

# Trace Element Analysis of some Medicinal and Aromatic Plant Taxa by ICP-MS

Ebubekir İZOL1\*, İsa ÇİÇEK<sup>2</sup>, Lütfi BEHÇET<sup>2</sup>, Enes KAYA<sup>1</sup>, Abbas TARHAN<sup>3</sup>

<sup>1</sup> Bingöl University, Bee and Natural Products R&D and P&D Application and Research Center, Bingöl, Türkiye <sup>2</sup> Bingöl University, Science and Art Faculty, Molecular Biology and Genetics Department, Bingöl, Türkiye <sup>3</sup> Dicle University, Science and Technology Application and Research Center, Diyarbakır, Türkiye Ebubekir İZOL ORCID No: 0000-0003-0788-4999 İsa ÇİÇEK ORCID No: 0000-0001-7241-6599 Lütfi BEHÇET ORCID No: 0000-0001-8334-7816 Enes KAYA ORCID No: 0000-0003-3973-168X Abbas TARHAN ORCID No: 00000-0001-5196-3892

\*Corresponding author: eizol@bingol.edu.tr

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Keywords ICP-MS, Çermik, Trace element analysis, Plants, Minerals **Abstract:** In this study, analysis of trace elements (Al, V, Cr, Ni, Cu, Zn, As, Ag, Cd, Sn, Hg, Pb) in medicinally important taxa, such as *Alkanna trichophila* Hub.-Mor. var. *trichophila*, *Anchusa azurea* Mill. var. *azurea* (Boraginaceae), *Achillea biebersteinii* Afan., *Centaurea iberica* Trev. ex Sprengel (Asteraceae), *Ajuga vestita* Boiss. (Endemic), *Teucrium polium* L. (Lamiaceae), collected in Çermik district of Türkiye's Diyarbakır province, was conducted quantitatively and qualitatively using the ICP-MS technique. Today, ICP-MS technology is one of the most sensitive metal analysis methods. As a result of the analysis, Sn, Hg, and Pb elements in the studied plant taxa could not be determined since they were below the LOD value. It is essential for consumers that these three toxic elements are not specified in plant species. In general, it was determined that the concentrations of heavy metals, which have harmful effects on health, were low in the investigated plants. Of all the elements, Al (26.04-193.5 mg/kg) had the highest concentration in the studied taxa. As a consequence, several trace elements were characterized, and their concentrations were identified in the studied medicinal and aromatic six ethnobotanically important plant species.

# Bazı Tıbbi ve Aromatik Bitki Taksonlarının ICP-MS ile Eser Element Analizi

**Anahtar Kelimeler** Öz: Bu çalışmada Türkiye'nin Diyarbakır ilinin Çermik ilçesinde toplanmış, folklorik veya tıbbi ICP-MS. amaclar icin kullanılan Anchusa azurea Mill. var. azurea (Boraginaceae). Achillea biebersteinii Cermik Afan. (Asteraceae), Ajuga vestita Boiss. (Endemik) (Lamaceae), Teucrium polium L. (Lamiaceae), Alkanna trichophila Hub.-Mor. (Boraginaceae), Centaurea ibericaTrev. ex Eser element Sprengel (Asteraceae) bitki türlerinin ICP-MS tekniği ile eser element (Al, V, Cr, Ni, Cu, Zn, analizleri. As, Ag, Cd, Sn, Hg, Pb) analizi kantitatif ve kalitatif olarak yapılmıştır. ICP-MS teknolojisi Bitkiler. günümüzde en hassas metal analiz yöntemlerindendir. Yapılan analiz sonucunda altı bitki Mineraller türünün tamamında Sn, Hg, Pb elementleri LOD değerinin altında kaldığından belirlenememiştir. Toksik olan bu üç elementin bitki türlerinde belirlenmemesi tüketiciler için önemlidir. Genel olarak araştırılan bitkilerde sağlığa zararlı etkileri olan ağır metal konsantrasyonlarının düşük olduğu belirlenmiştir. En yüksek konsantrasyon ise Al (26,04-193,5 mg/kg) elementinde belirlenmiştir. Sonuç olarak, etnobotanik açıdan önemli altı tıbbi ve aromatik bitki türünde çeşitli eser elementlerin karekterizasyonu ve konsantrasyonları belirlenmiştir.

## **1. INTRODUCTION**

For centuries, plants have been used for medicinal purposes to treat various diseases, including enteritis [1]. The development, regulation and application of traditional or herbal medicines in distinct parts of the world often present challenges. Common challenges in many countries are those connected to regulatory status, quality control, assessment of safety and effectiveness, safety monitoring, and insufficient knowledge of customary, complementary/alternative and herbal medicines within public drug regulatory authorities [2]. Metals with a density of more than 5 g /  $cm^3$  are defined as "heavy metals". In another definition, metals that are harmful when they enter the body in high concentrations are called toxic metals or heavy metals. More than 60 metals are in this group, including Pb, Cr, Cd, Co, Ni, Cu, Zn, Hg and Fe. Due to their nature, these elements are generally found in stable compounds or silicates in the form of oxide, carbonate, sulfur and silicate in the earth crust. To maintain their everyday activities, all living things need heavy metals in the environment. Iron (Fe), copper (Cu), manganese (Mn), cadmium (Cd), molybdenum (Mo), silicon (Si) and boron (B) are heavy metals required for plant metabolism. Cu, Co, Fe, Mn, Mo, Zn, Se, and I are also heavy metals needed for animals. Co, Cu, Cr, Fe, Mn, Ni, Mo, Zn, U, V are also toxic substances. The primary sources of heavy metals are mineral fertilizers, some base stones, sewage wastes, biocides, wastewater, urban wastes, motor vehicle exhaust gases and mining [3].

Trace elements play an essential role in the formation of active chemicals in medicinal plants and are also responsible for the toxicity of medicinal plants [4]. The grade of toxic heavy metals in plants can be affected by the geochemical parameters of the soil, air, water pollution and the ability of plants to amass certain elements selectively. Besides, metals may be connected to the geographical origin, harvest or gathering of these plant materials. Some metals (such as Fe, Cr, Mo, Ni Zn, Co, Mn, Cu, Al) are essential plant nutrients, but at higher concentrations, they are phytotoxic. However, most heavy metals are initially micronutrients, namely, they are necessary (in small amounts) for the expected growth of plants and animals. Manganese (Mn), molybdenum (Mo), copper (Cu), zinc (Zn), and nickel (Ni) are heavy metals required for higher plants. For humans and animals, copper (Cu), Manganese (Mn), cobalt (Co), chromium (Cr), molybdenum (Mo), zinc (Zn), vanadium (V), and selenium (Se) are micronutrient heavy metals. Iron (Fe), which is not generally considered a heavy metal, is essential for both plants and animals. Several other elements, including cadmium (Cd), lead (Pb), arsenic (As), and tin (Sn), could play a significant role at very low concentrations. Toxicities and deficiencies of micronutrients adversely affect animal and plant health, causing declines in growth rate (and yield), obvious physiological stress symptoms, and, in extreme cases, the death of the animal or plant [5]. The consumption of plants is significant for humanity. Commonly consumed plants may be needed for their chemical content, and they may need to be avoided due

to their harmful chemicals. [6]. For example, onion and garlic (*Allium* species) are widely consumed worldwide. Scientific studies have shown that these plants are beneficial, but they can be harmful due to their highly toxic element contents.

One of the most effective methods used to determine the amounts of elements in plants is the inductively coupled plasma-mass spectrometry (ICP-MS) method, an analytical technique in which the molecular bonds are broken, and atoms are ionized by sending argon to a high-temperature plasma. The sample is generally delivered as a solution to the nebulizer and spray chamber via the sample intake system. Here, thanks to the high-velocity argon flow, the sample solution is fogged. Only tiny droplets move into the argon plasma, and others go directly to waste. Plasma at temperatures of 7000 °K evaporates and ionizes the sample. Ion flow goes from atmospheric pressure to a high vacuum environment through sample and skimmer cones. The ion stream is then directed through the ion lenses to the mass filter, focusing on the quadruple. Ions are separated in the mass spectrometer according to their mass to charge ratio and are measured by the detector [7]. Essential components of ICP-MS are sample entry system, ICP torch, interface, vacuum system, lenses, DRC (Dynamic reaction cell), quadruple, detector, data processing and system controller [8]. ICP-MS is suitable for the determination of trace elements in solution with its fast analysis rate and convenient mass range. Simple spectra, low detection limit and compatibility with isotope ratios are the features that make ICP-MS attractive. The detection limit for most elements is below ng/L. Thanks to its ability to determine multiple elements, it is used in qualitative analysis and determination of isotope ratios, as well as in the quantitative and semi-qualitative analysis of the majority of the elements in the periodic table, including metallic elements, in various samples. Calibration graphs can be drawn between pg/L and mg/L for many elements. For this reason, many elements with different concentrations can be determined at the same time. Since the development of different sample introduction systems, the ICP-MS technique has been able to analyze solid samples as well as liquid samples. ICP-MS is widely used in wastewater, drinking water, food, hydrogeology, geochemistry, geology, and petrochemistry [9].

When the metal content of plants is considered, the concentrations of the elements must be determined in order not to exceed the concentration limits set by WHO, to be evaluated as a medicinal plant or food, to be used as a herbal drug and to be utilized ethnobotanically.

In this study, the trace element concentrations of six ethnobotanically important plant species (*A. trichophila*, *A. azurea*, *A. biebersteinii*, *C. iberica*, *A. vestita*, *T. polium*) were determined by inductively coupled plasmamass spectrometry (ICP-MS) technique. Following is detailed information on the studied plant taxa.

Anchusa azurea: The local name of the plant is Guriz or Gelizvan. It is called by various local names in different

geographies. The gathering periods are between April and May. Above ground parts are used for food and treatment purposes [10]. In the literature, its leaves and flowering branches, known as wound healing externally, are used widely as they are suitable for kidney diseases and lip cracking and have urinary-enhancing effects. The leaves can be used as a decoction or infusion as a diaphoretic, urinary enhancer and ulcer remedy. As an antidote against snake bites by crushing the leaves, the water obtained from boiling the leaves and flowers can be used in the treatment of eczema, and the aboveground parts can be used as decoction in asthma [11-20].

Achillea biebersteinii: The regional name of the plant is Gihaye Zerg. Likewise, it is called by various local names in different geographies. The gathering periods are between May and June. Flower parts are used for treatment [10]. In the use of the literature, the main used part of the plant is flower conditions, but it is found in the stem and leaf in the drugs sold, albeit a little. It effectively relieves abdominal pain in treating asthma, kidney pain, skin spots, urine enhancer, as an appetizer, and in treating gynaecological diseases. In the form of infusion against urinary tract inflammations (5%), rheumatic illnesses, anti-inflammatory, menstrual, hepatitis, sinusitis, menstrual pain, toothache, shortness of breath, abdominal pain, asthma as a decoction of all parts, flowers and leaves are powdered after drying. It can be used in wound treatments by pouring it on the wound and leaving the leaves on the wound when fresh. In the treatment of decoction ulcers prepared from the above-ground parts, the infusion trained from the aboveground parts can be used as a urinary tract antiseptic, including the infusion prepared from the flowering parts (capitula) [20-26].

*Ajuga vestita*: The local name of the plant is Abamayasıl herb. The gathering periods are between April and May. Above ground, parts are used for treatment. There is no use of literature in ethnobotanical terms. It is a plant that is collected when fresh, and eaten raw and brewed after drying due to its bitter taste and drunk with various sweeteners to reduce sugar in case of diabetes [10].

*Teucrium polium* L.: The local name of the plant is Meryemhot and Meyero. Likewise, in different geographies, it is named with many various local names and these names take place in the literature. The gathering periods are between May-June. Above ground, parts are used for treatment and belief [10]. In the literature, they are used to relieve headache and ear pain, wound healing, pain-relieving, stimulant, appetite, stomach ailments, digestive and excretory system ailments, stomach aches, appetite and diabetes, intestinal inflammation and laziness. It is also used in the treatment of tuberculosis, relieving stomach pain, cancer treatment, rheumatic pain, colds and diabetes [27-35].

*Alkanna trichophila*: The local name of the plant is Gurız Dervin. It is also included in the literature with different names. The gathering periods are between April and May. Root parts are used for treatment. Its roots are used as an expectorant to heal stomach and intestinal ulcers [10].

*Centaurea iberica*: The vernacular name of the plant is Kerbeşik, Çavbelok. Like other plants, they are named with many vernacular names in different geographies and these names are included in the literature. The gathering periods are between March-May. Fresh and young parts of above-ground parts are used for food and treatment purposes. In the use of the literature, the decoction of flowers and branches is prepared and used against rheumatic pain, malaria, antipyretic, menstrual, constipation, appetite, against goitre disease, stomach pain, snake and scorpion bites and malaria. It is also used in the treatment of sugar reducers, infusions, and internal antipyretics, wounds and boils [36-39].

# 2. MATERIAL AND METHODS

#### 2.1. Preparation of plant samples

Plant taxa were collected from the Çermik district in Diyarbakir province of Turkey. The plants collected were identified and recorded in the herbarium of Bingöl University. The names of the species, their herbarium numbers and the collection sites and times were given in Table 1.

Tablo 1. Names of plants species, place and time of gathering, herbarium numbers

| Name of Plant              | Collection | Herbarium | Collection        |
|----------------------------|------------|-----------|-------------------|
| taxa                       | localities | numbers   | period            |
| Alkanna<br>trichophila     | Diyarbakır | BIN9405   | Apr-May<br>2017   |
| Centaurea<br>iberica       | Diyarbakır | BIN9406   | March-May<br>2017 |
| Anchusa azurea             | Diyarbakır | BIN9402   | Apr- May<br>2017  |
| Achillea<br>biebersteinii. | Diyarbakır | BIN9401   | May- June<br>2017 |
| Ajuga vestita.             | Diyarbakır | BIN9404   | Apr- May<br>2017  |
| Teucrium<br>polium L.      | Diyarbakır | BIN9403   | May- June<br>2017 |

#### 2.2. Reagents

Ultrapure water (18.3 M $\Omega$  cm – 1 obtained from the Human power I device) was used in all of the experimental stages. Agilent Technologies (USA) brand multi-element calibration standard was used as the calibration standard for the elements determined for analysis reliability. In addition to the calibration standard, the internal standard Agilent Technologies brand standard internal mix is used. The nitric acid used is 65% Supra pure Merck (Darmstadt, Germany) brand.

#### 2.3. Digestion of The Samples

The dissolution process was done before the samples were analyzed with the ICP-MS device. For this, the ground samples were weighed 1 g, and 6 mL of supra pure nitric acid and 2 mL of hydrogen peroxide were added. The prepared samples were dissolved in CEM brand MARS6 ONE TOUCH (USA) model microwave shredder oven. The dissolved samples were diluted to 50 mL with 1% supra pure nitric acid prepared with ultrapure water [40]. Additional dilution was made so that the prepared samples coincided with the standard calibration range.

## 2.4. Instrumentation and Statistical Analysis

Standard solutions were prepared with 1% supra pure nitric acid at the concentrations given in Table 2.

| Table | 2. Calibration Sta  | indards         |                   |                  |
|-------|---|-----------------|-------------------|------------------|
| 1.Sd  | 1 (µg/kg)   | 4.Sd            | 50 (µg/kg)        | Internal<br>Sd   |
| 2.Sd  | 10 (µg/kg)  | 5.Sd            | 100 (µg/kg)       |                  |
| 3.Sd  | 25 (µg/kg)  | 6.Sd            | $200\;(\mu g/kg)$ |                  |
| tes   | <sup>27</sup> Al, <sup>51</sup> V, <sup>52</sup> Cr, <sup>60</sup> Ni, <sup>63</sup> Cu, <sup>66</sup> Zn |                 |                   | <sup>45</sup> Sc |
| Analy | <sup>75</sup> As, <sup>107</sup> Ag, <sup>1</sup>   | <sup>89</sup> Y |                   |                  |

Sd: Standard

Quantitative and qualitative analyses were performed with the ICP-MS (Agilent 7700X (Tokyo, Japan)) device. Before the sample analysis, the ICP-MS device was brought to optimum conditions and calibrated. <sup>45</sup>Sc, <sup>89</sup>Y elements are used as internal standards. After the calibration charts were created, the elements were analyzed with the ICP-MS device. A high level of helium gas is used to prevent interference. Samples diluted in the standard calibration range were sent to the cyclonic spray chamber with a peristaltic pump, high purity argon gas flow. Besides, for the reliability of the analysis, standard analysis and device calibration was performed after each sample. The operating parameters of the ICP-MS device are given in Table 3.

| Parameter                 | Description / Value |
|---------------------------|---------------------|
| Plasma gas                | Ar X50S 5.0         |
| Makeup gas                | 0.9 L/min           |
| Carrier gas (inner)       | 1.1 L/min           |
| Plasma gas flow (Ar)      | 15 L/min            |
| Radio frequency power     | 1550 W              |
| Radio frequency matching  | 1.80 V              |
| Radio frequency           | 27.12 MHz           |
| Injector                  | 2.0 mm              |
| Cones                     | Ni                  |
| Nebulizer pump            | 0.1 rps             |
| Background                | <5 cps (9 amu)      |
| Short-term stability      | <3% RSD             |
| Long-term stability       | <4% RSD/2 h         |
| Resolution m/z            | 244 amu             |
| Spray chamber temperature | 2°C                 |
| Rinse time                | 45 sec              |
| Sample intake             | 0.5 mL/min          |

In the analysis, linear range, regression and correlation coefficient (R) values, detection limit (LOD) and measurement limit (LOQ) of the calibration chart drawn under optimal operating conditions for twelve elements are shown in Table 4. The LOD and LOQ values of the studied metal elements were calculated using 10 independent blank solutions. LOD and LOQ were found as  $3.\sigma$  and  $10.\sigma$ , respectively.

Table 4. Analytical parameters of the ICP-MS method

| Element | Linear<br>range<br>(µg/kg) | Regression                   | Correlation<br>coefficient<br>(r) | Limit of<br>Detection<br>(µg/kg) | Limit of<br>Quantificat<br>ion<br>(µg/kg) |
|---------|----------------------------|------------------------------|-----------------------------------|----------------------------------|---|
| Al      | 0–200                      | y=0.006x                     | 0.9983                            | 1.1637                           | 3.4911                                    |
| v       | 0–200                      | y=0.002x                     | 0.9989                            | 0.0100                           | 0.0300                                    |
| Cr      | 0–200                      | -0.004<br>y=0.002x<br>-0.005 | 0.9990                            | 0.0115                           | 0.0345                                    |
| Ni      | 0–200                      | y=0.001x                     | 0.9994                            | 0.0328                           | 0.0984                                    |
| C<br>11 | 0–200                      | -0.002<br>y=0.004x<br>-0.007 | 0.9995                            | 0.0683                           | 0.2049                                    |
| Z       | 0–200                      | y=0.054x                     | 0.9885                            | 0.4126                           | 1.2378                                    |
| A       | 0–200                      | y=0.004x                     | 0.9999                            | 0.0747                           | 0.2241                                    |
| A       | 0–200                      | y=0.003x                     | 0.9747                            | 0.0358                           | 0.1074                                    |
| g<br>C  | 0–200                      | +0.041<br>y=0.001x           | 0.9991                            | 0.0607                           | 0.1821                                    |
| u<br>Sn | 0–200                      | -0.002<br>y=0.001x           | 0.9987                            | 0.0195                           | 0.0585                                    |
| H<br>g  | 0–200                      | -0.005<br>y=0.004x<br>-0.001 | 0.9999                            | 0.1355                           | 0.4065                                    |
| Pb      | 0–200                      | y=0.014x                     | 0.9952                            | 0.0427                           | 0.1281                                    |

Values expressed are means  $\pm$ standard deviation of three parallel measurements (p < 0.05).

# 3. RESULTS AND DISCUSSION

The concentration results of the analyzed elements are given in Table 5 with the average of three parallel readings and standard deviation values.

#### Table 5. Elemental analysis results of plants by ICP-MS<sup>a</sup>

|   | Al 27           | V 51              | Cr 52             |
|---|-----------------|-------------------|-------------------|
| Sample Id                               | (mg/kg)         | (µg/kg)           | (µg/kg)           |
|   |                 |                   |                   |
| Alkanna trichophila                     | $38.2 \pm 0.8$  | $97.0{\pm}2.1$    | $163.0 \pm 3.5$   |
| Centaurea iberica                       | $38.3 \pm 0.6$  | 2041.7±99         | $969.8 \pm 27.9$  |
| Anchusa azurea                          | 83.1±1.2        | 234.5±11          | 202.7±11.2        |
| Achillea biebersteinii Afan.            | 193.5±3.5       | 474.5±17          | $1000.6 \pm 33.5$ |
| Ajuga vestita.                          | 191.6±2.7       | 387.1±13          | 677.9±21.7        |
| Teucrium polium L.                      | $26.04{\pm}0.7$ | 97.0±9.3          | 79.4±3.5          |
|   | Ni 60           | Cu 63             | Zn 66             |
|   | (mg/kg)         | (mg/kg)           | (mg/kg)           |
| Alkanna trichophila Hub                 |                 |                   |                   |
| Mor.                                    | $0.83{\pm}0.05$ | $2.74 \pm 0.08$   | 23.8±1.5          |
| Centaurea iberica Trev. ex              |                 |                   |                   |
| Sprengel                                | $1.66{\pm}0.07$ | $4.02{\pm}0.09$   | 20.1±1.3          |
| Anchusa azurea Mill. var.               |                 |                   |                   |
| azurea                                  | $1.52 \pm 0.06$ | $4.46 \pm 0.09$   | $15.2 \pm 1.1$    |
| Achillea biebersteinii Afan.            | 6.27±0.11       | $3.79{\pm}0.09$   | 63.1±2.3          |
| Ajuga vestita Boiss.                    | $3.75 \pm 0.07$ | $5.87 \pm 0.11$   | $14.1 \pm 1.3$    |
| Teucrium polium L.                      | $0.69{\pm}0.03$ | $6.73 {\pm} 0.13$ | $17.8 \pm 1.7$    |
| <sup>a</sup> Results are the mean $\pm$ | standard de     | eviation of       | three parallel    |

measurements. (p < 0.05).

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 Table
 5.
 Elemental analysis results of plants by ICP-MS<sup>a</sup> (continuation)

| Sample Id                               | As 75<br>(μg/kg)  | Ag 107<br>(μg/kg)                               | Cd 111<br>(µg/kg)   |
|---|---|---|---------------------|
| Alkanna trichophila                     | $8.7 \pm 0.03$  | 75.1±5  | 230.5±15            |
| Centaurea iberica                       | $20.6 \pm 0.11$   | 53.6±3  | <lod< td=""></lod<> |
| Anchusa azurea                          | 29.3±0.15   | 33.3±3  | 31.9±4              |
| Achillea biebersteinii                  | $67.0{\pm}4.5$  | 163.2±11  | $17.8 \pm 1$        |
| Ajuga vestita                           | 30.6±1.2  | 7.31±0.9  | 81.3±7              |
| Teucrium polium L.                      | <lod< td=""><td>89.3±7</td><td>24.2±2</td></lod<>                           | 89.3±7  | 24.2±2              |
|   | Sn 118  | Hg 202  | Pb 208              |
|   | (µg/kg)   | (µg/kg)   | (µg/kg)             |
| Alkanna trichophila                     | <lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<> | <lod< td=""><td><lod< td=""></lod<></td></lod<> | <lod< td=""></lod<> |
| Centaurea iberica                       | <lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<> | <lod< td=""><td><lod< td=""></lod<></td></lod<> | <lod< td=""></lod<> |
| Anchusa azurea                          | <lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<> | <lod< td=""><td><lod< td=""></lod<></td></lod<> | <lod< td=""></lod<> |
| Achillea biebersteinii                  | <lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<> | <lod< td=""><td><lod< td=""></lod<></td></lod<> | <lod< td=""></lod<> |
| Ajuga vestita.                          | <lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<> | <lod< td=""><td><lod< td=""></lod<></td></lod<> | <lod< td=""></lod<> |
| Teucrium polium L.                      | <lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<> | <lod< td=""><td><lod< td=""></lod<></td></lod<> | <lod< td=""></lod<> |
| <sup>a</sup> Results are the mean $\pm$ | standard dev  | iation of th                                    | ree parallel        |

measurements. (p < 0.05).

In the literature review, it was determined that among the plant species, Anchusa azurea Mill., which was collekted only in Iraq, was analyzed by ICP-OES. In this study by Peshawa S. Osw and Faiq H.S. Hussain [41], Al concentration was found in the range of 25-303 mg/kg in seed, stem, branch and leaf. It was determined that the result we found  $(83.1 \pm 1.2 \text{ mg/kg})$  was within this range. V concentration was determined in the range 0.1-1.7 mg / kg. It was found to be close to the result we found (0.2 mg/kg). While the element Cr was found in the range of 0.4-1.8 mg/kg, we found it to be 0.2 mg/kg. While Ni was found to be 0.9-6.5 mg / kg, we found it 1.52 mg / kg. The concentrations of Cu, Zn, As, Ag, Cd elements we found were determined to be below the values found in this study. While Pb could not be determined in our study, it was found below 1 mg/kg in this study. It was seen that the values in the study were performed to a large extent and the results in our study were close to each other [41].

Aluminum (Al) is a heavy metal taken into the human body from drinking water and other sources. Its excess accumulation in the body increases the possibility of getting Alzheimer. It has been determined that the amount of Al in the brains of Alzheimer's patient increases [42]. Besides, adverse effects on the nervous system and lungs were detected [43]. For these reasons, it is an element that is important for human health. In his study, Yener found the concentration of the element Al in plants in the range of 30-1424 mg/kg [4]. In this study, the Al concentration range in plant species was 26-193 mg/kg. It was determined that the plant with the lowest Al concentration was *Teucrium polium* L. and the highest was *Achillea biebersteinii* Afan.

Studies have shown that vanadium (V) has both positive and negative effects on human health. It has been determined that the compounds it creates cause hypoglycemia by causing low blood sugar in humans. It has also been stated that it may be an antineoplastic agent against cancer [44]. The concentration range of vanadium element in the plants studied was found to be 97-2041  $\mu$ g / kg. At the same time, the highest concentration was observed in *Centaurea iberica*Trev. ex Sprengel plant, the lowest concentration was found in

# Alkanna trichophila Hub.-Mor. and Teucrium polium L. plants.

Chromium (Cr) element is crucial for human health. It acts as a cofactor in the synthesis of the insulin hormone and cholesterol. In a study, it was determined that Cr concentration varies between 0.15-4.8 mg/kg. In a different study, the Cr concentration was found in the range of 2-35 mg/kg [45]. According to WHO data, toxicity values for arsenic, lead, chromium and cadmium in wild plants were determined as 5, 10, 2 and 0.3 mg/kg, respectively [46, 47]. The range of values we found was determined as 79-1000  $\mu$ g / kg. It was seen that the values found were below the WHO data. While the highest measurement was observed in *Achillea biebersteinii* Afan. plant, the lowest measure was found in *Teucrium polium* L. plant species.

Nickel (Ni) is a metal whose concentration is limited by WHO in consumed plants. WHO data reported that the limit of Ni element in edible plants was 1.63 mg/kg [46]. It has been stated that the Ni concentration needed for human health can vary between 80-100  $\mu$ g / day. In general, the Ni content of foods is desired to be less than 0.5 mg/kg, but it has been reported that some foods may be higher [48]. A study determined that the Ni limit in plants was 0.5-10 mg/kg. In another study, Ni concentration was reported to range from 24-4740 µg / kg [45]. Ni concentration in our study was found in the range of 0.6-6 mg/kg. It was seen that these values were both above and below the WHO limit. It was determined that the highest concentration was in the Achillea biebersteinii Afan. plant species, and the lowest concentration was in the Teucrium polium L. plant.

Copper (Cu) is a heavy metal that is toxic when taken in excess. Also, it has been reported that copper can reduce hypertension and increase the infertility effect of lead [49]. Cu is a micronutrient element for plants [50]. In the study of Akgüç et al., They found the Cu limits in plants as 4-15 mg/kg [51]. In one study, Cu values were found as 0.2-24 mg/kg [45]. In this research, Cu levels in plants were found to be 2-6 mg/kg. It was determined that these values are below the WHO data.

Plants need nutrients containing trace elements found in the soil. Zinc (Zn) is an essential component for plant growth [52]. WHO has determined the Zn limit as 27.4 mg/kg in edible plants [46]. In the study of Potortì et al., They found the Zn concentration range as 1-5240 mg/kg. In this study, it was determined that the Zn concentration in plants was in the range of 14-23 mg/kg. The results we found were determined to be below the WHO limit.

Arsenic (As) is generally found in foods. Its source is legumes, vegetables, grains and herbs. Due to its toxic effect, the amount of exposure to human is important. Therefore, it needs to be controlled [53]. In the study on *Allium* species, As concentration was found in the range of 13-325  $\mu$ g / kg [54]. The concentration of As in the *Murraya koenigii* plant grown for medicinal purposes in different cities of India was found in the range of 55-111  $\mu$ g / kg [55]. Since the concentration of As in *Teucrium* 

*polium* L. plant remained below the lod value, it could not be determined. The As range of other species was determined to be  $8-67 \ \mu g / kg$ .

The concentration range for the silver (Ag) metal element was determined to be 7-163  $\mu$ g / kg. The concentration varies according to the plant species. Tin (Sn) metal element could not be detected since it is below the loq value in all plant species. In a study on cadmium (Cd) metal, the concentration range was found to be 20-9000  $\mu$ g / kg [46]. A different study determined that it was above 0.25 mg/kg [56]. WHO reported the Cd limit as 200  $\mu$ g / kg in edible plants [46],[57]. Cd could not be determined in plant *Centaurea iberica*Trev. ex Sprengel. In other plant species, the Cd range is found as 17-230  $\mu$ g / kg. *Alkanna trichophila* Hub.-Mor. while exceeding the plant, other species were determined to be below the limit.

Mercury (Hg) is a harmful metal for human health. It has been reported that the nervous system, in particular, has a high sensitivity to Hg compounds. Studies have shown that it causes severe damage to the brain and kidneys. The source of Hg can be industrial and thermal power plants, in particular, mercury-filled thermometers and amalgam fillings in homes [58]. According to WHO data, the Hg limit is specified as 0.2-0.5 mg/kg. The Hg concentration could not be determined in all plant species.

Lead (Pb) must rise to a certain level to have a toxic effect on the human body. Pb concentration in the blood varies due to many factors such as age, physiological conditions and nutrition. [59]. It has been stated that it may negatively affect the nervous system in the range of 100-1000 µg / L Pb limit in the blood [60]. It has also been reported to cause health problems such as diarrhoea, headache, anaemia, behavioural disorders, mental retardation and tremors [61]. WHO specified the 10 mg/kg limit for Pb [46],[57]. States such as the Republic of Korea and China have set a toxic metal limit in the range of 20-30 mg/kg [46]. In a study, the concentration of Pb in plants is 20-5100 µg / kg, 0.22-1.15 mg/kg in a different study [4] were found in the range. In this study, it could not be determined because the Pb concentration was below the LOD value.

The accumulation and absorption of trace elements in plant tissue depend on several factors [62]. Differences in concentrations of heavy metal elements are due to differences in the structure of certain parts of the plant and the chemical composition of the soil in distinct regions [63]. Besides, the uptake and transfer of heavy metals may vary, counting on the elements' properties and the structure and species of the plant [64],[65].

One of the most advanced techniques in heavy metal and mineral analysis is ICP-MS technology. With the advantage of wide concentration, the analysis of low concentrations is more reliable and sensitive than other techniques [66]. For this reason, quantitative and qualitative metal element analyzes of plants were made with ICP-MS.

# 4. CONCLUSION

Al, V, Cr, Ni, Cu, Zn, As, Ag, Cd, Sn, Hg, Pb trace element analysis of aromatic and medicinally consumed plant species Anchusa azurea Mill. var. azurea, Achillea biebersteinii Afan., Ajuga vestita Boiss., Teucrium polium L., Alkanna trichophila Hub.-Mor., Centaurea *iberica* Trev. ex Sprengel was determined quantitatively and qualitatively with this study. It is vital to use the studied plant species, especially for medicinal purposes. In the studied species, the highest concentration was detected in element Al. Failure to determine the toxic properties of Sn, Hg, and Pb heavy metals in all plants is critical in consumption and has reduced risk factors. Since Cd element exceeds WHO limit in Alkanna trichophila Hub.-Mor. plant, attention should be paid to its consumption. In other species, it was determined to be below the WHO limit. As the ace element limits cannot be determined for Teucrium polium L. plant species, it is found below the WHO limit. Even if it is by the literature data on other plant species, it should be cautious in its consumption and used in low limits because it exceeds the WHO data. Concentration limits of other elements were determined to be following WHO data. Metal concentrations can have positive and negative effects on human health. While high concentrations of some metals have a harmful effect, insufficient intake of some metals causes the same effect. The fact that metals act as catalysts in many biological reactions also makes them valuable. In this study, the heavy metal characterization and concentrations of these species used as medicinal and aromatic plants were determined, and thus it was stated that it was a significant study for consumers.

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