

## Multi-elemental analysis of wine samples using ICP-OES and ICP-MS methods. Anthropogenic gadolinium in wine

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*The study presented in this article has been focused on developing a method for elemental analysis of wine samples. A wide sample set of 200 wines contained white, rosé and red still wines; the wine vintages being 2013, 2014, 2015, 2016, 2017 and 2019. Samples were taken from wine festivals in Pardubice and Hradec Králové and private wineries in the Czech Republic. The analysis was performed using inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS); the determined elements being As, Ba, Ca, Cd, Ce, Co, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, S, Sm, Sr, Tb, Tm, Y, Yb, and Zn. The data obtained were processed statistically and the Sr/Ba, Sr/Ca and Sr/Mg ratios were determined as potential indicators for the identification and classification of the wine origin. The existence of the so-called gadolinium anomaly for selected wine samples was investigated as evidence of the presence of anthropogenic gadolinium.*

**Keywords:** Minerals; Heavy metals; Rare earth elements; Wine; ICP-OES; ICP-MS

### Introduction

Chemically, wine is a very complex liquid [1] produced from grape berries by the process of alcoholic fermentation of mash or must [2,3]. It is one of the most popular and widely consumed alcoholic beverages worldwide [1,2,4] and its commercial

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value is obvious [1]. Wine is a source of numerous organic and inorganic biologically active substances with considerable health benefit [1,3,5], such as polyphenols, antioxidants, vitamins and minerals [3,5]. The presence of minerals in the wine is ensured by their transport from the soil through the plant to the berries and the subsequent processing of the berries into the wine [3,5–7]. In the same way, heavy metals can get into the wine [3]. Minerals and heavy metals may also originate from winemaking equipment, from the process of filtering and purifying wine or from fertilisers and vine treatment chemicals [1,3,8]. The importance of minerals lies in biochemical and physicochemical processes [3]. The total mineral content in a wine is between 1.5 and 4 g L<sup>-1</sup> [3,5] consisting, in particular, of potassium, phosphorus, calcium, sulphur, magnesium, silicon, chlorine, sodium, iron, and boron [3]. The mineral content in grape berries and wine is affected by many factors, such as soil and its geological origin, weather, climate, heavy-metal pollution, vine variety, fertilisation, use of vine protection products, winemaking practices, transport and storage [1,5,7–9]. However, the grape harvest area is considered a key factor [7].

The origin of wines can be determined and classified, and possible falsification of both origin and authenticity can be identified using the multi-element analysis combined with multivariate statistical approaches, so-called fingerprint techniques [8–10]. These properties of food products are usually associated with the overall judgment of quality by the consumer, which results in an impact on the commercial value of the product [10]. The European Commission (EC) and the International Organisation of Vine and Wine (OIV) strictly regulate the components of wine [4] and therefore, elemental analysis of wine is needed for both wine industry and customers [4,9]. For elemental analysis of wine, various techniques are used, namely: electrothermal atomic absorption spectrometry (ETAAS), flame atomic absorption spectrometry (FAAS), and especially ICP-OES and ICP-MS [3,4,5,7,9,10]. The amount of minerals is determined as the ash of inorganic origin [3,5]. Major and trace elements, rare earth elements (REEs), and isotope ratios are often monitored as fingerprints to determine the origin of wines [1,7,9,10,11].

Attention is often paid to REEs in the case of classification of wines [9,11]. They are naturally found in the environment [12–15] and used in various fields (agriculture, industry, medicine) [12,15–18]. Due to their widespread use, concentrations of REE from anthropogenic activities are increased in the environment (soil, surface water, wastewater) [19]. Through the subsequent bioaccumulation of REEs in organisms, e.g. by algae and bivalves [19], they can enter the food chain and adversely affect human health [13,17]. After ingestion of food, dermal absorption and inhalation, REEs can accumulate in the human body [13,18] (blood, bones, brain) [13] and causing serious health problems [17,18], such as functional neurological disorders, pneumoconiosis, male sterility, fibrotic tissue injury, cytotoxicity, and oxidative stress [17]. One of these emerging contaminants is gadolinium [15], which is, for example, used in contrast agents for magnetic resonance imaging (MRI), electronics, iron and steel industry [15,16,20].

Gadolinium represents non-negligible impurity of phosphate fertilisers [13–15,21] or it may be a part of livestock feeds as a growth stimulator [15,22]. Anthropogenic gadolinium enters the environment from various sources (emissions in hospitals with MRI workplace [16], disposal of home electronics [20], etc.) Due to the fact that anthropogenic gadolinium occurs in more bioavailable and more soluble forms [12,19], it accumulates in soil and is spread in water (surface and wastewater) [15,16,20]. The result is an increase in the total gadolinium concentration by an anthropogenic increase compared to the natural gadolinium content and also compared to the concentrations of other REEs [15,16,20], which is then called the gadolinium anomaly [15,16,]. From this soil and water, anthropogenic gadolinium can enter agricultural products and, consequently, the food chain through [13], for example irrigation, which is common in vineyards to regulate water availability to the plant [23], or soil contamination with REEs [19].

This work is focused on the development of suitable analytical methods for determining the elemental composition (minerals, heavy metals, REEs) of wine samples using ICP-OES and ICP-MS methods. Subsequently, the possible use of these methods to monitor the geographical origin of wines is investigated. For these purposes, the element ratios Sr/Ba, Sr/Ca, Sr/Mg are evaluated. The content of anthropogenic gadolinium and gadolinium anomaly is also determined.

## Materials and methods

### Reagents and standards

All the used reagents were of analytical reagent grade. Distilled water was purified using an Ultra Clear GP TWF UV UF TM ultra-pure water preparation equipment (Evoqua Water Technologies, Günzburg, Germany). Nitric acid (65%) (Lach-Ner, Neratovice, the Czech Republic) was distilled in sub-boiling distillation equipment BSB-939-IR (Berghof, Eningen, Germany) for ICP-MS analysis.

For instrument calibration, multi-elemental calibration standards were prepared from the commercially available single-element standard solutions of As, Ba, Ca, Cd, Co, Cu, Fe, In, K, Mg, Mn, Na, Ni, P, Pb, S, Sr, and Zn (Analytika, Prague, the Czech Republic; SCP Science, Baie-D'Urfe, Canada; Merck, Darmstadt, Germany) with a concentration of 1 g L<sup>-1</sup>. Further, commercially available multi-elemental standard solution M008 containing 100 mg L<sup>-1</sup> of Ce, La, Nd, Pr and 20 mg L<sup>-1</sup> of Dy, Er, Eu, Gd, Ho, Lu, Sm, Tb, Tm, Y, Yb (Analytika) was used. Ethanol (96%) (Lach-Ner), nitric acid (65%) and ultra-pure water were also used to prepare all calibration standards.

The mixed calibration standards contained Ba, Ca, Fe, K, Mg, Mn, Na, P, S, Sr, Zn for ICP-OES analysis and As, Cd, Ce, Co, Cu, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Ni, Pb, Pr, Sm, Tb, Tm, Y, Yb for ICP-MS analysis. To stabilise the calibration solutions, 65% nitric acid for ICP-OES analysis and sub-boiled 65%

nitric acid for ICP-MS analysis were added with a final concentration of 0.65 % in both cases. The ICP-MS standards contained an internal standard indium in the final concentration of  $1 \mu\text{g L}^{-1}$ .

To validate the method, a calibration set containing ethanol and a calibration set without the addition of ethanol were prepared. Subsequently, 96% ethanol was added to the calibration standards in an amount corresponding to the composition of the analysed wine samples. To the calibration standards for ICP-OES analysis, 96% ethanol was added in an amount of 1.5 mL per 100 mL of solution. For ICP-MS analysis, calibration solutions were prepared with the addition of 96% ethanol with a final content of 0.15 mL per 10 mL of solution.

The blanks were prepared to contain the same amount of 65% nitric acid and 96% ethanol and, in the case of ICP-MS analysis, with the addition of indium as calibration standards. Table 1 lists the concentrations of the individual groups of elements in the relevant standards for ICP-OES and ICP-MS analyses.

**Table 1** Concentrations of calibration standards for ICP-OES and ICP-MS analyses

Standards	ICP-OES*					ICP-MS**	
	A	B	C	D	E	F	G
S1	200	100	50	1	0.1	10	2
S2	100	50	25	0.5	0.05	5	1
S3	40	20	10	0.1	0.01	1	0.2
S4	20	10	5	0.05	0.005	0.5	0.1
S5	4	2	1	0.02	0.002	0.1	0.02
S6						0.05	0.01
S7						0.01	0.002

\* –  $c$ ,  $\text{mg L}^{-1}$ ; \*\* –  $c$ ,  $\mu\text{g L}^{-1}$ ;

A: K; B: P, S; C: Ca, Mg, Na; D: Fe, Mn, Zn; E: Ba, Sr; F: As, Cd, Ce, Co, Cu, La, Nd, Ni, Pb, Pr; G: Dy, Er, Eu, Gd, Ho, Lu, Sm, Tb, Tm, Y, and Yb

## Samples

In total, the wine sample set contained 185 samples from wine festivals in Pardubice and Hradec Králové (collected by employees of the Upper Secondary School of Chemistry Pardubice) and 15 samples from private wineries. The wines were white, rosé and red, and all were still wines. The wine vintages were 2013, 2014, 2015, 2016, 2017 and 2019. The wine origin was mainly from the Czech Republic (Moravia and Bohemia regions), but also from abroad (France, Romania, Hungary, and Slovakia). The diversity of grape varieties represented a wide range, such as Chardonnay, Děvín, Grüner Veltliner, Pálava, Pinot Blanc, Pinot Gris, Riesling, Sauvignon Blanc, Silvaner, Welschriesling, Blauer Portugieser, Blaufränkisch, Cabernet Moravia, Cabernet Sauvignon, Dornfelder, Pinot Noir and others.

The samples were stored in 100mL polyethene (PE) bottles in a freezer at  $-18\text{ }^{\circ}\text{C}$ . Samples were thawed and tempered to room temperature before analysis. All the samples were diluted ten-times with ultra-pure water prior to ICP-OES and ICP-MS analyses. An internal standard indium was added to the sample solutions to achieve the final concentration of  $1\text{ }\mu\text{g L}^{-1}$  for ICP-MS analysis.

## Instrumentation

Elemental analysis of the wine samples and calibration standards were performed using an ICP optical emission spectrometer (moxsel Integra XL; GBC, Regents Park, Australia) and an ICP orthogonal acceleration time-of-flight mass spectrometer (ICP-*oa*-TOFMS) OptiMass 9500 (GBC).

The operating conditions of ICP-OES analysis were as follows: power, 1 000 W; view height, 5 mm; gas, Ar 99.999%; plasma, auxiliary and nebuliser gas flow rates were 10, 0.4 and  $0.52\text{ L min}^{-1}$ ; read time, 1 s; fixed point background correction, 3 replicates, and radial view. The most sensitive spectral lines or lines not affected by the interference of other elements present were used for the quantification of selected elements (Ba, Ca, Fe, K, Mg, Mn, Na, P, S, Sr, and Zn). Table 2 summarises the spectral lines on which the selected elements were measured using the ICP-OES spectrometer, photomultiplier voltage, background correction, and limits of detection (LODs) of the instrument and the method. The instrumental LOD was calculated as concentration related to the three times the standard deviation of the signal at the place of the background correction. Calculation of the method LOD was performed by multiplying the instrumental LODs by the sample dilution factor.

**Table 2** Spectral lines, photomultiplier voltages, background correction, instrumental LODs and method LODs of selected elements for ICP-OES analysis

Element	$\lambda$ [nm]	PTM [V]	BC [nm]	$\text{LOD}_I$ [ $\text{mg L}^{-1}$ ]	$\text{LOD}_M$ [ $\text{mg L}^{-1}$ ]
Ba	493.409	580	-0.050	0.0001	0.001
Ca	317.933	430	+0.040	0.0001	0.001
Fe	259.940	600	-0.020	0.0002	0.002
K	769.896	600	-0.055	0.3	3
Mg	280.270	300	+0.020	0.0001	0.001
Mn	257.610	550	-0.020	0.001	0.01
Na	589.592	600	-0.045	0.01	0.1
P	213.618	600	+0.020	0.02	0.2
S	180.731	600	+0.020	0.1	1
Sr	407.771	500	+0.040	0.0001	0.001
Zn	213.856	600	-0.020	0.001	0.01

$\lambda$  – wavelength; PTM – photomultiplier voltages; BC – background correction;  $\text{LOD}_I$  – instrumental limit of detection;  $\text{LOD}_M$  – method limit of detection

The operating conditions of ICP-MS analysis were as follows: power, 1 200 W; multiplier gain, 2700 V; plasma, auxiliary and nebuliser gas flow rates were 13, 0.55 and 0.9 L min<sup>-1</sup>, 3 replicates and five-second data acquisition time. For quantification, the external calibration using the internal standard indium was used. Using the device's "smart gateway", selected unwanted m/z ranges were excluded from detection. Working isotopes were <sup>59</sup>Co, <sup>60</sup>Ni, <sup>63</sup>Cu, <sup>75</sup>As, <sup>89</sup>Y, <sup>112</sup>Cd, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>153</sup>Eu, <sup>158</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm, <sup>172</sup>Yb, <sup>175</sup>Lu, and <sup>206+207+208</sup>Pb. They were selected on the basis of their sensitivity and with regard to possible isobaric overlaps of the interfering ions with the same mass. Table 3 summarises the instrumental LODs and method LODs of selected element isotopes for ICP-MS analysis. The instrumental LOD was expressed as the concentration corresponding to three times the standard deviation of the integrated peak area, which was measured near the ion peak observed. The method LOD was calculated as a multiple of the instrumental LOD using the sample dilution factor.

**Table 3** Instrumental LODs and method LODs of selected isotopes of elements for ICP-MS analysis

Isotope	LOD <sub>I</sub>	LOD <sub>M</sub>	Isotope	LOD <sub>I</sub>	LOD <sub>M</sub>
<sup>59</sup> Co	0.8	0.008	<sup>153</sup> Eu	0.4	0.004
<sup>60</sup> Ni	2.4	0.024	<sup>158</sup> Gd	0.4	0.004
<sup>63</sup> Cu	0.2	0.002	<sup>159</sup> Tb	0.1	0.001
<sup>75</sup> As	0.4	0.004	<sup>163</sup> Dy	0.4	0.004
<sup>89</sup> Y	0.6	0.006	<sup>165</sup> Ho	0.3	0.003
<sup>112</sup> Cd	0.5	0.005	<sup>166</sup> Er	0.4	0.004
<sup>139</sup> La	0.5	0.005	<sup>169</sup> Tm	0.1	0.001
<sup>140</sup> Ce	0.3	0.003	<sup>172</sup> Yb	0.4	0.004
<sup>141</sup> Pr	0.1	0.001	<sup>175</sup> Lu	0.1	0.001
<sup>146</sup> Nd	0.5	0.005	<sup>206+207+208</sup> Pb	0.1	0.001
<sup>147</sup> Sm	0.8	0.008			

LOD<sub>I</sub> – instrumental limit of detection in ng L<sup>-1</sup>; LOD<sub>M</sub> – method limit of detection in µg L<sup>-1</sup>

## Results and discussion

This work aimed to develop suitable methods for elemental analysis of minerals, heavy metals, and REEs in wine samples using ICP-OES and ICP-MS methods. Furthermore, attention was paid to determining the suitability of Sr/Ba, Sr/Ca and Sr/Mg ratios as indicators for the identification and classification of wine origin and determining the gadolinium anomaly in these samples.

Thirty-two elements (As, Ba, Ca, Cd, Ce, Co, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, S, Sm, Sr, Tb, Tm, Y, Yb, Zn) were analysed using ICP-OES and ICP-*oa*-TOFMS spectrometers. The sample set contained 131 white, 51 red and 18 rosé wines from the years 2013 to 2017, and 2019 originated from the Czech Republic but also from abroad.

## Method validation

Validation of the method for elemental analysis of wine samples was performed. The effect of ethanol present in the sample matrix on the analysis was investigated. For this purpose, the calibration series of standards with and without the addition of ethanol were analysed and compared. The effect of ethanol on the results of the determination was demonstrated. The differences in slopes of calibration lines with and without ethanol ranged from 6 to 40 % for ICP-OES and from –73 to 12 % for ICP-MS. For this reason, a 1.5% addition of ethanol to the calibration series was necessary for both ICP-OES and ICP-MS analysis of wine samples. Table 4 summarises the changes in the slopes of the calibration line for elements.

The verification of the reliability of ICP-OES and ICP-MS method differed slightly. To verify the recovery and long-term repeatability of analysis by ICP-OES, recalibration was performed after every 15 samples using calibration standard S1 (see Table 1 for concentration) and a blank. For ICP-MS, verification was performed after every 20 samples by analysing calibration standards S2, S3, S4 and S5 (see again Table 1). Both methods were validated by monitoring recovery and long-term repeatability and the instrumental LODs and method LODs were calculated, as shown in Table 2 (for ICP-OES analysis) and in Table 3 (for ICP-MS). The recovery of the analysis results was expressed as the obtained and the theoretical concentration ratio when ranging from 84 to 110 % for ICP-OES analysis and from 81 to 120 % for ICP-MS. Long-term repeatability expressed as the relative standard deviation (RSD) ranged from 1.77 to 2.49 % for ICP-OES and from 0.07 to 15.0 % for ICP-MS. Table 4 summarises the results of determining the recovery and repeatability of ICP-MS and ICP-OES methods for all the elements.

**Table 4** Method validation – the changes in the slopes, recovery and long-term repeatability of ICP-OES and ICP-MS methods

	Element	Slope difference [%]	Recovery [%]	Repeatability [%]
ICP-OES	Ba	17	103–110	1.84
	Ca	8	86–92	1.86
	Fe	26	90–98	2.28
	K	6	96–104	2.21
	Mg	14	93–100	1.77
	Mn	26	88–95	2.46
	Na	6	100–106	1.88
	P	40	84–91	2.49
	S	10	86–92	2.24
	Sr	21	97–104	2.05
	Zn	33	89–95	2.04
ICP-MS	Co	9	88–110	0.19–13.8
	Ni	–16	81–117	0.67–7.46
	Cu	–21	82–117	0.32–6.79
	As	–73	86–117	0.17–9.53
	Y	–8	90–112	0.36–11.0
	Cd	–2	93–109	0.72–9.52
	La	–3	100–111	0.34–7.88
	Ce	–	96–109	0.14–6.72
	Pr	–	94–110	0.27–6.92
	Nd	–	95–117	0.53–12.8
	Sm	–	85–120	1.10–11.5
	Eu	–	99–115	1.04–9.04
	Gd	12	94–111	0.14–13.5
	Tb	–	98–113	0.27–10.3
	Dy	–	81–116	0.24–15.0
	Ho	–	95–117	0.60–10.7
	Er	–	100–115	0.54–10.4
	Tm	–	100–114	0.07–9.35
	Yb	9	96–115	0.44–14.2
	Lu	–	99–114	0.54–11.4
Pb	5	103–119	0.12–8.58	



## Statistical evaluation of the results

The results of measurements were presented using minimum, maximum, arithmetic mean, and standard deviation. Tables 5 and 6 summarise the statistical results for ICP-OES and ICP-MS measurements. Both also list the values of the common content of elements in wine or the limits of risk elements in wine set by the OIV [3,5,24].

The average concentrations of As, Ba, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, P, Pb, Sr, and Zn found in all wines were in the range of common contents of these elements found in wine wines or below the limits set by the OIV. As seen, the average values of the S content were lower than the typically occurring contents. However, the maximum values of S were in the range of common contents. The Ni content in all samples was higher than that for common Ni content found in wine and the highest ( $400 \mu\text{g L}^{-1}$ ) was in the sample Blaufränkisch, 2019, Vinařství Košulič (Hustopeče, the Czech Republic). Higher contents of Ni in the samples could be caused by pollution of wine in the winemaking process.

When comparing the concentrations of heavy metals with the maximum acceptable limits set by the OIV, 2 non-compliant samples were found in the sample set. One is St. Laurent Claret, 2015, Vinařství Zemčik (Horní Věstonice, the Czech Republic) in which  $160 \mu\text{g L}^{-1}$  Pb and  $1700 \mu\text{g L}^{-1}$  Cu were found and thus the limits for Pb content ( $<150 \mu\text{g L}^{-1}$ ) and Cu content ( $<1000 \mu\text{g L}^{-1}$ ) were exceeded. The limits for the content of Cu, Pb, and Zn ( $<5 \text{mg L}^{-1}$ ) were exceeded in the sample Blaufränkisch, 2019, Vinařství Košulič (Hustopeče, the Czech Republic) with a concentration of Cu  $10000 \mu\text{g L}^{-1}$ , Pb  $4100 \mu\text{g L}^{-1}$  and Zn  $43 \text{mg L}^{-1}$ . In this sample, the permitted limit of Cu was exceeded 10 times, the limit for Pb more than 27 times and for Zn almost nine times. A possible reason for the increased presence of Cu in wine samples might be a high concentration of Cu in the soil and its subsequent transport by the plant into the grapes and by the production process into the wine. Cu, Pb and Zn may come from equipment used for wine production or from fungicides and fertilisers used in the vineyard. The high content of Cu and Zn in wine can harm the colour, aroma and taste of wine. The high content of Pb can have a detrimental effect on the health of consumers.

**Table 5** Statistical determination of measured concentrations for ICP-OES analysis of wine samples [3,5,24]

Element	Content*	WHITE				ROSE				RED			
		MIN	MAX	$\bar{x}$	SD	MIN	MAX	$\bar{x}$	SD	MIN	MAX	$\bar{x}$	SD
K	100–2500	92	1100	510	230	160	670	400	160	250	1800	750	300
Zn	<5 <sup>A</sup>	<0.033 <sup>B</sup>	1.9	0.41	0.31	0.036	0.95	0.33	0.25	<0.033 <sup>B</sup>	43	1.4	6.6
Na	2–250	<0.33 <sup>B</sup>	130	28	24	7.8	28	18	5.4	<0.33 <sup>B</sup>	520	23	75
Mg	50–200	36	140	90	19	58	120	85	17	64	180	100	23
S	400–1000	57	870	290	140	100	800	380	180	70	450	180	99
Fe	0.3–10	0.13	5.1	1.1	0.86	0.21	2.4	0.84	0.57	0.13	3.9	1.0	0.75
Mn	0–50	0.22	1.8	0.78	0.29	0.30	1.2	0.74	0.32	0.41	3.0	0.92	0.47
Ba	0.05–0,35	0.019	0.17	0.068	0.033	0.017	0.11	0.062	0.023	0.015	0.29	0.079	0.051
P	20–1600	40	730	140	80	64	160	110	28	46	280	150	67
Sr	0.2–3	0.14	1.2	0.50	0.21	0.23	0.71	0.47	0.15	0.18	1.3	0.58	0.24
Ca	10–200	15	230	79	23	39	110	76	19	30	110	57	16

\* – common content of element found in wine; MIN – minimum; MAX – maximum;  $\bar{x}$  – arithmetic mean; SD – standard deviation;  
<sup>A</sup> – the limit on the content of the element in wine set by the OIV; <sup>B</sup> – limit of quantification

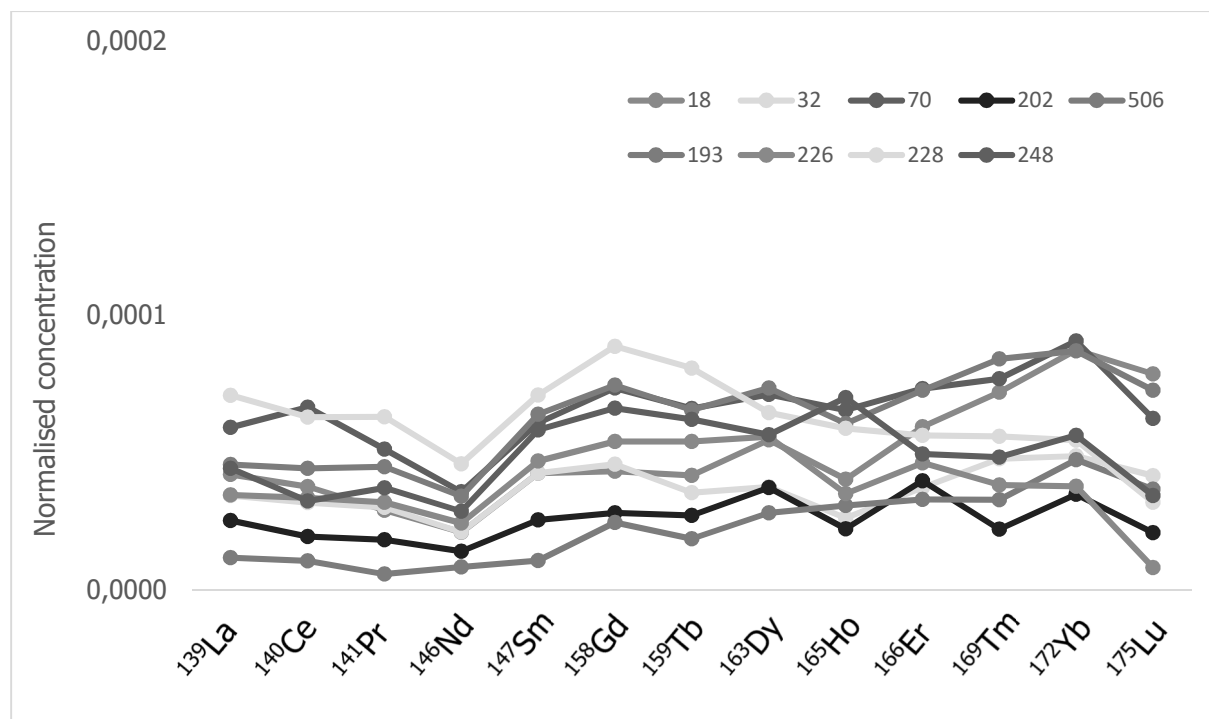
**Table 6** Statistical determination of measured concentrations for ICP-MS analysis of wine samples [3,5,24]

Element	Limit*	WHITE				ROSE				RED			
		MIN	MAX	$\bar{x}$	SD	MIN	MAX	$\bar{x}$	SD	MIN	MAX	$\bar{x}$	SD
Ni	0.1–1 <sup>A</sup>	9.5	120	37	15	24	76	41	13	6.1	400	44	53
Co	1–20 <sup>A</sup>	1.3	12	4.4	1.9	1.8	6.2	3.9	1.4	1.0	4.5	2.8	0.90
Cu	<1000	6.0	1700	130	200	8.2	1200	110	280	5.6	10000	300	1400
As	<200	0.36	22	3.2	2.8	0.59	6.8	2.1	1.5	0.28	8.8	2.0	2.0
Y	–	0.065	14	2.0	2.3	0.11	5.1	1.4	1.4	0.068	2.5	0.53	0.55
Cd	<10	0.063	2.1	0.45	0.29	0.12	0.65	0.32	0.13	0.069	11	0.50	1.5
La	–	0.026	7.9	1.0	1.3	0.060	4.0	0.74	1.1	0.023	2.7	0.34	0.52
Ce	–	<0.010 <sup>B</sup>	15	2.1	2.6	<0.010 <sup>B</sup>	9.9	1.8	2.9	<0.010 <sup>B</sup>	5.0	0.65	1.1
Pr	–	<0.0033 <sup>B</sup>	1.6	0.24	0.31	<0.0033 <sup>B</sup>	0.95	0.23	0.32	<0.0033 <sup>B</sup>	0.56	0.10	0.14
Nd	–	<0.017 <sup>B</sup>	4.8	0.75	0.95	<0.017 <sup>B</sup>	2.8	0.61	0.89	<0.017 <sup>B</sup>	1.6	0.29	0.41
Sm	–	<0.027 <sup>B</sup>	1.5	0.28	0.30	<0.027 <sup>B</sup>	0.94	0.23	0.30	<0.027 <sup>B</sup>	0.39	0.15	0.13
Eu	–	<0.013 <sup>B</sup>	0.53	0.11	0.090	0.016	0.31	0.085	0.078	0.016	0.34	0.095	0.061
Gd	–	<0.013 <sup>B</sup>	1.8	0.29	0.34	<0.013 <sup>B</sup>	0.90	0.21	0.28	<0.013 <sup>B</sup>	0.41	0.10	0.12
Tb	–	<0.0033 <sup>B</sup>	0.31	0.051	0.060	<0.0033 <sup>B</sup>	0.14	0.042	0.046	<0.0033 <sup>B</sup>	0.062	0.027	0.022
Dy	–	<0.013 <sup>B</sup>	2.2	0.32	0.38	<0.013 <sup>B</sup>	0.91	0.21	0.26	<0.013 <sup>B</sup>	0.40	0.11	0.11
Ho	–	<0.010 <sup>B</sup>	0.47	0.085	0.088	<0.010 <sup>B</sup>	0.18	0.072	0.051	<0.010 <sup>B</sup>	0.10	0.033	0.025
Er	–	<0.013 <sup>B</sup>	1.5	0.24	0.27	<0.013 <sup>B</sup>	0.59	0.19	0.17	<0.013 <sup>B</sup>	0.24	0.070	0.070
Tm	–	<0.0033 <sup>B</sup>	0.24	0.046	0.042	<0.0033 <sup>B</sup>	0.081	0.036	0.022	<0.0033 <sup>B</sup>	0.039	0.016	0.012
Yb	–	<0.013 <sup>B</sup>	1.6	0.35	0.31	<0.013 <sup>B</sup>	0.64	0.25	0.19	<0.013 <sup>B</sup>	0.37	0.10	0.093
Lu	–	<0.0033 <sup>B</sup>	0.30	0.064	0.053	<0.0033 <sup>B</sup>	0.10	0.053	0.027	<0.0033 <sup>B</sup>	0.058	0.019	0.016
Pb	<150	2.9	160	23	22	5.0	29	12	6.5	2.6	4100	96	580

\* – the limit on the content of the element in wine set by the OIV; MIN – minimum; MAX – maximum;  $\bar{x}$  – arithmetic mean; SD – standard deviation; <sup>A</sup> – common content of element found in wine; <sup>B</sup> – limit of quantification

## Gadolinium anomaly

This interesting phenomenon was monitored in wine samples. The REE concentrations found were normalised to the PAAS (post-Archean Australian Shale) geological standard [25]. The natural gadolinium content was calculated using the equation:  $Gd_{PAAS-geo} = 0.33 \times Sm_{PAAS} + 0.67 \times Tb_{PAAS}$  [16, 26]. The gadolinium anomaly ( $Gd_{anom}$ ) was further recalculated from the formula:  $Gd_{anom} = Gd_{N-total} / Gd_{N-geo}$  [16,26]. Subsequently, the profile of normalised REE concentrations in selected wine samples was created, which is shown in Figure 1. The specific wine samples used for the graph were selected to simplify visualization. Europium was excluded from the data for the graph due to suspicion of the possibility of a false Europium anomaly. The presence of barium oxide and the formation of light REE can cause significant middle REE interferences, especially isobaric interferences with  $^{151}Eu$  and  $^{153}Eu$  [27,28]. The graph shows no evidence of the gadolinium anomaly.



**Fig. 1** Normalised REE concentrations for selected wine samples

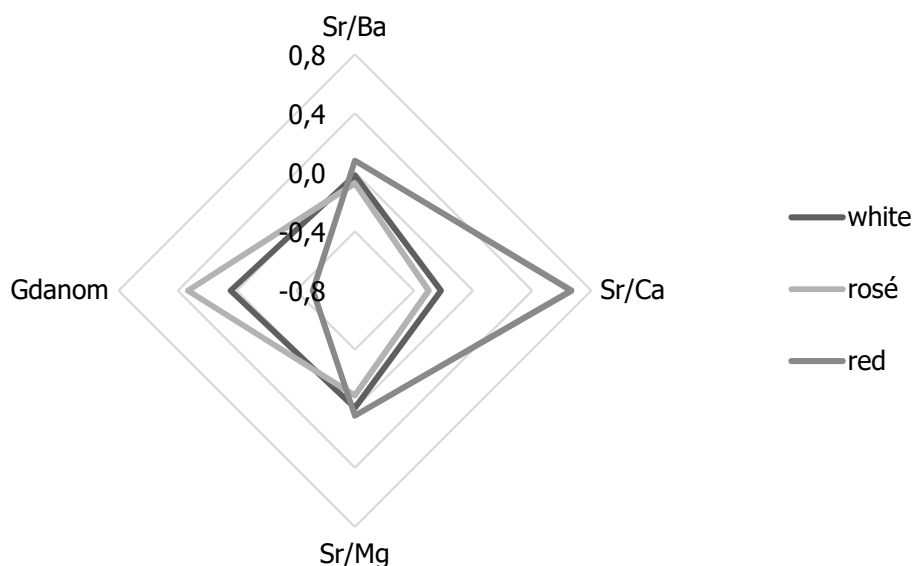
18, 32, 70, 202, 506 – samples of white wines; 193, 226, 228, 248 – samples of red wines

The gadolinium anomaly values in the wine samples ranged from 0.54 to 1.53. According to the literature, the threshold value for determining the gadolinium anomaly is being 1.5 [29]. Proximity to the threshold value was reached by five samples only from the whole set and one sample was found whose gadolinium anomaly value was at the threshold. The concentrations of anthropogenic gadolinium in the samples ranged from 0.0012 to 0.14  $\mu\text{g L}^{-1}$ ;

however, in some samples, anthropogenic gadolinium was not found. Overall, it can be said that anthropogenic gadolinium has been present in the wine samples analysed, but only in an amount that did not exceed the threshold value of the gadolinium anomaly. This phenomenon is an evidence of the intervention of human activity in the gadolinium biochemical cycle. The presence of anthropogenic gadolinium in soil or surface water and wastewater is caused by various sources. Examples are the disposal of household equipment (electronics), over-fertilisation with phosphate fertilisers produced in China or the widespread use of very stable gadolinium-based contrast agents for MRI that enter wastewater through a patient's urine. Subsequently, anthropogenic gadolinium comes into the living organisms from soil and water and enters food chains.

### Element ratios

The Sr/Ba, Sr/Ca, Sr/Mg ratios were calculated according to the study of Šperková and Suchánek, who had dealt with the multidimensional classification of wines from different Czech regions [1]. These ratios were evaluated by the study as one of the best indicators for identifying the origin of wines. The obtained data were standardised using Microsoft Excel. The determined standardised element ratios and gadolinium anomaly are plotted in Figure 2. The Sr/Ca ratio appears to be the most variable and most suitable indicator from the selected ratios for the identification of wine samples, which is illustrated by Figure 2.



**Fig. 2** Observed standardised element ratios and gadolinium anomaly ( $G_{danom}$ ) in wine samples

## Conclusions

In our study, methods for multi-elemental analysis of wine samples using ICP-OES and ICP-MS spectrometers have been developed. These methods were used to determine 32 elements among which were minerals, heavy metals and REEs. The methods' limits of detection were verified and proved to be sufficient for the purpose of the work. Furthermore, the effect of ethanol on the calibration curve was demonstrated. For this reason, the matrix of the calibration standards was modelled by the addition of ethanol and the wine samples were diluted ten times.

The determined range of concentrations of the elements measured in the samples was wide, in the order of a thousandth of  $\mu\text{g L}^{-1}$  to thousands of  $\text{mg L}^{-1}$ . The data was evaluated in terms of mineral and heavy metal content and the work described possible causes of the increased heavy metal contents.

This work has also been determined the element ratios Sr/Ba, Sr/Ca, Sr/Mg as indicators for determining the origin of wines, and the content of anthropogenic gadolinium, including the so-called gadolinium anomaly as evidence of human activities in the environment. Using the gadolinium anomaly as a possible indicator for determining the origin of wines was also shown.

Our methods described herein can be used for multi-elemental analysis of wine samples, for the identification and classification of the origin of wines and the subsequent detection of their possible adulteration and, of course, for the determination of gadolinium anomaly.

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