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Analysis of traditional Tibetan pills

Martin Cesnek[1] · Milan Štefánik[1] · Marcel Miglierini[1] · Tomáš Kmječ[2] · L'ubomír Sklenka[1]

Abstract Traditional Tibetan medicine starts to be a very popular complementary medicine in USA and Europe. These pills contain many elements essential for the human body. However, they might also contain heavy metals such as mercury, iron, arsenic, etc. This paper focuses on elemental composition of two Tibetan pills and investigation of forms of iron in them. X-ray fluorescence spectroscopy and neutron activation analysis identified the presence of several heavy metals such as mercury, iron and copper. Mőssbauer spectroscopy revealed the possible presence of $\alpha - Fe_2O_3$ (hematite) and $\alpha - FeOOH$ (goethite) in both of the investigated samples.

Keywords Tibetan medicine · Mőssbauer spectroscopy

1 Introduction

Traditional Tibetan medicine is known all around the world and it is a very important part of the Chinese and Tibetan health care system [1]. Tibetan pills contain many elements which play an important role in the human body and help to prevent and treat diseases. These pills might also contain relatively high concentration of mercury which is used as one of the tradi-

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✉ Martin Cesnek
martin.cesnek@fjfi.cvut.cz

[1] Department of Nuclear Reactors, Czech Technical University, V Holesovickach 2, 180 00 Prague, Czech Republic

[2] Faculty of Mathematics and Physics, Charles University, V Holesovickach 2, 180 00 Prague, Czech Republic

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tional pharmaceutical components and as toxic element it undergoes detoxifying processes [2]. It was found earlier [3] that some Tibetan pills also contain other heavy metals such as arsenic or lead. Such a medicine has become also popular complementary medication and some products can be found in USA [4] and Europe [5]. Thus, it has attracted attention of many scientists and has been recently studied from different points of view [6–9].

This paper focuses on elemental composition of two analyzed Tibetan pills called Rinchen Chakril Chenmo and Rinchen Mangyor Chenmo. Moreover, it deals with characterization of iron in these two kinds of pills. Iron is one of the most important trace elements in the human body and participates in many essential biological processes [10] and as a heavy metal can be toxic for the body [11]. Thus, it is very interesting to study forms of iron in such alternative and natural medicine.

Rinchen Chakril Chenmo (RCC) is used to treat different eye diseases/conditions, ailments of liver and spleen caused by impure blood, etc. Rinchen Mangyor Chenmo (RMC) is used to treat ailments which are caused by blood disorders such as sore throat, pulmonary diseases, etc.

2 Samples and methods

Two samples of traditional Tibetan medicine mentioned earlier were analyzed by Mőssbauer spectroscopy (MS), X-ray fluorescence spectroscopy (XRF) and neutron activation analysis (NAA).

XRF was performed with the help of EAGLE III μ-Probe (X-ray tube voltage 40 kV). Samples were analyzed in a powder form. XRF spectra were obtained from five different spots of the both samples and the results were obtained as an average from these five measurements. Concentrations of elements are only approximately given by the semi quantitative method.

NAA was performed in Prague at the Czech Technical University at the Department of Nuclear Reactors. The samples (whole pills) were placed inside a dry vertical channel of the VR-1 training reactor, and they were irradiated by neutrons for 20 minutes at maximum reactor power (1E8 cps). Activated samples were repeatedly measured using the semiconductor HPGe detector (six measurements per one pill). Analysis of measured gamma-ray spectra was carried out using the GENIE-2000 spectroscopy software and gamma-spectroscopic on-line database.

MS was performed in transmission geometry with constant acceleration spectrometer using a ^{57}Co/Rh gamma-ray source. The resulting isomer shifts are given relative to the MS spectrum of $\alpha - Fe$ foil recorded at room temperature. MS spectra of both samples in the form of powder were recorded at room temperature (RT) and at 4.2 K using helium bath cryostat. The spectral parameters comprising isomer shift (IS), quadrupole splitting\shift (QS), hyperfine magnetic field (B), line width (Γ), and area (A) of spectral components were refined by the CONFIT curve-fitting program [12].

3 Results and discussion

XRF analysis revealed presence of elements which are listed in Table 1. It can be seen that from a qualitative point of view RMC and RCC are very similar. RCC contains, in comparison with RMC, also As and Zn. Both pills contain mineral elements which play an important role in human body. Moreover, XRF revealed relatively high concentrations of

Table 1 Results of semiqualitative XRF analysis. Listed average values are given with the following errors: content >1 % - ±1 % of the value, content <1 % - ±50 % of the value

Element	RMC ΦWt%	RMC ΦAt%	RCC ΦWt%	RCC ΦAt%
Mg	3.64	6.76	1.66	3.04
Al	2.29	3.83	0.97	1.60
Si	5.15	8.21	1.45	2.30
P	4.67	6.76	2.51	3.61
S	4.89	6.87	4.72	6.56
Cl	5.18	6.59	9.98	12.56
K	10.66	12.28	7.60	8.67
Ca	30.35	34.24	40.75	45.29
Mn	0.45	0.37	0.19	0.16
Fe	10.09	8.17	15.78	12.60
Cu	1.14	0.81	0.11	0.08
Zn	0.63	0.43	0.20	0.14
Hg	20.86	4.69	13.25	2.95
As	–	–	0.57	0.34
Zr	–	–	0.24	0.12

Table 2 Results of NAA

Observed isotope	RCC	RMC	Nuclear reaction	Half-life period
^{23}Na	X	X	^{23}Na(n,γ)^{24}Na	15 h
^{26}Mg	–	X	^{26}Mg(n,γ)^{27}Mg	9.5 m
^{37}Cl	X	X	^{37}Cl(n,γ)^{38}Cl	37 m
^{41}K	X	X	^{41}K(n,γ)^{42}K	12.4 h
^{75}As	X	–	^{75}As(n,γ)^{76}As	1.1 d
^{55}Mn	X	X	^{55}Mn(n,γ)^{56}Mn	2.6 h
^{58}Fe	X	–	^{58}Fe(n,γ)^{59}Fe	44.5 d
^{81}Br	–	X	^{81}Br(n,γ)^{82}Br	35.3 h
^{121}Sb	X	–	^{121}Sb(n,γ)^{122}Sb	2.7 d
^{123}Sb	X	–	^{123}Sb(n,γ)^{124}Sb	60 d
^{197}Au	–	X	^{197}Au(n,γ)^{198}Au	2.6 d
^{196}Hg	X	X	^{196}Hg(n,γ)^{197}Hg	64 h
^{196}Hg	X	X	^{196}Hg(n,γ)^{197m}Hg	24 h
^{198}Hg	X	X	^{198}Hg(n,γ)^{199m}Hg	42.6 m

heavy metals such as Fe, Hg which are characteristic for traditional Tibetan medicine. It also revealed a trace amount of Al and Cu.

Results from XRF are in good agreement with qualitative results obtained by NAA. Nuclides found with the help of NAA are listed in Table 2. Furthermore, NAA revealed presence of isotopes of other heavy metals as Au, Sb and Br.

MS spectra of both pills obtained at RT are shown in Figs. 1 and 2 together with their components. Corresponding hyperfine parameters are listed in Table 3. RT spectrum of

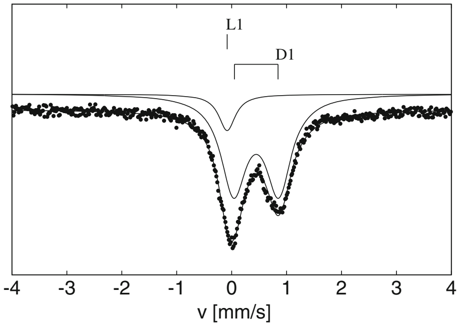

Fig. 1 MS spectrum of RMC obtained at RT

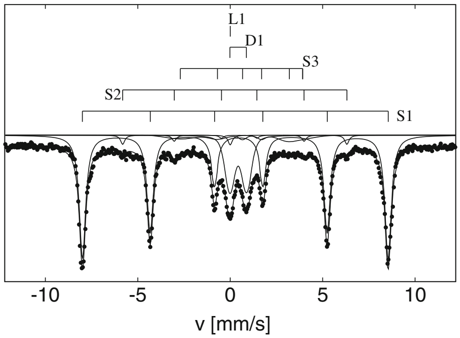

Fig. 2 MS spectrum of RCC obtained at RT

RMC exhibits an asymmetrical doublet with no trace of magnetic components. This spectrum was fitted using one doublet and one singlet. On the other hand, RT spectrum of RCC exhibits major six-line magnetic component (S1) which has very close hyperfine parameters to the hyperfine parameters of $\alpha - Fe_2O_3$ [13]. Sextet (S2) with small contribution to the spectrum has very similar hyperfine parameters as $\alpha - FeOOH$ [13]. Sextet S3 represents a component which exhibits superparamagnetic relaxation. Doublet (D1) and singlet (L1) have very similar hyperfine parameters to those in the RMC. Singlet in both spectra might suggest some contamination of pills during the process of preparation by $\gamma - Fe$ possibly from stainless steel.

In order to obtain more information, the samples were measured at 4 K. Low temperature spectra together with their components are shown in Figs. 3 and 4. Corresponding hyperfine parameters can be found in Tab. 3. Both spectra contain broadened doublet even at 4 K. This doublet is major part of spectrum in case of RMC. Unfortunately, the origin of this component is not clear and the corresponding iron phase was not precisely determined. Minor sextets S1 and S2 might be possibly assigned to $\alpha - Fe_2O_3$ and $\alpha - FeOOH$, respectively. Sextets S3 and S4 exhibit superparamagnetic relaxation. Low temperature spectrum of RCC also revealed possible presence of $\alpha - Fe_2O_3$ and $\alpha - FeOOH$ which is in good agreement with its RT spectrum. Sextet S1 might be assigned to very small particles of $\alpha - Fe_2O_3$ which have not undergone the Morin transition. On contrary, sextet S2 might be assigned to bigger particles of $\alpha - Fe_2O_3$. Sextets S3 might be assigned to $\alpha - FeOOH$. Sextet S4 exhibits superparamagnetic relaxation.

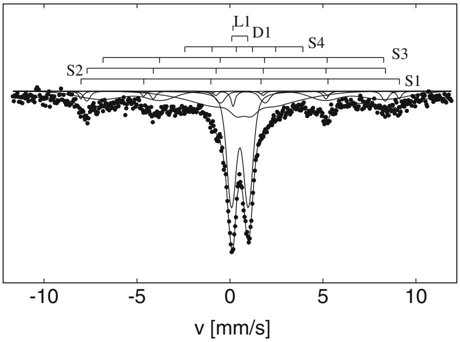

Fig. 3 MS spectrum of RMC obtained at 4 K

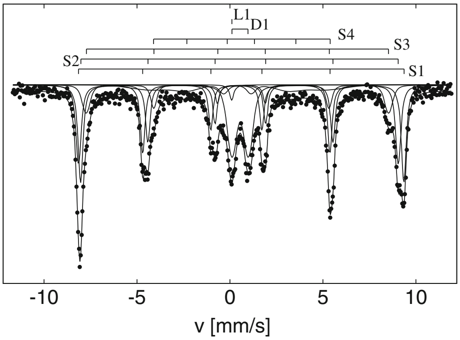

Fig. 4 MS spectrum of RCC obtained at 4 K

Table 3 Hyperfine parameters of spectral components of RMC and RCC MS spectra

Sample	Temperature		IS [mm/s]	QS [mm/s]	Bhf [T]	A [%]
RMC	RT	L1	−0.08 ± 0.02	–	–	11 ± 1
		D1	0.45 ± 0.02	0.82 ± 0.04	–	89 ± 1
	4 K	L1	0.17 ± 0.03	–	–	2 ± 1
		D1	0.53 ± 0.02	0.90 ± 0.04	–	39 ± 1
		S1	0.43 ± 0.03	0.23 ± 0.05	53.18 ± 0.17	3 ± 1
		S2	0.42 ± 0.02	−0.19 ± 0.04	49.88 ± 0.16	5 ± 1
		S3	0.62 ± 0.05	−0.11 ± 0.09	46.95 ± 0.53	25 ± 1
		S4	0.70 ± 0.08	−0.19 ± 0.16	14.55 ± 0.80	26 ± 1
RCC	RT	L1	0.00 ± 0.04	–	–	1 ± 1
		D1	0.43 ± 0.02	0.90 ± 0.04	–	19 ± 1
		S1	0.37 ± 0.02	−0.18 ± 0.04	51.36 ± 0.16	72 ± 1
		S2	0.36 ± 0.02	−0.24 ± 0.04	37.68 ± 0.16	3 ± 1
		S3	0.86 ± 0.07	−0.64 ± 0.14	20.12 ± 0.69	6 ± 1
	4 K	L1	0.09 ± 0.04	–	–	1 ± 1
		D1	0.55 ± 0.02	0.88 ± 0.04	–	18 ± 1
		S1	0.51 ± 0.02	−0.18 ± 0.04	53.42 ± 0.16	31 ± 1
		S2	0.50 ± 0.02	0.31 ± 0.04	54.01 ± 0.16	27 ± 1
		S3	0.51 ± 0.02	−0.21 ± 0.04	50.54 ± 0.16	13 ± 1
		S4	0.37 ± 0.09	−0.15 ± 0.15	29.78 ± 0.88	10 ± 1

4 Conclusion

Two samples of traditional Tibetan pills called Rinchen Chakril Chenmo and Rinchen Mangyor Chenmo were analyzed by X-ray fluorescence spectroscopy (XRF), neutron activation analysis (NAA) and Mőssbauer spectroscopy (MS) aimed to get information about elemental/isotopic composition of both samples and/or forms of iron.

XRF and NAA revealed presence of many mineral elements which are essential for the human body but also relatively high concentrations of heavy metals such as iron, copper, mercury, arsenic, etc. Further investigation of the Tibetan pills revealed possible presence of $\alpha - Fe_2O_3$ and $\alpha - FeOOH$ in both investigated samples. Furthermore, room temperature and even low temperature MS spectra exhibit non-magnetic doublet. Its origin is, however still not clear.

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