



## Determination of trace elements in illicit spice samples by using ICP-MS



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### ABSTRACT

The narcotic and toxic effects of synthetic cannabinoids have been intensely investigated by scientists in recent years. Most of these studies have been about the effects of synthetic cannabinoid compounds on the human body. However, in this study, we aimed to determine trace element concentrations in seized “spice” products and observe whether they were above the limit values. The investigated spice product plants contained brooklime, which was the most popular raw material in illicit spice drugs in Turkey. The synthetic cannabinoid contents of the samples were identified by GC-MS. All samples were analyzed by ICP-MS after microwave digestion. The concentration values of Ba, Be, Co, Cr, Cu, Ni, Li, Pb, U, and Zn in three brooklime samples and twenty-nine spice samples containing brooklime were reported. Certified standard reference material CRM SRM 1573a tomato leaves were used to assess the accuracy of the method. After checking the accuracy, excess amounts of the digested CRM were also used to check the precision of the method. Trace element contents in the analyzed samples were likely to be of negligible concern. Barium was the only distinctive element determined. To our knowledge, this is the first study in this field.

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### 1. Introduction

Synthetic cannabinoids (SCs) were first marketed as legal marijuana alternatives in Europe in the early 2000s [1]. The first SCs were in herbal form and small packages. “Street chemists” named and launched these smokable herbal products under the “Spice” brand [2]. The popularity of “spice” rapidly increased with the help of their legal sales [3]. Although package labels clearly indicate “not for human consumption”, “incense”, or “for aromatherapy use only”, clinical toxicologists understand these products are commonly used to obtain  $\Delta^9$ -THC-like psychological effects [4].

In recent years, SCs have frequently been observed in seized materials all over the world [5]. Therefore, countries began to control the abuse and distribution of SC compounds due to their narcotic and toxic effects. In Europe, starting from 2009, some countries (Austria, Germany, France, Luxembourg, Poland, Lithuania, Sweden, UK and Estonia) subjected all products containing synthetic cannabinoid compounds to the Narcotics Law [6].

Although SC containing herbal products were marketed under the spice brand in Europe, the first spice products were launched and sold under the “Bonsai” brand in Turkey. The first capture of a SC compound (JWH-018) in Turkey by the police departments was in May 2010. After this date, synthetic cannabinoid seizures increased very quickly and

reached to 11,139 cases annually in 2013. Legal regulation of the first fourteen SCs including JWH-015, JWH-018, JWH-019, JWH-073, 4-methyl-JWH-073, JWH-081, JWH-122, JWH-200, JWH-203, JWH-210, JWH-250, JWH-398, CP-47,497 and HU-210 was in February 2011. The number of controlled new psychoactive substances increased with the help of advanced early warning systems compatible with European countries so that in 2014, according to Turkish Drug Laws, there were 428 controlled substances composed of 125 SCs [7].

SC containing herbal products are typically produced in two steps: synthesis and mix. Raw SC compounds have been synthesized in clandestine laboratories mostly located in China [2]. Afterwards, synthetic drugs were sprayed on dried plant materials like spice or incense [8,9]. Plant materials are only a mask to hide synthetic chemicals. These products are also advertised as herbal tea, incense, and aromatherapy with their pleasant smell. Brooklime (*Veronica beccabunga*), sage (*Salvia officinalis*), damiana (*Turnera diffusa*) and mint (*mentha*) are the most common plant materials used in SC-containing drugs in Turkey.

Brooklime, which is the focus of this study, is considered a member of the family Plantaginaceae and grows naturally in Turkey. Its dried plant particles are typically green and brown. Brooklime is used in natural medicines or herbal tea mixtures with all parts except the roots. Mannitol, muscaenosidic acid, 8-epiloganic acid, gardsoside, arborescosidic acid, its acetyl ester alpinoside, aucubin, catalpol, catalpol esters, iridoid glucosides salidroside and caffeoyl phenylethanoid glycoside are the organic chemicals naturally found in brooklime [10–15].

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Although most recent studies focus on synthetic compound content and toxicology of illicit spices, concerns have been raised that some spice products may contain heavy metal residues that may be harmful to health [2]. However, there are only few studies about metal residues for raw brooklime in the literature. Dudel et al. investigated U concentrations in brooklime samples grown near abandoned uranium mines [16]. Živković et al. analyzed Cr, Zn and Cu levels in *Veronica* samples [17]. Moreover, Hosseini et al. presented brooklime as an accumulator for Pb [18].

The metal contents of some illicit heroin and ecstasy tablets seized in Turkey were identified in previous studies [19,20]. Nevertheless, we could not find a comprehensive study about illicit spice products' trace metal ingredients. Thus, in this study, we aimed to determine trace element concentrations in seized spice products that contained the most popular raw material in Turkey: brooklime.

## 2. Materials and methods

### 2.1. Materials

Raw brooklime (*V. beccabunga*) samples grown in Turkey were purchased from three different producers, so we coded them as 1a, 1b and 1c (Fig. 1a).

SC-containing samples were collected for a period that lasted for 6 months, March 2013 to July 2013. All samples were provided from street seizures and only brooklime-containing spices were selected ( $n = 29$ ). Brooklime samples were coded by numbers, 2 to 30, and stored in plastic bags in a dark place. Three independent samples were taken from each spice seizure (Fig. 1b).

### 2.2. Sample preparation

Dried samples ( $0.300 \text{ g} \pm 0.001 \text{ g}$ ) were put into 10 ml glass bottles and solved with 5 ml methanol for GC-MS method. The undissolved parts were separated with 25 mm polyethylene syringe filters (Millex, Merck KGaA, Germany).

For ICP-MS method,  $0.300 \text{ g} (\pm 0.001 \text{ g})$  dried samples of plants were transferred to a Teflon vessel, digested with 6 mL of concentrated ultrapure nitric acid (65%) and 2 mL of ultrapure hydrogen peroxide (30%). Decomposition of the samples was carried out in a microwave digestion system (Milestone Srl, Ethos One, Italy). A one-step microwave program, ramping for 15 min up to  $200 \text{ }^\circ\text{C}$  at 1000 W, holding for 10 min at  $200 \text{ }^\circ\text{C}$  at 1000 W, was applied to the samples. The undissolved parts were separated with 25 mm polyethylene syringe filters (Millex, Merck KGaA, Germany).

### 2.3. Instruments

Imaging of spice samples was performed using a stereomicroscope (SZX16, Olympus Co., Tokyo, Japan) with a  $1 \times$  objective lens (Olympus).

The GC-MS system consisted of an Agilent Technologies (Santa Clara, CA, USA) 6890, a gas chromatograph and an Agilent 7683B auto injector coupled with a 240Agilent Ion Trap mass spectrometer. The GC was operated in Splitless mode with a helium flow rate of  $1.0 \text{ mL/min}$  and the column head pressure was 9.38 psi. The MS was operated in the electron impact (EI) mode using an ionization voltage of 50 eV and source temperature of  $230 \text{ }^\circ\text{C}$ . The GC injector was maintained at  $260 \text{ }^\circ\text{C}$  and the transfer line at  $270 \text{ }^\circ\text{C}$ . The GC studies were performed on an ultra-inert column ( $30 \text{ m} \times 0.25 \text{ mm}$ ) coated with  $0.25 \mu\text{m}$  5% phenylmethylsiloxane (HP5-MS) purchased from Agilent Technologies (Santa Clara, CA, USA). The separations were obtained using a temperature program consisting of an initial hold at  $80 \text{ }^\circ\text{C}$  for 3.0 min, ramped up to  $270 \text{ }^\circ\text{C}$  at a rate of  $10 \text{ }^\circ\text{C/min}$ , and held at  $270 \text{ }^\circ\text{C}$  for 2 min.

An Agilent 7700X model ICP-MS system was used for simultaneous multi-element detection of Ba, Be, Co, Cr, Cu, Li, Ni, Pb, U and Zn. The ICP-MS operating conditions are shown in Table 1. Syringe filters (Germany) were used to separate the undissolved parts of plant samples. A microwave oven equipped with PTFE vessels, Milestone Ethos One (Italy), was used for sample digestion.

### 2.4. Reagents and solutions

The methanol (Merck), nitric acid (Merck) and hydrogen peroxide (Merck) used were of analytical reagent grade. Ultrapure water (New Human UP 900, Human Corp., Seoul, Korea) was used in all experiments.

### 2.5. Method validation

Mixed internal standard solutions with a concentration of  $200 \mu\text{g L}^{-1}$   $^6\text{Li}$ ,  $^{45}\text{Sc}$ ,  $^{72}\text{Ge}$ ,  $^{115}\text{In}$  and  $^{209}\text{Bi}$  was used to correct changes in the sample uptake rate and plasma conditions for the ICP-MS measurements. The analytical characteristic of the proposed method were obtained for the ten elements studied under the optimized conditions. Table 2 presents the linear ranges used for calibration and the coefficients of determination ( $R$ ) used to assess the linearity ( $R > 0.99$ ). The limits of detection (LOD) and limits of quantification (LOQ) for each metal were determined as follows: 10 independent analyses of a blank solution spiked with the metal at a lower level of concentration of the analytical curve were performed. The LOD and LOQ were calculated from the standard deviation ( $\sigma$ ) of these determinations ( $\text{LOD} = 3\sigma$  and  $\text{LOQ} = 10\sigma$ ).

Certified standard reference material CRM SRM 1573a tomato leaves (National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA) was used to assess the accuracy of the method. After checking the accuracy, excess amounts of the digested CRM were also used to check the precision of the method. The results are shown in Table 3.

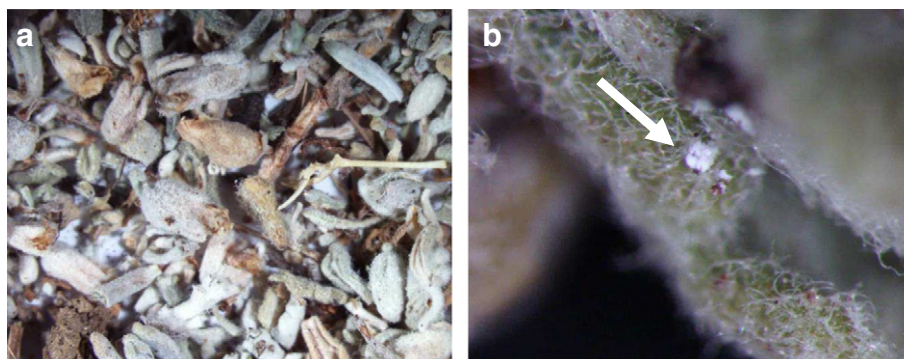


Fig. 1. Stereomicroscope images of brooklime (*V. beccabunga*) sample (a) and a SC particle on illicit spice sample (b).

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