Chemometric evidence for Sr and Rb isotopes due to the specific soil chemistry in different geographical regions

[1*]Biljana Balabanova, [2]Liping Fan

[1]Faculty of Agriculture, Goce Delcev University Stip, North Macedonia.

[2] College of Information Engineering, Shenyang, University of Chemical Technology, Shenyang, Liaoning Province, China.

*E-mail: biljana.balabanova@ugd.edu.mk

INTRODUCTION

Strontium and rubidium are the commonly used metals for isotope-ratio analysis. Moreover, this geochemical merker varies between different rock types and formations. The $^{87}Sr/^{86}Sr$ ratio has been shown to vary widely in surface rocks, so any Sr released into soils, rivers, and groundwaters has an isotopic signature that reflects its source. Sr and Rb isotopes have also been used to trace agricultural products, which have incorporated Sr, along with Ca, from soils incorporating the Sr-isotope ratios of the underlying rocks.

The specific conditions in the soil represent characteristic conditions of the environment which is reflected in a certain way in the plants. Despite uncertainty about the organic compounds in a sample, the content of selected elements (trace and rare earth elements, REEs) reflects the growing conditions in the environment. For that instance, in the present research we will give focus on the inorganic compounds' identifications, due to the more stable response to the lithogenic nature of the soil-plant interaction.

For the present study, the target isotopes were ^{88}Sr, ^{87}Sr, ^{86}Sr and ^{85}Rb. The isotope analysis was conducted with application of ICP-MS, following the protocol provided in the EPA METHOD 6020. In the validation process, no significant interference occurred that could affect the sensitivity of the measurement of the selected isotopes. Data analysis has been applied within the comparative issues between Sr and Rb content in soil from North Macedonia and selected regions in China. Moreover, the same chemometric model was applied for data analysis for selected plant species for both regions.

In addition, multi-isotope or single-isotope ratios (e.g., strontium and lead) can provide unique, representative fingerprints that make it possible to discriminate the origin of plant food samples. Over the past decade, with the development of new advanced analytical techniques we can successfully retrieve elemental and isotopic compositions, of any given food sample and determine the geographic origin successfully. The growing concern of the consumers stimulated scientific research and publications in recent years, including multi-element and isotope-ratio methods of analysis in food authentication after statistical evaluation of the data.

EXPERIMENTAL DESIGN

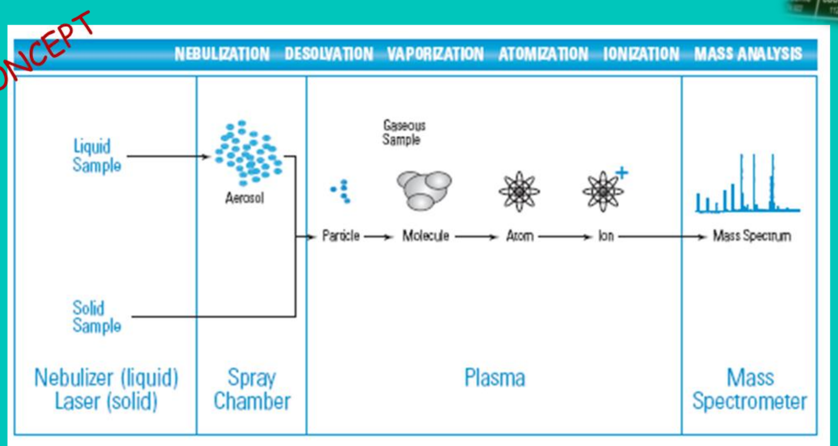
The $^{87}Sr/^{86}Sr$ ratio therefore varies between different rock types and formations. Since Rb is an alkali metal and Sr is an alkaline earth, these elements behave differently in geological processes, creating large variations in Rb/Sr, and, so, large variations in $^{87}Sr/^{86}Sr$. The $^{87}Sr/^{86}Sr$ ratio has been shown to vary widely in surface rocks, so any Sr released into soils, rivers, and groundwaters has an isotopic signature that reflects its source. Sr isotopes have also been used to trace agricultural products, which have incorporated Sr, along with Ca, from soils incorporating the Sr-isotope ratios of the underlying rocks.

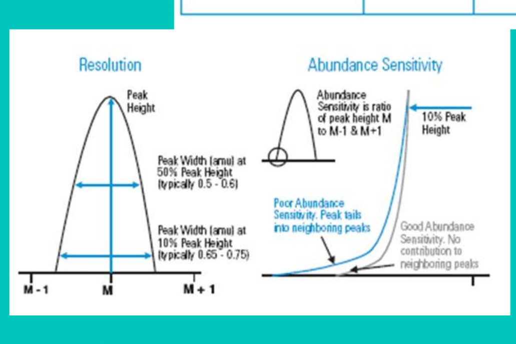
MATERIALS AND METHODS

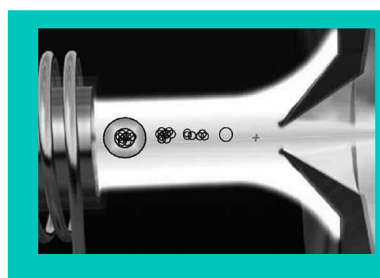
The aim of this case study was to evaluate strontium and rubidium lithogenic occurrence in soil *vs.* the geochemical impact to the herbal plant yellow wort (*Blackstonia perfoliate*). Total content and isotope ratios were determined regarding regional occurrence in the area of the Republic of North Macedonia, compared to selected areas from China. Furthermore, the elements' isotope ratios were corelated with the average data for the corresponding elements in soil samples (top layer). Samples of yellow wort (*Blackstonia perfoliate*) were used for comparative analysis to the same species obtained in market in China.

Isotopes measurements

BASIC CONCEPT







Standard QA/QC variables were used to prove the validity of the method. All set parameters indicate satisfactory analytical sensitivity, accuracy and precision of analysis. During the measurements, dual gas phases were used for the analytes: a) normal mode using basic carrier gas argon and b) helium mode, using optional helium gas. From the parameters obtained, it can be determined that the first analytical mode provides greater sensitivity and linearity of the applied method.

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CHEMOMETRIC TOOLS APPLIED

Sample collection has been conducted in the South-eastern region in the country. For collection of each plant species, we have choose 5 network points, from each location two differ samples were collected. In total, 2 samples from each location, we collected 10 samples for each specie. The samples have been cleaned form dust, airdry to constant mass, then homogenized and subjected to acid digestion. For digestion of samples, the microwave digestion system (model Mars, CEM) was applied. Precisely was measured 0.5 g of each sample and placed in Teflon digestion vessels. In total, 5 mL concentrated nitric acid, HNO_3 (69%, 108 m/V) and 2 mL hydrogen peroxide, H_2O_2 (30%, m/V) were added. The Teflon vessels were carefully closed and placed in microwave digestion system. Samples were digested in two steps for total dissolving at 180°C. After the digestion method was finished, digested samples were quantitatively transferred into 25 mL volumetric flaks, following the protocol of EPA METHOD 3052. The isotope analysis was conducted with application of inductively coupled plasma with mass spectrometry (ICP-MS), following the protocol provided in the EPA METHOD 6020. ICP-MS technique was used due to the high sensitivity (LOD <0.1 ppb), as well for the improved accuracy and reproducibility in isotope measurements. Target masses for strontium were 86, 87 and 88, while for rubidium was selected the 85 mass as most abundant isotope. In the validation process, no significant interference occurred that could affect the sensitivity of the measurement of both elements.

Table 1. Data summary of the instrumental condition and validation of the applied methodology

Element	Isotope	ORS mode	Integration Time (s)	Linear range (µg/L)	Slope	Intercept	R	LOD (µg/L)	LOQ (µg/L)
Sr	86	Normal	0.1	1-50	1.526	10.93	0.9998	0.27	0.872
Sr	86	Helium	0.5	1-100	0.0092	-6.271	0.9994	0.15	0.519
Sr	87	Normal	0.1	1-100	2.125	391.2	0.9999	0.12	0.401
Sr	87	Helium	0.5	0.5-50	1.150	2.483	0.9992	0.096	0.321
Sr	88	Normal	0.1	5-50	1.680	10.27	0.9995	0.77	2.572
Sr	88	Helium	0.5	1-50	2.019	-5.94	0.9991	0,10	0.334
Rb	85	Normal	0.1	1-100	0.058	-0.0063	0.9994	0.29	0.969
Rb	85	Helium	0.5	0.1-10	0.0079	0.0022	0.9991	0.0033	0.011

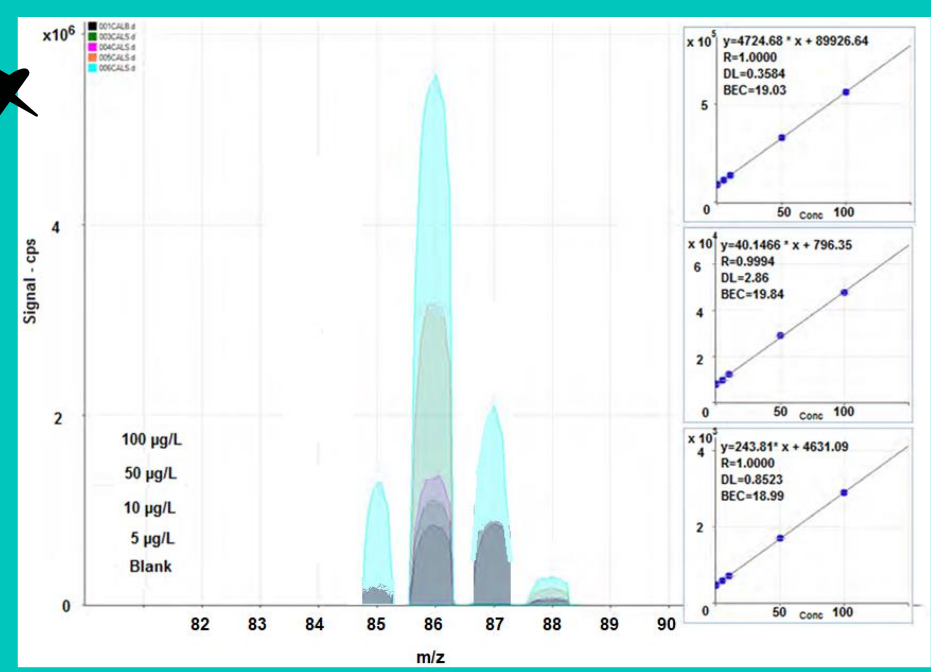

Fig. 1. Calibration data for the analyzed isotopes, within the range of 5 µg/L to 100 µg/L.

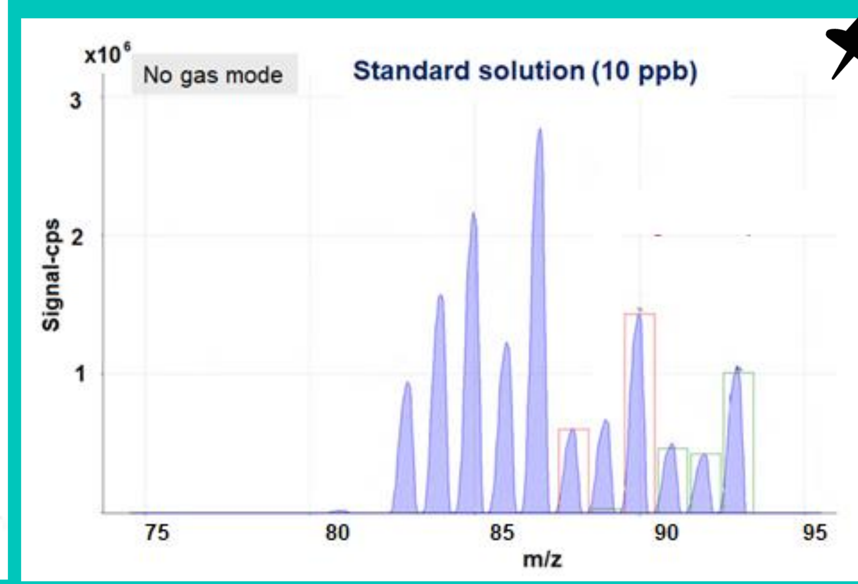

Fig. 2. The cps signals of 10 µg/L calibration standard, indicate stability for CCV Recovery (>80%)

The total content of lrubidium and strontium was determined in herbal species collected in North Macedonia. A comparative analysis was made on the species Yellow wort (*Blackstonia perfoliat*), available in Macedonia *vs.* China. In order to determine the potential of soil enrichment with rubidium and strontium due to the influence of the contents of these elements in the biaccumulation, the average values for these two elements in the soil are given in comparison in both countries. From the data on the content of rubdium and strontium in the soil, it indicates a greater enrichment of these elements in the soils in North Macedonia, compared to the soils in China

Table 2. Total content of lead and strontium in herbal samples-comparative analysis (N=10)

Sample	Data description	Rb (mg/kg)		Sr (mg/kg)	
		Range	Average	Range	Average
Yellow wort - NMK	Blackstonia perfoliat	12.6-133	54.3	10.8 – 210	77.4
Yellow wort - Ch	Blackstonia perfoliat	0.78 – 77.8	21.4	29.7 – 413	116
Soil data – North Macedonia, NMK	Data for automorphic soil for North Macedonia [1]	58.9 - 1930	534	21 - 1400	140
Soil data - China, CH	Data for agricultural soil in China [2]	39-573	201	67.3 – 116	98.6

Geochemical markers of isotopic ratios of rubidium and strontium were determined in order to determine the correlation of the bioaccumulation of rubidium and strontium in relation to the specific soil chemistry in different regions (North Macedonia vs. China), for the *Blackstonia perfoliate* herbal specie. According to the obtained results, there is a significant difference in the isotopic ratios of rubidium and strontium isotopes (Table 3). This indicates that these parameters can represent significant segments in determining the geographic origin of species.

Geochemical markers represent a significant factor in determining the geographical authenticity of plant foods. This research was aimed at the possibility of using rubidium and strontium isotopes as typical indicative markers in correlation with soil chemistry. The analysis indicated that the natural and anthropogenic indication of these two elements in the soil does not provide significant geochemical marking for the plant species. Herbal plants that have been confirmed as typical metal bio-accumulators were used. The total content of lead and strontium in plant herbal spices did not show specificity with the geographical region.

Table 3. Data summary for the Rb and Sr isotopes ratios

Sample	N	$^{85}Rb/^{86}Sr$	$^{86}Sr/^{87}Sr$	$^{87}Sr/^{88}Sr$
Yellow wort - NMK	10	1.471 ± 0.26	0.811 ± 0.16	2.087± 0.22
Yellow wort – Ch [2]	10	2.852 ± 0.85	0.872± 0.25	1.903± 0.18

The target isotopes ^{88}Sr, ^{87}Sr, ^{86}Sr and ^{85}Rb and isotopic ratios $^{86}Sr/^{87}Sr$ and $^{87}Sr/^{88}Sr$) showed a significant difference in the same species and different geographical region. This indicates that isotopic ratios of lead and strontium can be used as a geochemical marker to determine the geographical authenticity of herbal species. However, isotopic ratios, by themselves, do not represent an isolated geochemical marker. This indicates the multi-cluster nature in determining the geographic origin of plant foods.

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