

**DETERMINATION OF TRACE METALS IN GARLIC BULBS (*Allium sativum* L.):  
A VARIETY DISCRIMINATION BY INDUCTIVELY COUPLED  
PLASMA MASS SPECTROMETRY \*\***

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Thirteen trace metals (Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Nb, and Mo) and two toxic metals (Cd and Pb) in two kinds of garlic bulbs have been quantified. Following the dehydration process, the garlic residues are digested using 10.0 mL of an acid mixture of HNO<sub>3</sub>:H<sub>2</sub>O<sub>2</sub>:HCl (3:1:1, v/v/v). The trace metal assay is accomplished by inductively coupled plasma mass spectrometry (ICP-MS). Results reveal that the metal levels for the garlic bulbs with purple skin in dry weight are 14.5, 1.32, 3.03, 3.88, 13.0, 2.50, 1.00, 64.1, 139.6, 13.6, 18.4, 0.29, 0.11, 1.60, and 0.52 mg/kg for Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Nb, Mo, Cd, and Pb, respectively, while the corresponding metal concentrations in the garlics with white skin are 22.9, 2.70, 3.95, 6.60, 19.7, 3.72, 1.16, 79.9, 149.8, 19.7, 24.0, 0.33, 0.43, 0.84, and 0.30 mg/kg, respectively. In general, the trace metals in both varieties are clearly under the FAO/WHO maximum permissible limits. However, it is observed that the garlics with white skin show higher quantities of essential/possible essential metals and lower levels of toxic metals, demonstrating the garlics with white skin exhibit a higher nutrition quality and are a better source of essential minerals.

**Keywords:** trace minerals, garlic bulbs, variety discrimination, nutrition quality assessment, inductively coupled plasma mass spectrometry.

**ОПРЕДЕЛЕНИЕ СОДЕРЖАНИЯ МИКРОЭЛЕМЕНТОВ В ЛУКОВИЦАХ ЧЕСНОКА  
(*Allium sativum* L.): РАЗЛИЧЕНИЕ СОРТОВ МЕТОДОМ МАСС-СПЕКТРОМЕТРИИ  
С ИНДУКТИВНО-СВЯЗАННОЙ ПЛАЗМОЙ**

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Проведен количественный анализ следов 13 металлов (Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Nb и Mo) и двух токсичных металлов (Cd и Pb) в двух сортах чеснока. После дегидратации остатки чеснока перерабатывали с использованием 10.0 мл смеси кислот HNO<sub>3</sub>:H<sub>2</sub>O<sub>2</sub>:HCl (3:1:1). Анализ следов металлов осуществлялся методом масс-спектрометрии с индуктивно-связанной плазмой (ИСП-МС). Содержание металлов (Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Nb, Mo, Cd и Pb) в луковичах чеснока с пурпурной кожурой в сухом весе составляет 14.5, 1.32, 3.03, 3.88, 13.0, 2.50, 1.00, 64.1, 139.6, 13.6, 18.4, 0.29, 0.11, 1.60 и 0.52 мг/кг, соответственно, в то время как в чесноке с белой кожурой 22.9, 2.70, 3.95, 6.60, 19.7, 3.72, 1.16, 79.9, 149.8, 19.7, 24.0, 0.33, 0.43, 0.84 и 0.30 мг/кг. В целом содержание металлов в обоих сортах явно не превышает максимально допустимых пределов ФАО/ВОЗ. Обнаружено, что чеснок с белой кожурой содержит более высокие количества жизнен-

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но необходимых (возможно существенных) металлов и более низкие уровни токсичных металлов, из чего следует, что чеснок с белой кожурой обладает более высокими питательными качествами и является лучшим источником необходимых минералов.

**Ключевые слова:** микроэлементы, чеснок, различение сортов, оценка питательных свойств, масс-спектрометрия с индуктивно-связанной плазмой.

**Introduction.** Trace elements, which are also known as trace minerals, show highly close relationship with human health. They are declared to be essential for the human body with respect to the immune system, tissue development and maintenance, and cell metabolic rate optimization [1]. Metals including Li, V, Cr, Mn, Fe, Co, Cu, Zn, and Mo belong to the category of essential minerals, while Ni, Rb, Sr, and Nb are possible essential minerals. However, some xenobiotic metals involving Cd and Pb present no obvious benefits in body function and can cause harmful effects at minor levels [2]. With the property of nonbiodegradable and bioaccumulation in living tissues, even those essential or possible essential metals for the human body can exert toxic effects at high levels of exposure [3, 4]. As we all know, food chains are crucial resources of trace minerals for human beings [5, 6]; the trace metals in foodstuffs have become excellent indicators not only for the nutritious index but also for the cultured soil quality [7, 8]. In recent years, quality assessment via trace mineral quantification in commonly edible foodstuffs has received great interest from the point of safety certification to consumers [9, 10].

Garlic (*Allium sativum* L.) is the second important Allium crop with culinary and medicinal usage traced back to ancient civilizations, such as Chinese, Indian, Egyptian, and Greek [11, 12]. Nowadays, this Allium crop is widely used as a popular condiment and green vegetable for its pungent flavor [13]. Meanwhile, garlic is claimed to have antibacterial, antifungal, anticancer and antiviral properties [14], and helps prevent various diseases, including atherosclerosis, high cholesterol, high blood pressure, and cancer [15–18]. According to the literature, besides research work on the potential medical value of garlic, the multielement determination of trace metals in garlic samples has been carried out to assess heavy metal contamination [19–21], evaluate the mineral content [22, 23], and discriminate the product variety [24–27].

Many laboratory methods were reported for trace metal determination in garlies, among which atomic absorption spectrometry (AAS) was the extensively utilized method. Based on this technology, Grijalba et al. [28] analyzed inorganic arsenic species of As(III) and As(V) from garlic samples by dispersive micro-solid phase extraction. Ramezani et al. [29] estimated Pb and Cd levels, Izgi et al. [30] and Martinis et al. [31] determined Se contents, and Kaplan et al. [32] quantified Te element. There were also studies applying AAS to assay Fe, Mn, Cu, Co, Ni, Cr, Zn, Pb, and Cd in garlies to illustrate possible health hazards and obtain knowledge on environmental pollution [33, 34]. Neutronic activation analysis (NAA) [25], atomic-fluorescence spectrometry (AFS) [35], cathodic stripping voltammetry (CSV) [36], and inductively coupled plasma atomic emission spectrometry (ICP-AES) [23, 26, 7, 37] were also proposed for the trace metal quantification in garlies.

ICP mass spectrometry (ICP-MS) is an outstanding technique for the trace element determination due to its conspicuous merits of a low detection limit, high sensitivity, wide dynamic range, and excellent spectral resolution [38, 39]. During the last two decades, this analytical tool has been applied in scientific fields from the environment to biochemistry [40–42]. Through trace element quantification by an ICP-MS system, Liu et al. [27] used isotopic datasets ( $^2\text{H}/^1\text{H}$ ,  $^{18}\text{O}/^{16}\text{O}$ ,  $^{13}\text{C}/^{12}\text{C}$ , and  $^{15}\text{N}/^{14}\text{N}$ ) to discriminate the geographic origin of Asian garlies, Zhu et al. [37] studied the element size-fractional distribution in garlic, Smith [24] analyzed Li, B, Na, Mg, P, S, Ca, Ti, Mn, Fe, Cu, Ni, Zn, Rb, Sr, Mo, Cd, and Ba in garlies from different countries to create a suitable database to predict country of origin and monitor seasonal changes, and Oral et al. [43] gave detailed metal levels in 12 Allium species including garlic from Turkey in order to characterize the species in detail. Herein, the first aim of the present work is to accurately determine eleven trace metals (Li, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Nb, and Mo) and two toxic elements (Cd and Pb) in local garlic bulbs with purple or white skins by using ICP-MS. The second aim of this work is to characterize the trace metal differences between the two popular varieties, which can provide potential data clue for assessing nutrition quality and further variety discrimination.

**Experimental. Reagents and standard solutions.** High-purity acids and ultrapure water were used throughout the sample assay. All commercially available acids including  $\text{HNO}_3$  (68% v/v, AR grade) and  $\text{HCl}$  (36% v/v, AR grade), which were purchased from Luoyang Haohua Chemical Reagent Co. Ltd, China, were heated by sub-boiling distillation in Teflon stills (Savillex DST-1000-PFA, USA) to remove metallic or cationic impurities prior to usage. Herein,  $\text{H}_2\text{O}_2$  of guaranteed reagent grade (30% v/v) was used without

further purification. Deionized water passed through a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to produce high-purity water with the resistivity of 18.2 M $\Omega$ ·cm.

All the standard solutions stored in a refrigerator at 4 °C were prepared using ultrapure water and kept in polytetrafluoroethylene (PFA) bottles. The PFA bottle and pipet tips were cleaned in 50% (v/v) HNO<sub>3</sub> for 12 h and carefully rinsed three times with Milli-Q water before use. Four solutions (5, 10, 20, 50 ng/mL for all the elements) in 2% HNO<sub>3</sub> (v/v), all which were used as the external calibrators, were prepared by gravimetric dilution from 10  $\mu$ g/mL multi-element calibration standard solutions (Agilent Technologies, Tokyo, Japan). Multi mono-element solutions were prepared from 1.0 mg/mL of single element standard solutions, which were purchased from the National Institute of standards and technology, China. In this work, all the calibration standard solutions were progressively diluted from the above stock standard solution using 2% HNO<sub>3</sub> (v/v).

**Instrumental apparatus.** Here, the instrument is a Thermo Fisher Scientific X series ICP-MS (Waltham, MA, USA) in the Laboratory of Mineralization and Dynamics, Chang'an University. This apparatus is equipped with a concentric nebulizer for sample injection, a cyclonic spray chamber with an impact bead of 2°C, a standard quartz torch, a pair of nickel Xi sample/skimmer cones (1.1/0.75 mm), and a quadrupole mass analyzer. Before quantification, the instrument was first optimized to obtain stable relative maximum intensities for Li, Co, In, and U using a 10 ng/mL of tuning solution containing Li, Co, In, Ce, U, etc. At the same time, the ratios for oxide formation (CeO<sup>+</sup>/Ce<sup>+</sup>) and doubly charged species (Ce<sup>2+</sup>/Ce<sup>+</sup>) were well controlled at 3.0%. Considering the effect of organic matrix on ICP-MS analysis [44], Rh was selected as the online internal standard, and the signal drift corrections were done by repeatedly analyzing a standard solution. Here, the data are collected using peak jumping and a standard resolution mode with a dwell time of 10 ms. The operating parameters of the output power, the analogue/PC detector voltages, and the sample depth are 1250 W, 1800/2900 V, and 100, respectively.

*Garlic sample treatment for trace element analysis.* Two varieties of fresh garlic bulbs from the local market, which were cultivated in the same farm, were taken for this study. Having been peeled out by a stainless steel Teflon knife, the garlic samples were thoroughly washed with tap water to eliminate absorbed mud and dust particles. After being rinsed by pure water, the garlic samples were dried in air for several days and subsequently in a drying oven at the temperature of 80°C until a constant weight was obtained. After dehydration, the samples were ground into powder using a mortar and pestle and then digested using a wet acid method. Briefly, the samples with weight about 3.00 g were transferred into Teflon vessels, and a mixture of 10.0 mL of concentrated HNO<sub>3</sub>:H<sub>2</sub>O<sub>2</sub>:HCl (3:1:1, v/v/v) was carefully added. Then, the samples in the sealed vessels were placed on a hotplate at 135°C. After half an hour, the vessels were openly evaporated until incipient dryness. Thereafter, 1.0 mL of HNO<sub>3</sub> was added twice to eliminate excess HCl. Finally, 3.0 mL of 2% HNO<sub>3</sub> (v/v) was introduced into the samples, and the sample solutions were heated to a bright color. The digested samples were then diluted using 2% HNO<sub>3</sub> (v/v) to a calibrated mark of 14.5-mL. Following filtration through the filter paper (0.22  $\mu$ m), the samples were directly assayed by ICP-MS.

*Spiking procedures.* Concerning the overall repeatability of ICP-MS detector, the calibration procedures were carried out on three different days. The method precision was evaluated by determining all the analytes in standard solutions and digested garlic samples with the RSDs studied. Considering there are no standard reference materials (SRMs) available in this current work, the accuracy of this proposed approach was estimated using the following procedure. In brief, a set of different quantities of aqueous multi-element standard solutions was introduced into the solution with a trace element content equal to the garlic SRM material of GBW10022 (GSB-13) except Nb and Cd. After a homogenous solution was obtained, the analogue garlic SRM sample was diluted 100-fold and then a suitable aliquot was taken for ICP-MS analysis with spiked-recoveries studied.

**Results and discussion.** *Experimental condition optimization for ICP-MS.* The effects of experimental conditions for the determination of garlic metal were studied including the gas (Ar) flow rate of the coolant/auxiliary/nebulizer, the nebulizer inserting depth, the sampling depth and flow rate, as well as the dwell time. Figure 1 shows an increase of m/z signals for low, medium, and high isotopes (Li, Co, In, and U) with increasing coolant Ar rate up to 14.0 L/min and then declining (testing standard solution: 10 ng/mL). Hence, 14.0 L/min of coolant Ar is chosen in this work. Here, the effect of auxiliary and nebulizer gas flow rates on the m/z signals are tested from 0.6 to 0.85 L/min, showing the optimal values of 0.8 and 0.70 L/min, respectively.

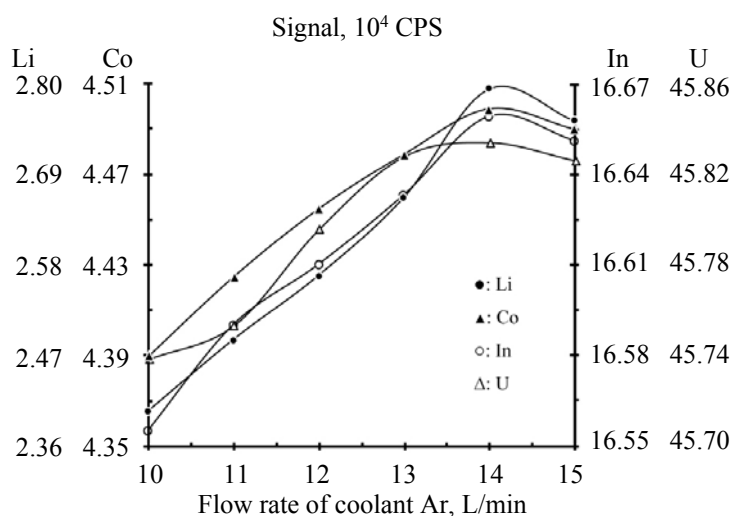


Fig. 1. ICP-MS signal vs flow rate of coolant Ar.

To enhance the sensitivity and precision of this method, the nebulizer noninserting depth from 4.0 to 11.0 mm was examined in detail, and the result given in Fig. 2. It is obvious that the nebulizer inserting depth shows a great influence on the  $m/z$  signals. As Fig. 2 shows, the  $m/z$  signals for Li, Co, In, and U increase sharply from 4.0 to 10.0 mm of the nebulizer length outside the spray chamber  $\Delta L$  (herein, the length is defined as  $\Delta L = L_0 - L_1$ , where  $L_0$  is the nebulizer length, which is 40 mm, and  $L_1$  is the nebulizer inserting depth). However, the  $m/z$  signals for Li and U decrease from 10.0 mm. Hence,  $\Delta L=10$  mm (namely 30 mm of the nebulizer inserting depth) is selected as the optimal. By considering the stability and efficiency of the reagents, 100 of sampling depth, 1.0 mL/min of peristaltic pump, and 10 ms of dwell time are selected in the subsequent work.

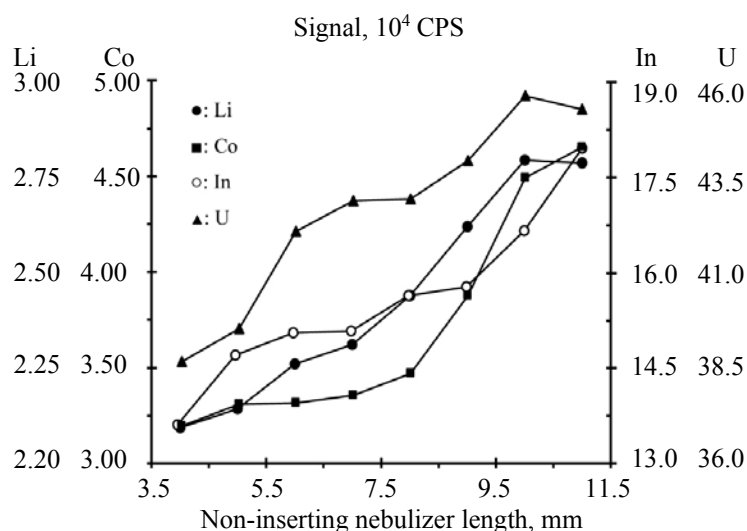


Fig. 2. The influence of the nebulizer inserting length on the ICP-MS signal.

*Accuracy study of the proposed method.* Generally, the garlic SRM is usually analyzed to assess the accuracy of the proposed method, which is based on a comparison between the obtained result and the certified one with the calculated absolute or relative error. However, there is no garlic SRM material available in this present work. Therefore, the accuracy of the proposed approach was tested by examining the determination recovery of the analytes in a similar garlic SRM of GBW10022 (GSB-13). After the spiked analogue garlic sample was prepared as mentioned above, the trace element levels were quantified by ICP-MS under the optimum operating conditions (see Table 1). Clearly, the recoveries for the analyzed metals in the spiked

analogue garlic sample range from 94.3 to 105.2% with RSDs less than 3.2% ( $n = 5$ ), demonstrating the good accuracy of the proposed method for the trace element determination.

TABLE 1. Results for Accuracy Study of the Proposed ICP-MS Method ( $n = 5$ )

Element	Content <sup>a</sup> , µg/g	Added, ng/mL	Found, ng/mL	RSD, %	Recovery, %
Li	0.13	20	33.5	2.7	102.5
V	0.20	20	39.8	2.8	99.2
Cr	0.30	30	60.5	2.6	101.7
Mn	13.4	1000	2326	1.3	98.6
Fe	205	5000	25620	0.8	102.4
Co	0.056	10	15.4	3.2	98.3
Ni	0.92	100	197.2	2.3	105.2
Cu	4.60	500	942.0	2.2	96.4
Zn	21.7	2000	4057	1.2	94.3
Rb	6.50	500	1139	1.5	97.8
Sr	12.3	1000	2235	1.1	100.5
Nb	0.52	50	103.5	1.9	103.0
Mo	0.21	20	40.5	2.4	97.5
Cd	0.62	50	113.7	1.8	103.4
Pb	0.72	50	120.0	2.1	96.0

<sup>a</sup> The trace elements in the solution except Nb and Cd are the same as the referred values of garlic SRM of GBW10022 (GSB-13).

*Precision and repeatability study.* The precision of the garlic determination method was evaluated by RSDs of repetitive measurements carried out in solutions containing the analytes. In this work, RSDs for determining trace elements are in the range from 0.8 to 3.2%, and RSD variations are in the same range for all digested samples tested. The repeatability of this approach was also investigated. Herein, low, medium and high concentrations of standard solutions (5, 10, 100 ng/mL) were repetitively quantified in three consecutive days. The RSD values for intra- and inter-day measurements were less than 4.5% ( $n = 5$ ). Obviously, the proposed method shows good applicability for the trace element determination.

*Trace element analysis in real garlic bulb samples.* The garlic bulb samples with purple skin or white skin from the same farm were decomposed as described in the sample treatment section. Under the optimum ICP-MS experimental conditions, the trace elements including Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Nb, Mo, Cd, and Pb in the two varieties were quantified, with the results summarized in Table 2. As shown

TABLE 2. Analytical Results for Trace Elements in Two Varieties of Garlic Bulbs ( $n = 5$ )

Element	White skin sample, mg/kg	RSD, %	Purple skin sample, mg/kg	RSD, %
Li	14.5	1.6	22.9	1.4
V	1.32	2.2	2.70	2.4
Cr	3.03	2.0	3.95	2.8
Mn	3.88	1.8	6.60	2.2
Fe	13.0	1.5	19.7	2.1
Co	2.50	1.8	3.72	1.6
Ni	1.00	2.3	1.16	2.3
Cu	64.1	1.7	79.9	1.1
Zn	139.6	1.5	149.8	0.9
Rb	13.6	1.4	19.7	1.6
Sr	18.4	2.0	24.0	1.7
Nb	0.29	2.5	0.33	2.9
Mo	0.11	3.5	0.43	3.2
Cd	1.60	3.0	0.84	2.1
Pb	0.52	2.9	0.30	2.7

in Table 2, the determination RSDs for the garlic samples are less than 3.5% ( $n = 5$ ), demonstrating the good precision of this method for trace element assay in garlic bulbs. Additionally, the metal levels for the garlic bulbs with purple skin in dry weight are found to be 14.5, 1.32, 3.03, 3.88, 13.0, 2.50, 1.00, 64.1, 139.6, 13.6, 18.4, 0.29, 0.11, 1.60, and 0.52 mg/kg for Li, V, Cr, Mn, Fe, Co, Cu, Zn, Ni, Rb, Sr, Nb, Mo, Cd, and Pb, respectively, while the corresponding metal concentrations in garlic bulbs with white skin are 22.9, 2.70, 3.95, 6.60, 19.7, 3.72, 1.16, 79.9, 149.8, 19.7, 24.0, 0.33, 0.43, 0.84, and 0.30 mg/kg, respectively. Compared with the FAO/WHO maximum permissible limits in garlies, the trace metal levels in both varieties are clearly within healthy values.

For further data analysis, it is interesting to know that garlic samples with white skin show higher levels of essential/possible essential metals and lower levels of toxic metals as compared to samples with purple skin. That indicates a higher nutrition quality and a better source of essential metals for garlic bulbs with white skin. Meanwhile, despite small differences in trace metals in the two varieties, this work provides valuable variety identification data, showing the possibility of the variety discrimination by trace element levels in garlic species.

**Conclusion.** The ICP-MS technique coupled with the wet acid digestion method was developed for the quantification of 13 trace metals (Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Nb, Mo, Cd, and Pb) in two common varieties of garlic. The determination recoveries of 94.3–105.2% and RSDs  $< 3.2\%$  ( $n = 5$ ) obviously demonstrated the reliability and potential of the proposed approach for metal determination in garlic. The trace metal levels in garlic bulbs were found to be well under the FAO/WHO maximum permissible limits, confirming the safety of consumption of both garlic bulbs. By comparing garlic bulbs with purple and white skins, it was found that garlic bulbs with white skin have higher levels of essential/possible essential metals (Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Nb, and Mo) and lower contents of toxic metals (Cd and Pb), showing higher nutrition quality and a better source of essential metals. This study also shows potential for variety discrimination for garlic species via trace element characteristics.

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