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**MINERALS AND HEAVY METALS CONSTITUENTS OF A SPIDER WEB MADE BY  
*ARANEUS DIADEMATUS* (ARANEIDAE)**

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**ABSTRACT**

The objective of this study was to investigate the minerals and heavy metals composition in the web-silk of two populations of the spider *Araneus diadematus* (Araneidae) by Atomic Absorption Spectrophotometer. Minerals forming (59 %) and heavy metals forming (41 %) of the total content were found in the web-silk of the two populations. The major component was Calcium (Ca) that formed (38.9% - 41%) followed by Aluminium (AL) that formed (20.2 - 21.2%) of the total constituents. Calcium formed (65.7%) of total minerals in population (1) followed by Mg (12.2%), Na (11%) and K (9%); and (69.1%) of total minerals in population (2) followed by Mg (11%) and Na (7%). Low content (0.6 – 1.4 %) of phosphate and manganese was detected in both populations. Aluminium and iron constituted, respectively, (52% and 45.3%) of total heavy metals in population (1) and (49.4% and 47.8%) in population (2). The content of Zn, Ba, Cu, Cr and Ni was very low in both populations. The present results indicate that the silk-webs of the spider *Araneus diadematus* is rich of minerals and metals beneficial for human uses in different medical and industrial products. Slight differences observed could be related to different compositions in the diet of each population. Further investigations may reveal undiscovered important contents of the spider webs.

**Keywords: Alumimium, *Araneus diadematus*, Calcium, Heavy Metals, Iron, Minerals,  
Spider-Web**

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**INTRODUCTION**

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Many species of spider have different glands to produce silk with different properties for different purposes, including housing, web construction, capturing and detaining prey, egg protection, and mobility [1, 2, 3]. They may also help to protect the spider from predators such as birds and wasps. Every spider produces silk in several different kinds of glands, each gland is responsible for its own protein chemistry [4]. Spider silk is one of the strongest naturally occurring fibers [5]. The strength lies in the protein structure of the fiber, which changes as the silk goes from the liquid state inside the spider to the solid state outside the spider [6]. The basic structure of spider silk is complex molecules of amino acid, where glycine and alanine are the primary constituents [7]. The spider silk in native and super contracted states have been analyzed by spectroscopy [8]. [9], studied the variation in the chemical composition of orb webs built by different populations of the spider *Nephilaclavipes* (Araneae, Tetragnathidae) and found the adhesive droplets in the orb webs to contain, among other constituents, an aqueous solution of organic low-molecular-weight compounds which varied in different populations.

The tensile strength of spider silk is greater than the same weight of steel and has much

greater elasticity [10]. However, spider silk is much less dense than steel; its ratio of tensile strength to density is perhaps 5 times better than steel [11].

The combination of strength and ductility gives the spider silk a very high toughness [12], which equals that of commercial polyaramid (aromatic nylon) filaments, which themselves are benchmarks of modern polymer fiber technology [13]. Various compounds other than protein were found in spider silks, such as sugars, lipids, ions, and pigments that might affect the aggregation behavior and act as a protection layer in the final fiber.

The properties of spider silk have impressed naturalists for thousands of years. Its microstructure is under investigation for potential applications in industry, including bullet-proof vests, and artificial tendons [14]. Researchers have used genetically modified mammals to produce the proteins needed to make these materials [15]. The genes encoding spider silk were cloned and expressed in the laboratory [16, 17, 18].

The composition of spider silk is not well known and research is going on to discover the constituents of different silks. Therefore, the present study focused on the minerals and heavy metals constituents in the web-silk of

two populations of the spider: *Araneus diadematus*. The main objective of the study is to determine qualitatively and quantitatively the composition of minerals and metals which are, probably, behind the strength and antiseptic properties of the spider silk.

## MATERIALS AND METHODS

### Handling Spider Webs

The spider webs were collected onto clean glass rods (one rod per population of spider). The webs were collected by cutting radii with a clean scalpel (wiped with 50% ethanol between samples), winding it upon a section of the rod and left to reset according to [9]. Each web was scraped off of the rod with a clean razor blade and was stored inside a clean sampling bottle. The collection was repeated several times until an adequate quantity of each orb was obtained. After all webs had been collected, the orb webs were washed twice in 50mL distilled, deionized water; without agitation at room temperature. The webs from a given population of the spider were then combined, dried and used for analysis.

### Minerals and heavy metals analysis

The concentrations of minerals and heavy metals were analyzed from dry samples of spider web and determined after wet digestion with a mixture of nitric, sulphuric and

hydrochloric acid using Atomic Absorption Spectrophotometer (AAS Model SP9). Each analysis was carried out in triplicates. The results are provided as (ppm,  $\mu\text{g/g}$  dry weight).

## RESULTS AND DISCUSSION

**Table 1** represents the content (p.p.m.,  $\mu\text{g/g}$ . DW) and percentage (%) of minerals and heavy metals in the web-silk of the spider *Araneus diadematus*. Six minerals forming almost (59 %) and seven heavy metals forming (41 %) of the total content was found in the web-silk of the two populations of the species. The major component of the silk was Calcium (Ca) that formed (38.9%) and (41%), followed by Aluminium (AL) that formed (21.2%) and (20.1%) of the total constituents in the two populations (**Figure 1a & 1b**).

Calcium formed (65.7%) of total minerals in population 1 (**Figure 2a**), followed by Mg (12.2%), Na (11%) and K (9%). Calcium formed (69.1%) of total minerals in population 2 (**Figure 2b**), followed by Mg and K (11%) and Na (7%). Low content (0.6 – 1.4 %) of phosphate and manganese was detected in both populations. The major heavy metals were aluminium and iron which constitute, respectively, (52% and 45.3%) of total heavy metals in population 1 (**Figure 3a**); and (49.4% and 47.8%) in population 2 (**Figure 3b**). The content (0.03 – 1.2 %) of

Zn, Ba, Cu, Cr and Ni was very low in both populations

The results of the present study showed that the silk of the spider-webs contains considerable amounts of minerals which could explain the effectiveness of spider-webs in wound healing. Peasants in the southern Carpathian Mountains used to cut up tubes built by *Atypus* and cover wounds with the inner lining. It was reported to facilitate healing, and even connected with the skin. This is believed to be due to antiseptic properties of spider silk [19], and because the silk is rich in vitamin K, which plays a direct role in clotting of the blood. The high content of calcium ions can also be another healing component of the spider-web required in the presence of vitamin-K to convert the prothrombin, a plasma proenzyme, into thrombin, a proteolytic enzyme. Thrombin, in turn, converts fibrinogen into fibrin which makes the clot [20]. Calcium ions, with other proteins, transfer fibrin from a soft clot to a hard one. On the other hand, phosphate might forms hydrogen phosphate that make the silk acidic thus protect its protein from bacteria and fungi. Since the spider silk was proved to be composed of a natural protein polypeptide of amino acids, the detected amounts of sodium and potassium salts might prevent denaturing of these proteins in this acidic

medium. The silk of *Nephila clavipes* has recently been used to help in mammalian neuronal regeneration [21].

The high content of aluminium and iron found in studied webs could be behind the strength of silk of the spider webs. Both aluminium and iron are used in many industries to make millions of different products, and is very important to the world economy. Structural components made from aluminium are vital to the aerospace industry and very important in other areas of transportation and building in which light weight, durability, and strength are needed. Aluminium is a soft, lightweight but strong metal. Aluminium weighs about one-third as much as steel or copper and has excellent corrosion resistance and good heat conduction [22]. It is also nonmagnetic and nonsparking and is the second most malleable metal and the sixth most ductile. Due to the presence of these characters, fishermen in the Indo-Pacific Ocean use the web of *Nephila* to catch small fish. People in Madagascar work to collect over one million golden orb spiders and extract silk from them to make a textile with golden tint. It was also used to make leather garment interwoven with spider silk to protect the soldiers from enemy arrows. This protection could be due to the high content of aluminium in the silk [23].

Spider silk is commonly used as a thread for crosshairs in optical instruments such as telescopes, microscopes, and telescopic rifle sights. Spider silk fibers were used in the field of optics to generate very fine diffraction patterns over N-slit interferometric signals utilized in optical communications [24, 25]. Spider silk was also used to suspend inertial confinement fusion targets during laser ignition, as it remains considerably elastic and has a high energy to break at temperatures as low as 10-20K. In addition, it is made from "light" atomic number elements that won't emit x-rays during irradiation that could preheat the target so that the pressure differential required for fusion is not achieved. Spider silk fibers were used to create a set of violin strings [26].

A molecular biologist is planning to use the proteins from super strong dragline silk to build artificial tendons and ligaments. Recent work characterizing the proteins responsible for the incredible strength and elasticity of spider silks could lead to durable and resilient new materials for artificial human tissues, surgical sutures, and ultrastrong armor [23, 27].

The amount of minerals and heavy metals was not significantly different among the two populations. The slight difference observed could be related to different compositions of

the diet of each population. The present results indicate that the silk-webs of the spider *Araneus diadematus* is rich of minerals and metals beneficial for human uses and can be extracted for different medical and industrial products such as antiseptic bandages and solutions. Because spider silk is rich in aluminium and iron it can be used in industry of transportation (automobiles, airplanes, trucks, railcars, marine vessels), packaging (cans, foil), construction (windows, doors, siding), consumer durable goods (appliances, cooking utensils), electrical transmission lines (because of its light weight, even though its electrical conductivity is only 60% of copper's) and machinery. Spider silk could also be a potential resource of other important components. The full realization of this potential will be facilitated by further investigation which may reveal undiscovered contents of the spider webs.

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**Table 1: Minerals and Heavy Metals Contents in a Spider web made by Two Populations of *Araneus diadematus***

Mineral	Population (1)		Population (2)	
	Ppm ( $\mu\text{g/g}$ , dry weight)	%	Ppm ( $\mu\text{g/g}$ , dry weight)	%
Ca	65300	38.9	55700	41
Mg	12200	7.3	8840	6.5
Na	10900	6.5	5780	4.3
K	8990	5.4	8670	6.4
P	1262	0.8	1159	0.9
Mn	670	0.4	506	0.4
Total minerals	99322	59.2	80655	59.4
Al	35600	21.2	27300	20.1
Fe	31000	18.5	26400	19.4
Zn	828	0.5	802	0.6
Ba	824	0.5	608	0.5
Cu	105	0.06	51.7	0.04
Cr	48	0.03	42	0.03
Ni	21	0.01	18	0.01
Total heavy metals	68426	40.8	55221.7	40.6

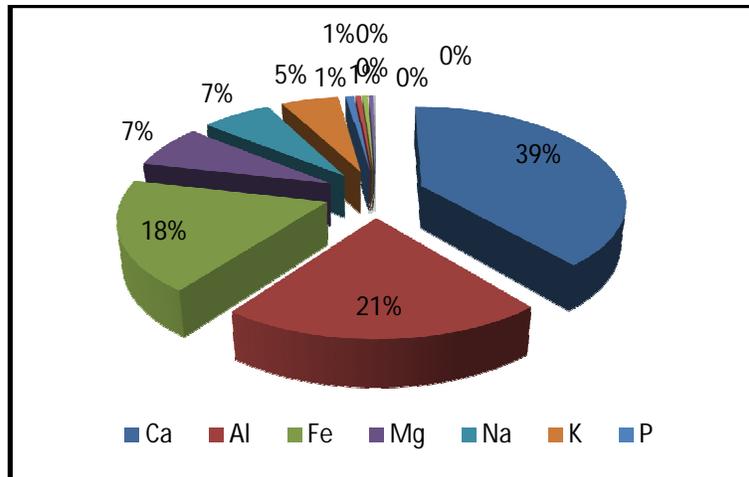


Figure 1a: Percentage of Minerals and Heavy Metals Contents in a Silk-Web Made by Spider *Araneus diadematus* (Population 1)

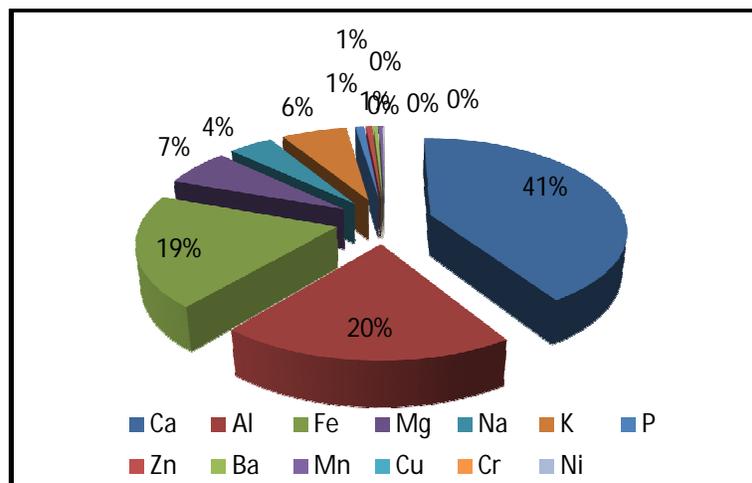


Figure 1b: Percentage of Minerals and Heavy Metals Contents in a Silk-Web Made by Spider *Araneus diadematus* (Population 2)

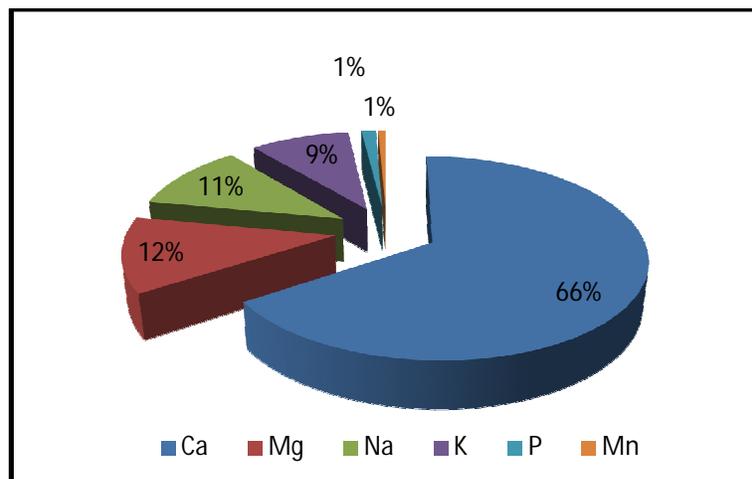


Figure 2a: Percentage of Individual Mineral (%TM) Content in a Silk-Web Made by Spider *Araneus diadematus* (Population 1)

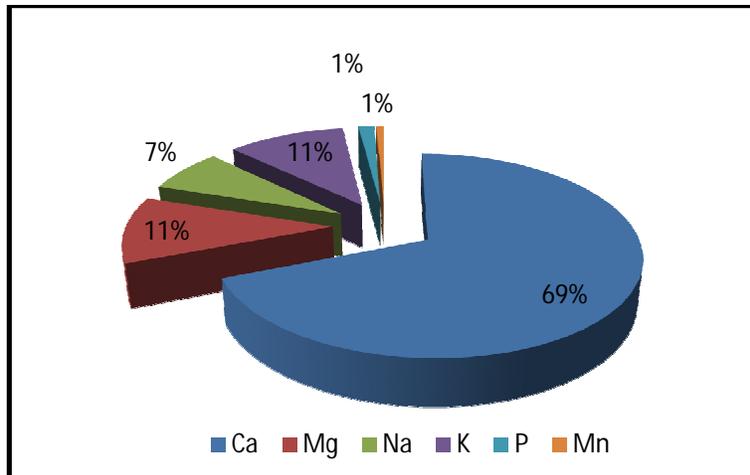


Figure 2b: Percentage of Individual Mineral (%TM) Content in a Silk- Web Made by Spider *Araneus diadematus* (Population 2)

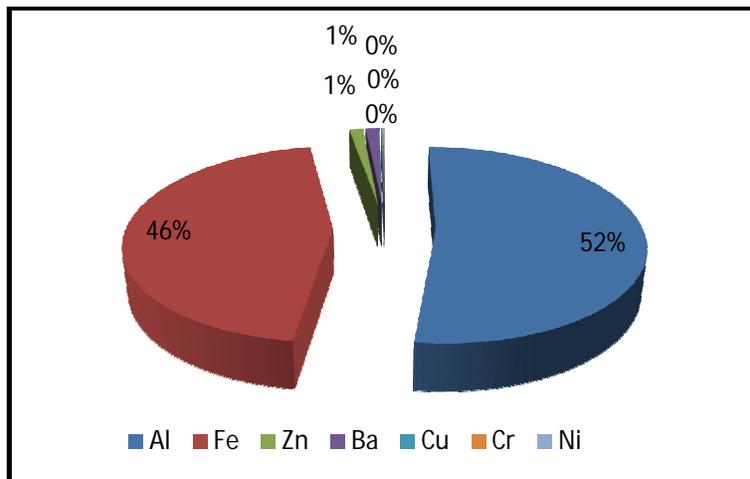


Figure 3a: Percentage of Individual Metal (%THM) Content in a Silk- Web Made by Spider *Araneus diadematus* (Population 1)

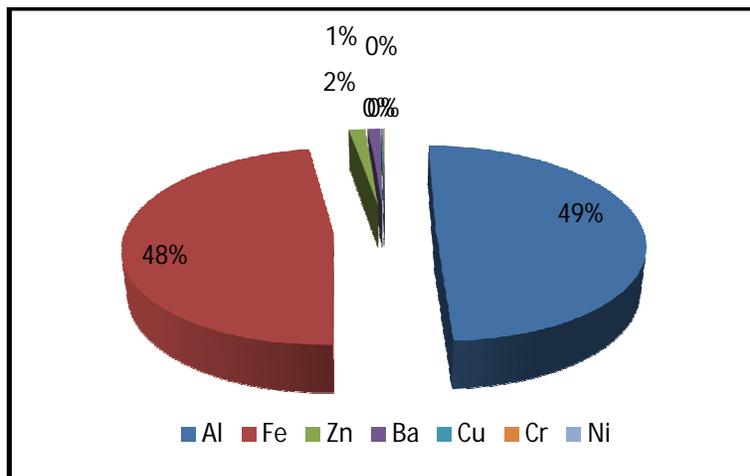


Figure 3b: Percentage of Individual Metal (%THM) Content in a Silk-Web Made by Spider *Araneus diadematus* (Population 2)