INSIGHTS ON CONSUMER HEALTH: THE MINERAL CONTENT OF SELECTED VEGETABLES AVAILABLE ON THE ROMANIAN MARKET

Andrei-Vlad Bădulescu*, Anița Luncan**

*Emanuil Gojdu National College, 3-5 Spiru Haret St., 410066, Oradea, Romania, email: andibadulescu@gmail.com
** Emanuil Gojdu National College, 3-5 Spiru Haret St., 410066, Oradea, Romania, email: anita_chimie@yahoo.com

Abstract

The accurate determination of the mineral content (and, subsequently, of the quality) of food products is essential for a truthful and honest information of consumers. It is also relevant to orienting the efforts of producers and suppliers, as to obtain and market the most adequate cultivar complying with customers' preferences and expectations. In this paper we present the results of several determinations on the mineral content of selected vegetables commonly encountered on the Romanian market, namely in the city of Oradea. The concentration of calcium, magnesium and iron in vegetables was determined by means of complexometric EDTA titrations using Eriochrome black T and salicylic acid as indicators. Vegetables belonging to different genera (i.e. Allium-onion, leeks), families (i.e. Apiaceae-carrots, celery) and even cultivars of the same species (i.e. Brassica oleracea-cabbage, cauliflower, kohlrabi) were analyzed, and experimental results were then sorted both hierarchically and in terms of taxonomic similarities. Most results are similar to the findings in the literature, yet the existence of certain differences highlights a need for subsequent research. A better understanding of such differences, as well as a correlation between the mineral content (and thus the quality), and genetic similarity of commonly cultivated species could ultimately contribute to achieving a better knowledge of the individual characteristics of marketed cultivars, and hence improve the efficiency of producing and marketing such products.

Keywords: consumer health; vegetables; mineral content; Romanian market.

INTRODUCTION

An analysis and classification of cultivars based on a sought-after indicator of their quality (the mineral content) is not only of interest to customers, but also to producers attempting to satisfy the customers' demand for a specific quantity of a certain mineral ion.

For example, a dietary calcium deficiency leads to a diminished body weight gain, impedes skeletal bone growth, and lowers serum calcium levels (Fujita et al., 2016). On the other hand, an excessive maternal intake of calcium is associated with neonatal seizures (Borkenhagen et al., 2013). It can be concluded that different customers are interested in a different amount of a certain mineral, prompting producers to adapt in order to satisfy a particular group.

Moreover, a certain concentration of a mineral, or a ratio of their concentrations, can be associated with various disorders. For example, the development of bitter pit in apples is linked to a low Ca/Mg content (do Amarante et al., 2013), while a lack of magnesium in vegetables would result in carbohydrate metabolism dysfunctions, leading to effects ranging from leaf yellowing and degradation to a diminished root growth (Farhat et al., 2016).

Previous studies (Ekkholm et al., 2007) have shown a significant variation in the concentration of inorganic ions in dietary produce, especially a noticeable drop in the concentration of trace minerals, as well as an increase in the consumption of vegetables.

The evolution of the mineral content has been attributed to various factors, from weather conditions to agricultural practices (the use of specific fertilizers) or the use of leaded fuels. The bioaccumulation of certain ions (ranging from essential ions such as iron to cadmium or lead) has been linked to industrial activity, typically due to wastewater discharge (De Melo Gurgel et al., 2016) or by means of air pollution due to mining activities (Arrivabene et al., 2015). The high concentration of metallic ions is most evident in aquatic organisms, but is also encountered in the consumers of such organisms (Cardwell et al., 2013).

Such variation highlights the need for constant research in the field, in order to obtain accurate and, most importantly, up-to-date information. Therefore, the method employed for this study (complexometric titrations) was devised to be practical, quick and of a suitable accuracy.

Using this method, calcium and magnesium can easily be distinguished from iron by use of a buffer solution, since iron precipitates at a significantly lower pH than either calcium or magnesium.

A formula for the precipitation pH can easily be inferred from the expression of K_{sp} of a given $M(OH)_n$ hydroxide:

$$K_{sp} = [M^{n+}][HO^-]^n$$

$$[HO^-] = \sqrt[n]{\frac{K_{sp}}{[M^{n+}]}}$$

$$pH = 14 - pOH$$

The precipitation pH, calculated for a M^{n+} concentration of 10 mmol/L (for calcium and magnesium) and 0.1 mmol/L (for both iron species), was registered in Table 2, alongside the K_{sp} values used for the calculations (Badea, 2004; Vlădescu, 2003).

Alongside the stability constants of the encountered coordination complexes, the stability of calcium and magnesium hydroxides is relevant in order to prove the accuracy of the titration. The stability constants of poorly soluble hydroxides can be calculated using the expression of K_{sp} and β, and their values are registered in Table 1:

$$\beta = \frac{M(OH)_n}{[M^{n+}][HO^-]^n} = \frac{1}{K_{sp}}$$

$$lg\beta = -lgK_{sp}$$

Since the stability constants of magnesium and ferric hydroxides greatly exceed those of corresponding EDTA complexes, the pH of the buffer should by no means be higher than 10.37 (for magnesium) and 2.89 (for iron). The sample is therefore dissolved in an environment of a suitable acidity, either a pH buffer or an acidic solution, its pH chosen based on the above-mentioned calculations. Its components and chemical properties are detailed in the second part of this paper.

Table 1

The stability constants of relevant coordination complexes

Coordination complex	lgβ
Ca-EDTA	10.7
Ca-ErioT	5.3
Mg-EDTA	8.69
Mg-ErioT	4.5
Fe^{3+}-EDTA	25.7
Fe^{2+}-EDTA	14.3
Fe^{3+}-salicylate	16.35
Fe^{2+}-salicylate	6.55
$Ca(OH)_2$	4.5
$Mg(OH)_2$	11.26
$Fe(OH)_3$	37.42

Source: (Furia, 1972)

MATERIALS AND METHODS

1. Comparison of experimental procedures

Previous studies of trace ion contents have typically relied on physical methods, usually atomic absorbtion spectroscopy, plasma optical emission spectroscopy (do Amarante et al., 2013), mass spectrometry or a combination of the three (Ekkholm et al., 2007; Cunningham et al., 2001). While accurate, spectroscopic methods have a number of drawbacks, such as a bulky and expensive equipment and a difficult experimental procedure. The determination of the ionic content of vegetable extracts by means of a chemical procedure results in a slightly diminished precision (while suitable for its purpose), yet overall a more practical method, due to its easy to use and affordable equipment.

Table 2

Solubility products and precipitation pH of relevant species

Compound	K_{sp}	Precipitation pH
Ca(OH)2	$3.1 \cdot 10^{-5}$	12.75
Mg(OH)2	$5.5 \cdot 10^{-12}$	10.37
Fe(OH)2	$4.9 \cdot 10^{-16}$	8.34
Fe(OH)3	$3.8 \cdot 10^{-38}$	2.89

Source: (Badea, 2004)

2. Experimental setting

Vegetable samples were titrated using a 0.01 mol L-1 tetrasodium EDTA solution, obtained by dissolving 3.8 g of thermally-dehydrated Na_4EDTA in distilled water, up to a volume of 1 litre.

A magnesium chloride solution is prepared from metallic magnesium and pure (metal-free) hydrochloric acid solution, in order to be used for the standardisation of the EDTA solution. The factor of the solution was determined to be between 0.999-1.001, approximated to 1.

The titration of calcium and magnesium was run using an ammonia/ammonium chloride buffer (pH=10), in order to ensure the precipitation of interfering divalent or trivalent cations (most importantly iron), but not that of the two analysed ions

The indicator consisted of 0.2 g of Eriochrome Black T dissolved in 50 mL of 20% ammonia solution. Known for its instability towards light, being easily degraded by UV radiation or sunlight, especially if in contact with TiO_2 particles (Kansal et al., 2013), the indicator solution was freshly prepared for each titration. Its instability with respect to oxidation, even by a moderately weak oxidant, such as dilute H_2O_2 has also been reported (Zhu et al., 1997).

For the titration of trivalent iron, the sample was dissolved in a 0.1 M HCl solution, in order to maintain a pH below 2.89 (the precipitation pH of Fe^{3+}). The indicator consists of a saturated salicylic acid solution and, unlike the previous indicator, is stable with respect to hydrolysis and sunlight and therefore reusable.

The determination of trivalent iron can safely proceed in these conditions, even in the presence of calcium and magnesium, due to the greater stability of the Fe^{3+-}EDTA complex than the equivalent calcium, magnesium or Fe^{2+} complexes, as well as that of Fe^{3+}-salicylate than Fe^{2+}-salicylate.

A typical colour shift is red (or purple) to blue (for Eriochrome Black T) or crimson to colourless (for the salicylic acid-iron complex), but the colour of the vegetable sample is noticeable. This does not impede the titration, but may lead to a slightly different aspect of the end point, especially in the case of the eriochrome indicator. Thus, the Ca^{2+}&Mg^{2+} titration has a greenish-gray end point, while the titration of iron leads to a return to the diluted sample’s original colour. In both situations, the end point is easily discernible, if not the one expected. The eriochrome-induced colour shifts of vegetable samples and of a calcium chloride solution (for comparison) are presented in Tables 3, 4 and 5.

Table 3

The colour shift of a colourless Ca^{2+} solution

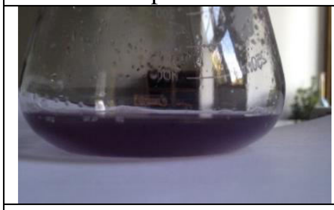
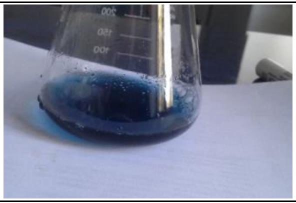
Expected eriochrome black T colour shift	
	
Beginning of titration	End point

Table 4

The colour shift of a diluted kohlrabi sample - typical for most samples

Commonly encountered eriochrome black T colour shift	
	
Beginning of titration	End point

Table 5

The atypical colour shift of a diluted carrot sample

The colour shift of a strongly coloured sample	
	
Beginning of titration	End point

RESULTS AND DISCUSSION

The titrations' results were averaged and registered in Table 6. It is easily noticeable that the titration of calcium and magnesium offered satisfactory results for all samples, whereas Fe^{3+} was in one case (cauliflower samples) found to have a concentration below the method's detection threshold, by not prompting the indicator's colour shift. All other samples were able to provide visible colour shifts and end points.

The findings were also recorded in Figures 1 and 2, in order to better highlight statistical correlations (or lack thereof) between the mineral content and genetic similarities (as stated in the abstract), or between the concentrations of the three ions.

Table 6

The experimental results

Cultivar	Ca^{2+}&Mg^{2+} total molarity (mmol/L)	Fe^{3+} molarity (mmol/L)	Ca^{2+}&Mg^{2+} average concentration (mg/L)	Fe^{3+} concentration (mg/L)	pH
Kohlrabi, stem	17	0.1	544	5.6	6
Cabbage, leaves	35	0.25	1120	14	5
Cauliflower, inflorescence	14	<0.1	448	<5	6.5
Carrot, root	16	0.15	512	8.4	7
Celery, root	20	0.1	640	5.6	5.5
Leek, bulb	21	0.3	672	16.8	6
Onion, bulb	14	0.2	448	11.2	5

The experimental findings highlight, first of all, the lack of a correlation between genetic similarities and ionic content, as highlighted in Figure 1. Thus, the lowest Ca^{2+}&Mg^{2+} content is encountered in cauliflowers (14 mmol/L) and the highest in cabbages (35 mmol/L), both cultivars belonging to *Brassica oleracea*.

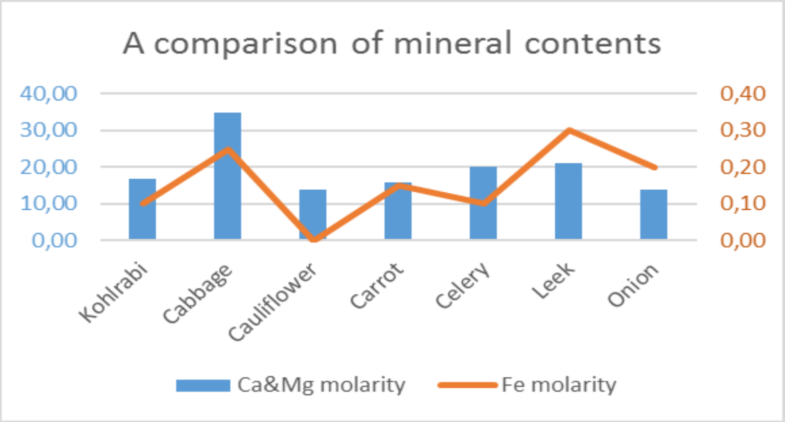


Fig. 1. The concentration of calcium, magnesium and ferric ions in seven common cultivars

Secondly, there is no noticeable relationship between the concentration of iron and that of Ca^{2+}&Mg^{2+}, as highlighted in Figures 1 and 2. For example, cabbage has a Ca^{2+}&Mg^{2+} content 1.66 times greater than that of leeks (35 and 21 mmol/L, respectively), yet its iron content is 1.2 times lower (0.25 and 0.3 mmol/L, respectively). The low R^2 value of 0.2933 proves the assumption.

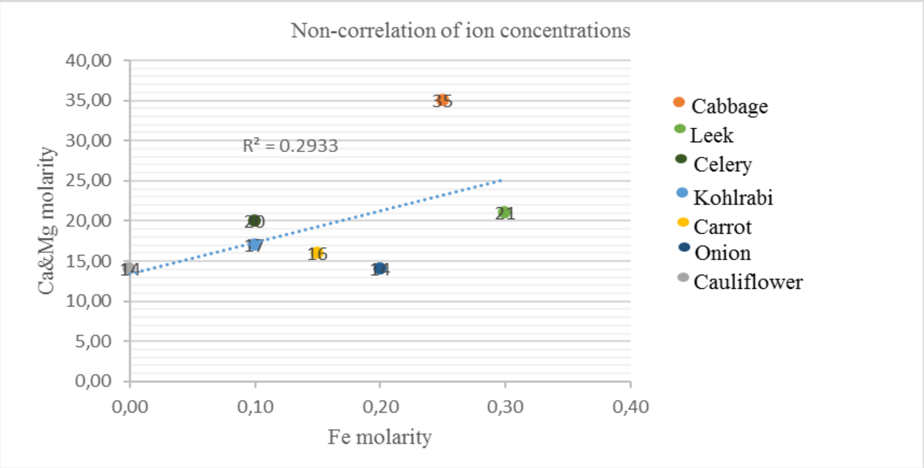


Fig. 2. The plot of the Ca^{2+}&Mg^{2+} molarity against that of Fe^{3+}, emphasising the lack of a correspondence between the two concentrations

CONCLUSIONS

The study indicates significant differences in the mineral content of selected vegetables, regardless of their taxonomic relatedness (for example, the concentration of Ca^{2+}&Mg^{2+} in cabbages is 150% greater than in cauliflowers). Moreover, there is no significant correlation between the concentration of iron and that of calcium and magnesium.

An ease in obtaining reliable and accurate information on the mineral content of a vegetable is convenient for producers interested in adapting to a growing demand for a certain cultivar due to its contents, to assess a mineral deficiency or even predict the development of certain disorders in a cultivar.

The experimental procedure has fulfilled its purpose with a satisfactory precision, a low cost and a quick procedure, and its accuracy can easily be improved by use of more concentrated samples. The method has proven to be reliable and easy to use, and can be adapted to various metallic ions by use of different pH buffers and indicators.

The method is most useful when a quick determination is required, and can assess the variation of ions over time due to the ease of repeating the analyses when needed. Thus, it is not only a convenient procedure to assess the quality of a vegetable product, but also a viable method to assess the extent of a pollutant's effects, by being a means of measuring the bioaccumulation of an ion in a plant.

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