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Inorganic Chemical Approaches to Pharmacognosy. I. Major and Trace Elements Determination in Crude Drug Samples by Energy-Dispersive X-Ray Fluorescence Spectrometry

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A convenient method requiring only one standard material was developed for the multi-elemental analysis (20 elements) of crude drug samples by energy-dispersive X-ray fluorescence spectrometry. The analytical method was based on the principle that when a sample powder is shaped into a very thin pellet, the excitation effect of the matrix is negligible, and a correction factor for the matrix absorption effect can be obtained by mathematical treatment. Percentage accuracies are better than $\pm 10\%$, and detection limits are in the low ppm range for most elements. The present method is suitable for the examination of metal-containing profiles of many crude drug samples because of its ease of application. Several samples were analyzed and each crude drug was found to apparently have a characteristic metal profile.

Keywords——energy-dispersive X-ray fluorescence spectrometry; crude drug; multi-elemental analysis; inorganic component; matrix absorption effect; matrix correction; thin pellet; metal-containing profile

Of the approximately eighty metallic elements, a considerable number have been identified as essential for life. Major ions such as Na^+, K^+, Mg^{2+}, and Ca^{2+} are important in maintaining electrolyte concentrations of body fluids and a skeletal constituents. Many transition metal ions are essential in trace amounts for the activation of enzyme systems. In many cases, these essential metal ions become toxic (or even carcinogenic) when present at sufficiently high levels to overwhelm the natural ligands and macromolecules that function as carriers for these ions. Under such conditions, they may act, as in the case of many toxic metals, by reacting with other biomolecules to distort or block their essential functions. Since the differences between essential and toxic levels are surprisingly narrow, these metal ions must be closely related to health.

On the other hand, a crude drug is a natural product usually containing various metals as ions or complexes with organic compounds. Only a limited amount of research has been carried out on these compounds[1-6] but the organic compounds in crude drugs have been studied extensively. Since the data on organic compounds obtained so far is insufficient to account for all the pharmacological effects of crude drugs, it may be assumed that inorganic components are also significantly responsible for the pharmacological effects. To elucidate the role of inorganic components in crude drugs, we have planned a series of studies.

Knowledge of the metal-containing profiles of many crude drugs is a prerequisite to understanding the significance of inorganic components in these crude drugs. Thus, the development of simple analytical procedures is desirable for measurement of many crude drug samples. The use of X-ray fluorescence spectrometry for measuring mineral components is attractive because it provides a simultaneous quantitative analysis of many important elements.

TABLE I. Operating Conditions

Secondary target	Measured elements	Tube	
		Voltage	Current
Ti	P, S, Cl	40 kV	10 mA
Ge	K, Ca, Ti, Cr, Mn Fe, Ni, Cu, Zn	40 kV	5 mA
Mo	As, Br, Pb($L\beta$), Rb, Sr	40 kV	20 mA
Gd	Mo, I, Ba	60 kV	40 mA

In this paper a multi-elemental analysis of crude drugs has been undertaken by energy-dispersive X-ray fluorescence spectrometry, and a convenient procedure requiring only one standard material has been established. This method was applied to the determination of 20 elements (P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Pb, Mo, I, and Ba) in some important crude drugs such as Cinnamomi Cortex and Glycyrrhizae Radix.

Experimental

Apparatus——X-Ray measurements were performed on thin samples (48 mg/cm^2) with a Rigaku-Kevex energy-dispersive X-ray spectrometer (ultra-trace system), consisting of a molybdenum anode X-ray tube, a secondary target and a filter assembly used to generate nearly bichromatic radiation, an Si(Li) detector, an X-ray amplifier, and a conventional multi-channel analyzer (model 1024). Secondary target systems used throughout this work were titanium, germanium, molybdenum, and gadolinium. The X-ray tube was operated at a voltage of 60 kV for gadolinium and at 40 kV for the other secondary targets. The exciting beam strikes the sample at 3° to the sample normal and the detected fluorescent X-rays leave the sample at 45° to the sample normal.

Materials——Crude drug samples were kindly provided by Mikuni Co., Ltd., Koshiro Chuji Co., Ltd., and Nihon Funmatsu Co., Ltd., Osaka. All other reagents were of the highest quality available.

Procedures——The crude drug samples were powdered in a National coffee mill (MK-51), and dried in an oven at 85 °C for about 5 h. Then 150 mg of each powdered sample was pressed into a 2.0 cm diameter pellet at 10 tons pressure (three pellets were prepared for the measurement of each sample). The fluorescent X-ray intensities ($L\beta$ for Pb; $K\alpha$ for the others) of twenty elements usually present in plants were measured successively under the operating conditions shown in Table I. Measurements using a gadolinium target were carried out on a pile of three pellets to obtain high sensitivity. The operating time was 300 s in each case. The intensity of each element was corrected for overlapping peaks (*e.g.*, K$K\beta$–Ca$K\alpha$ and Mn$K\beta$–Fe$K\alpha$) using the formula

$$C(j, \text{corrected}) = C(j) - K\beta^*(\text{int})/K\alpha^*(\text{int}) \times K\alpha(\text{int})$$

where $K\alpha$(int) is the count of the $K\alpha$ peak of the interfering element, and $K\alpha$*(int) and $K\beta$*(int) are the counts for the $K\alpha$ and $K\beta$ peaks, respectively, obtained when 20 μl of a standard solution of each interfering element was measured on a 5-μm polypropylene film. The apparent value [$C(j)$ ppm (or, j)/C (or, j)] in Eq. 5 was calculated from the intensity of the characteristic X-ray beams in the pre-measurement of the standard material (NBS SRM 1571, orchard leaves) under the same conditions. Furthermore, on the assumption that the sample material, in addition to detectable elements, consists primarily of cellulose, a matrix correction factor [F(sample)] was computed according to Eqs. (1)—(5). In the same manner, the matrix correction factor for orchard leaves [F(or)] was pre-computed from certified values. The elemental concentrations of the samples were recalculated by the use of Eqs. (1)—(6); the iterations were continued until each elemental concentration ceased to change by more than 0.1%.

Results and Discussion

Theoretical Considerations

Figure 1 shows a typical energy-dispersive X-ray fluorescence spectrum of Cinnamomi Cortex (*C. cassia*). The qualitative analysis was easily performed from the peak positions at the energy values of characteristic X-rays generated from sample materials, but the quantitative analysis required correction for preliminary (absorption) and secondary (exci-

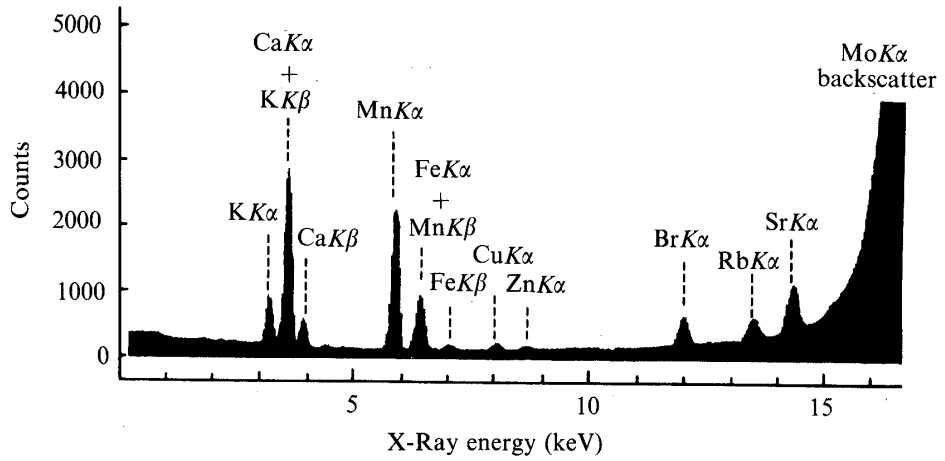

Fig. 1. X-Ray Fluorescence Spectrum (Mo K Excitation) of Cinnamomi Cortex

tation) effects of the matrix. These effects could be represented by very complex equations,[7] particularly in the case of secondary effects. Most of the crude drugs were taken from plants consisting mainly of light elements such as H, C, O, and N. When such samples were pressed into thin pellets, the secondary effects of the matrix were generally negligible. For such thin samples, element concentrations could be expressed by Eqs. (1)—(3).[8,9]

$$\text{ppm}\ (j) = C(j)F(j)m(s)/C(s)K(j)m \tag{1}$$

where $C(j)$ is the counts in the X-ray peak; $C(s)$, the counts from a single element standard; $F(j)$, a matrix correction factor; $K(j)$, the relative X-ray production probability normalized to the X-ray production probability of the standard element; and $m(s)$ (μg/cm^2) and m(g/cm^2), the area density of the standard and unknown samples, respectively.

For monoenergetic exciting X-rays,

$$F = \bar{\mu}m/(1-e^{-\bar{\mu}m}) \tag{2}$$

where

$$\bar{\mu} = \sum f(i)(\mu_i^{\text{ex}} \sec\alpha + \mu_i^{\text{fl}} \sec\beta) \tag{3}$$

Here $f(i)$ represents the fraction of each elemental constituent of the sample, μ^{ex} and μ^{fl} are the attenuation coefficients of the element for the exciting and fluorescent radiation, respectively, and α and β are the angles formed by the exciting beam and the fluorescent beam with the sample normal, respectively.

The concentration of the j-th element in orchard leaves as a reference material can be expressed by Eq. (4).

$$\text{ppm}\ (\text{or}, j) = C\,(\text{or}, j)\ F\,(\text{or}, j)\ m\ (s)/C(s)\ K(j)m(\text{or}) \tag{4}$$

On combining Eq. (4) with (1), we obtain,

$$\text{ppm}\ (j) = C(j)\ \text{ppm}\ (\text{or}, j)/C\ (\text{or}, j) \times F(j)m\ (\text{or})/F(\text{or}, j)m \tag{5}$$

Equation (5) indicates that when orchard leaves are used as reference material and the same amounts of sample material as of orchard leaves are weighed, the concentration of the j-th element in the sample can be calculated as a product of the apparent value and the ratio of the matrix correction factor of the sample to that of the orchard leaves.

The principal constituent in the plant sample is polysaccharide, such as cellulose $(C_6H_{10}O_5)_n$. Starch has the same general formula and other sugars are quite similar in

TABLE II. The Average Intensities (cpm) of 10 Measurements on Orchard Leaves (NBS SRM 1571) and Their Relative Standard Deviations

Time (s)		S	K	Ca	Cr	Mn	Fe	Cu	Br	Sr	Ba
50	$\bar{x}$	1201.2	9564.0	18828.0	24.0	697.2	2881.2	302.4	114.0	627.6	78.0
	σ	0.047	0.015	0.008	0.562	0.038	0.018	0.086	0.253	0.064	0.376
150	$\bar{x}$	1153.2	9512.0	18845.6	32.8	715.6	2918.4	304.2	127.6	613.6	81.2
	σ	0.033	0.005	0.005	0.244	0.022	0.014	0.053	0.085	0.043	0.287
300	$\bar{x}$	1153.8	9500.0	18884.6	32.0	714.0	2933.6	296.8	119.2	622.2	80.0
	σ	0.020	0.003	0.003	0.206	0.019	0.010	0.043	0.047	0.026	0.204
600	$\bar{x}$	1167.5	9521.0	18925.5	33.0	711.0	2917.8	302.2	122.6	623.2	81.4
	σ	0.014	0.004	0.003	0.173	0.013	0.008	0.027	0.037	0.018	0.102
1200	$\bar{x}$	1141.5	9385.4	19094.5	29.0	706.7	2889.5	299.3	121.0	619.4	93.2
	σ	0.013	0.006	0.004	0.066	0.011	0.004	0.018	0.027	0.017	0.081
2400	$\bar{x}$	1174.8	9547.2	18957.6	32.5	718.1	2931.5	305.9	118.6	624.1	87.1
	σ	0.005	0.002	0.001	0.057	0.008	0.003	0.029	0.022	0.011	0.081

TABLE III. The Average Intensities (cpm) of 10 Measurements on Orchard Leaves (NBS SRM 1571) and Their Relative Standard Deviations

Weight (mg)	Thickness (mg/cm^2)		S	K	Ca	Cr	Mn	Fe	Cu	Br	Sr	Ba
50	15.9	$\bar{x}$	1107.4	8042.8	15394.0	21.0	380.4	1393.3	122.6	40.2	196.0	31.2
		σ	0.052	0.038	0.059	0.237	0.087	0.068	0.108	0.131	0.073	0.134
100	31.8	$\bar{x}$	1178.8	9281.2	18580.4	31.6	615.0	2591.6	237.2	88.0	418.8	40.8
		σ	0.026	0.032	0.030	0.204	0.050	0.038	0.060	0.106	0.050	0.289
150	47.8	$\bar{x}$	1140.0	9363.2	18560.0	28.8	697.2	2942.6	302.2	117.8	601.6	84.2
		σ	0.027	0.012	0.016	0.277	0.030	0.027	0.053	0.051	0.026	0.099
200	63.7	$\bar{x}$	1163.2	9506.6	18857.8	27.6	733.0	3219.8	339.8	151.6	767.8	107.8
		σ	0.039	0.007	0.016	0.185	0.030	0.029	0.056	0.081	0.036	0.120
300	95.5	$\bar{x}$	1139.2	9275.2	18527.4	31.2	766.8	3328.0	399.0	236.2	1146.2	162.2
		σ	0.029	0.016	0.018	0.178	0.033	0.041	0.038	0.090	0.018	0.066

composition. The X-ray fluorescence technique should be applicable to nearly all plant constituents heavier than silicon or phosphorus. Only nitrogen among other unmeasurable elements often occurred in percent levels of concentration, *e.g.*, 2.76% in orchard leaves. The fraction f of cellulose could be calculated by subtraction. That is,

$$f_{(\text{cellulose})} = 1 - 0.0276 - \sum f(j) \qquad (6)$$

where j elements are measured by X-ray fluorescence. This procedure makes possible the determination of all parameters of Eqs. (2) and (5). The equations can be solved by iteration.

Effects of Accumulation Time and Sample Thickness on Reproducibility

First, the effects of accumulation time on the reproducibility of the fluorescence intensity were examined. One specimen of orchard leaves was measured ten times; the average intensities of some elements in the specimen and their relative standard deviations are summarized in Table II. Significant improvements in reproducibility were observed when the accumulation time was changed from 50 to 300 s. In the case of 300 s, the deviations were within 3% for all elements of higher intensity than 60 cpm.[10] The effects of sample thickness on reproducibility were then examined. Though it is desirable for the pellets to be as thin as possible, thin pellets tend to show variations in the sample preparation, *e.g.*, in the thickness or density of the part hit by the exciting X-ray beam. Ten pellets of orchard leaves were prepared for each sample thickness, and they were measured. Both the average intensities and their relative standard deviations are given in Table III. The results indicated that the preparations of sample pellets varied somewhat when 50 or 100 mg of sample powder was used. In the case of 150 mg (47.8 mg/cm^2), the deviations of most elements were about 5% or below. No significant improvement was observed on changing the amount from 150 to 300 mg. On the basis of these considerations, a suitable accumulation time and sample amount were fixed at 300 s and 150 mg, respectively.

X-Ray Detection Limit

In Fig. 2, the 3δ detection limits for elements in the standard material (orchard leaves) are shown along with those of the general method in which only characterized X-ray beams of molybdenum are used as the excitation source. Calculation was made using Eq. (1) and three times the square root of the background counts from the material run for 900 or 2700 s. The present method provides a highly sensitive analysis of many elements lighter than copper, most of which are biologically important, compared to the general method, whereas the latter is more sensitive for elements heavier than zinc because of the three times longer accumulation time compared to the present method. The detection limits of elements from chromium to strontium are less than 1 ppm. Therefore, the present method appears preferable.

The above results led to the recommended procedure described in Experimental for multi-elemental analysis of crude drug samples by energy-dispersive X-ray fluorescence spectrometry.

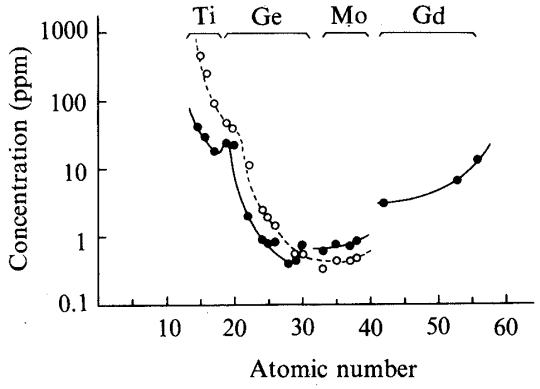

Fig. 2. X-Ray Detection Limits in Plant Material (NBS SRM 1571, Orchard Leaves)

—●—, secondary target (accumulation time, 900 s), ---○---, Mo target only (accumulation time, 2700 s).

Analytical Results

In order to determine the effectiveness of this matrix correction procedure, samples of known concentration were measured. The mean values and standard deviations of five separate measurements of both tomato leaves (NBS SRM 1573) and bovine liver (NBS SRM 1577) are shown together with their apparent values in Table IV. In the case of tomato leaves, the apparent values of elements lighter than bromine are smaller than the NBS values. This is because X-rays from these elements in tomato leaves are absorbed strongly by the higher levels of potassium and calcium than in the standard material (orchard leaves). When correction for absorption effects was performed according to the above method, the corrected values approximated well to the NBS values, *e.g.*, they changed from 2.16 (uncorrected) to 3.08% (corrected) for calcium and from 150 (uncorrected) to 210 ppm (corrected) for manganese. In particular, the analytical results for elements heavier than copper were in good agreement with the certified values. On the other hand, the determination of bovine liver was also possible with an accuracy of 10% or better for most elements tested. The present multi-elemental analysis thus appears suitable for crude drugs from animals as well as plants.

Some crude drugs were analyzed by the developed procedures, and the results are given in Table V, together with those from the reports of Itokawa *et al.*[4] and Matsuda *et al.*[5a] In the case of Cinnamomi Cortex, while the three analytical values for manganese are close, Matsuda *et al.* obtained about ten-fold higher values for iron and copper compared to the others. This is probably due to a difference in the samples tested. However, on looking at the overall results, each crude drug seems to have a characteristic metal profile; that is, the manganese content in the Cinnamomi Cortex lies in the range of 400—600 ppm, and is higher than the iron content in all cases. Also, the iron content in Carthami Flos reaches a high level

TABLE IV. Analytical Results (ppm) for NBS Standard Materials by X-Ray Fluorescence Spectrometry

Element	Tomato leaves			Bovine liver		
	Apparent value	Corrected value	NBS value	Apparent value	Corrected value	NBS value
P	0.277%	0.29±0.02%	0.34%	1.10%	1.07±0.02%	1.1%
S	0.473%	0.51±0.02%		0.74%	0.749±0.009%	
Cl	1.17%	1.32±0.04%		0.317%	0.33±0.01%	0.27%
K	3.42%	4.1±0.1%	4.46%	1.06%	1.06±0.04%	0.97%
Ca	2.16%	3.08±0.09%	3.00%	155	160±10	124
Ti	48.6	70±7			ND	
Cr	2.3	3±1	4.5	2.03	1.7±0.6	
Mn	150	210±3	238	11.6	10±2	10.3
Fe	450	620±30	690	345	300±10	268
Ni	0.47	0.6±0.2			ND	
Cu	8.5	10.8±0.4	11	201	182±8	193
Zn	48	60±2	62	143	131±8	130
As		ND	0.27		ND	
Br	22.7	24.8±0.9	26	10.2	9.9±0.5	
Rb	17.0	18.3±0.7	16.5	20.3	20±1	
Sr	42.1	45±2			ND	
Pb	5.2	6±1	6.3		ND	
Mo		ND			ND	
I		ND			ND	
Ba	29.1	29±3			ND	

ND: not detected.

TABLE V. Analytical Results (ppm) for Various Crude Drugs by X-Ray Fluorescence Spectrometry

Element	Cinnamomi Cortex			Glycyrrhizae Radix			Rhei Rhizoma			
	This work	Itokawa *et al.*	Matsuda *et al.*	This work	Itokawa *et al.*	Matsuda *et al.*	This work[a)]	This work[b)]	Itokawa *et al.*	Matsuda *et al.*
P	0.184%			970			0.143%	0.228%		
S	0.160%			960			760	940		
Cl	226			0.165%			0.116%	920		
K	0.96%			0.40%			1.13%	1.29%		
Ca	3.13%			0.55%			0.92%	1.10%		
Ti	44			20			10	46		
Cr	ND	ND		2.0	ND		1.7	2.0	0.5	
Mn	445	390	620	15.5	7.1	15	39.6	24.1	52.2	41
Fe	34	34	240	90	250	240	106	304	70	78
Ni	ND	ND	2.7	ND	ND	2.5	ND	3.9	1.9	3.4
Cu	5.4	3.8	46	6.0	6.6	9.2	4.2	7.4	1.9	2.1
Zn	1.9	7.5	4.8	4.5	11.8	9.2	13	21.5	8.4	7.6
As	ND			ND			ND	ND		
Br	42.4			63			42.7	3.4		
Rb	45			9.1			5.5	5.1		
Sr	260			520			37.9	64		
Pb	ND	ND	1.8	ND	0.3	0.34	ND	ND	ND	0.39
Mo	ND			ND			ND	ND		
I	ND			ND			ND	ND		
Ba	160			35			33	102		

a) Rheum palmatum (Merck).
b) Rhei Japonici Rhizoma (Osaka market).
ND: not detected.

of 2000—4000 ppm. From the analytical results, distinctive metal profile features in each crude drug are as follows:[11] 1) the cinnamomi Cortex contains manganese and barium at high levels, 2) the Glycyrrhizae Radix contains strontium and bromine at high levels, 3) the bromine contents in Rhei Rhizoma and Rhei Japonici rhizoma appear to be different, 4) the Sennae Folium contains barium at a high level, 5) Carthami Flos contains iron and nickel at high levels, 6) Cardamomi Fructus contains manganese at a high level and six times more potassium than calcium, 7) Ephedra Herba contains bromine at a high level, 8) Digenea contains calcium, molybdenum, and halides such as chlorine, bromine and iodine at high levels, 9) Moschus contains sulfur and barium at high levels. Thus, each crude drug seems to have a characteristics metal profile, although further research is necessary on sample variation, and the effects of geographical region of product collection, and the part used (*e.g.*, root, leaf, or flower) on the elemental content.

Conclusions

This method, in which only one standard material (orchard leaves) is required and the absorption effects of a matrix are corrected by mathematical treatment, was developed for the multi-elemental X-ray fluorescence analysis of crude drugs. This procedure does not require complex pretreatment, and the time required for analysis of 20 elements is short. Percentage accuracies achieved on standard samples were better than $\pm 10\%$ for most elements, and detection limits were in the low ppm range for elements from titanium to strontium. The present method was applied to several typical crude drugs, and the results suggest that each

TABLE V. (continued)

Element	Sennae Folium		Carthami Flos		Cardamomi Fructus		Arecae Semen	
	This work	Matsuda *et al.*	This work	Matsuda *et al.*	This work	Itokawa *et al.*	This work	Itokawa *et al.*
P	0.230%		0.13%		0.128%		880	
S	0.238%		0.409%		960		0.219%	
Cl	ND		1.03%		0.49%		800	
K	1.07%		2.50%		3.2%		0.46%	
Ca	3.20%		1.25%		0.48%		0.108%	
Ti	61		310		25		ND	
Cr	ND		44		7.6	ND	2.3	ND
Mn	40	37	75	53	260	270	16.9	32.6
Fe	253	310	0.376%	0.240%	190	160	116	45
Ni	ND	1.3	21.6	5.4	3.2	ND	ND	ND
Cu	7.0	7.7	17.8	19	8.8	8.3	11.5	13.2
Zn	33.8	29	42.2	34	47	590	7	11.7
As	ND		9.1		ND		ND	
Br	19		48		40		11.3	
Rb	26		28.4		50		13.9	
Sr	185		99		47.9		8.3	
Pb	ND	0.35	ND	2.1	ND	1.0	ND	ND
Mo	ND		ND		ND		ND	
I	ND		ND		ND		ND	
Ba	170		87		75		ND	

ND: not detected.

TABLE V. (continued)

Element	Ephedrae Herba			Digenea	Moschus
	This work	Itokawa *et al.*	Matsuda *et al.*		
P	0.238%			ND	0.356%
S	0.190%			0.30%	1.18%
Cl	0.82%			2.06%	0.307%
K	1.08%			1.77%	1.37%
Ca	3.33%			10.8%	0.436%
Ti	50			29	39
Cr	3.7	ND		15	3
Mn	28	33.3	32	19	8.8
Fe	520	120	470	480	370
Ni	ND	ND	5.1	13	0.9
Cu	5.4	3.2	4.3	2.7	9.4
Zn	14	12.1	9.2	6.1	52
As	ND			9.9	ND
Br	84.1			450	7.6
Rb	8.8			46	40
Sr	136			0.114%	14
Pb	ND	ND	1.3	ND	13
Mo	ND			30	ND
I	ND			400	ND
Ba	24			7.4	160

ND: not detected.

crude drug has a characteristic metal profile.

The differences in metal profiles according to geographical region and vegetation period have not yet been clarified. For this purpose, many samples must be analyzed for each crude drug.

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11) Note that the present values are simply the analytical results for a single specimen of each crude drug. The mean values and standard deviations obtained for many samples will be reported elsewhere.