: Simulation control group from other sites. The results did not differ significantly.**

Correlation	First reading	mean	Mg/l	Second reading	Mean	Mg/l
1	1.000	0.757	0.095	-0.238	0.909	-0.099
2	0.757	1.000	0.709	-0.543	0.895	0.270
3	0.095	0.709	1.000	-0.526	0.436	0.491
4	-0.238	-0.543	-0.526	1.000	-0.217	0.365
5	0.909	0.895	0.436	-0.217	1.000	0.207



**Figure 1: Total Cyanide concentration in ICP MASS (n = 5)**

### Conclusions

Limitations in results because to technical difficulties and lack of co-ordination between the relevant organizations, it was not possible to carry out samplings in regular months. In the current study, the concentration of cyanide in water samples were determined as a high mean level.

Consequently, there was no need to special statistical analysis the time of the examination, it is possible to verify the focus of periodic re-examination during the coming periods, especially during the months of growth and food enrichment, where the river's organisms are spread and the fish are prevented from growing along the river

supply in order to preserve the fish and aquatic organisms and preserve the purity of the water that is dependent on drinking and local use, Middle of the Euphrates River.

About limitations due to technical difficulties and lack of coordination between the relevant organizations, it was not possible to carry out samplings in regular after all the deaths that occurred in the Euphrates River, which caused a major environmental loss of fish wealth during the month of November. In the current study, the concentration of cyanide and mercury as a step to examine these elements in polluted water and there were no living organisms during the mortality were determined as a mean level.

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