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МЕТОД ЗА ОДРЕДУВАЊЕ НА СОДРЖИНАТА НА 35 ЕЛЕМЕНТИ ВО РАЗЛИЧНИ ПРИМЕРОЦИ СО ПРИМЕНА НА МИКРОБРАНОВА ДИГЕСТИЈА И ИНДУКТИВНО СПРЕГНАТА ПЛАЗМА СО МАСЕНА СПЕКТРОМЕТРИЈА (ICP-MS)

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Апстракт: Индуктивно спрегната плазма со масена спектрометрија (ICP-MS) и микробранов систем за дигестија беа користени како работни техники за одредување на содржината на 35 елементи (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, Ti, V и Zn) во примероци од масло за јадење, овошје, зеленчук и алкохолни пијалаци. Овој труд опфаќа оптимизација и валидација на условите за мерење на изотопите на елементите во дигестираните примероци. Валидацијата на методата е направена преку определување на границата на детекција и квантификација, линеарноста, мерниот опсег и мерната неодреденост, како и точноста и прецизноста (повторливост и репродуктивност) на мерењата. Испитуваните параметри укажуваат дека методата ги задоволува барањата за предвидената употреба.

Клучни зборови: *елементи, масло за јадење, овошје, зеленчук, алкохолни пијалаци, микробранова дигестија, ICP-MS*.

METHOD FOR DETERMINATION OF 35 ELEMENTS CONTENT IN VARIOUS SAMPLES WITH APPLICATION OF MICROWAVE DIGESTION AND INDUCTIVELY COUPLED PLASMA WITH MASS SPECTROMETRY (ICP-MS)

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Abstract: Inductively coupled plasma with mass spectrometry (ICP-MS) and microwave digestion system were used as working techniques for

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determining the content of 35 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, Ti, V and Zn) in various samples: edible oils, fruits, vegetables and alcoholic beverages. This paper includes optimization and validation of the conditions for measurement of the elements isotopes in prepared samples. Method validation was done using calculation of the limit of detection and quantification, lineary, measurement range and measurement uncertainty, as well as the accuracy and precision of the measurements. The examined parameters indicated that the method meets the requirements for the intended use.

Kew words: *elements, edible oils, fruits, vegetables, alcoholic beverages, microwave digestion, ICP-MS.*

1. Introduction

The objective of any analytical measurement is to obtain consistent, reliable and accurate data [1]. Validated analytical methods play a major role in achieving this goal. The results from method validation can be used to judge the quality, reliability and consistency of analytical results, which is an integral part of any good analytical practice. Validation of analytical methods is also required by most regulations and quality standards that impact laboratories. The objective of validating an analytical procedure is to demonstrate the "suitability for its intended purpose" [1, 2]. The intent of analytical measurement is to generate accurate and reliable data. Method validation alone cannot guarantee this, but it should be part of integrated quality assurance for analytical measurement. Instrument qualification and method validation are equally important. Instrument qualification means that the specifications are defined, tested and confirmed so that the instrument is suitable for the methods to be validated [3]. The analytical methods are then validated on qualified instruments to prove that the method works as intended. This is independent of any specific instrument. If we want to use the method with instruments from different vendors, the method should be validated on those instruments as well. Method validation occurs between analytical instrument qualification and system suitability testing and is linked to all other quality elements. Methods should be validated using qualified instruments [4-6]. During method validation, parameters and acceptance criteria for system suitability checks and quality control checks should be defined.

The main goal of this work was method development and validation of a multi-element analysis of various samples, such as edible oil, fruit and vegetable samples and alcoholic beverages. For that purpose, microwave digestion was applied for total digestion of the samples and inductively coupled plasma with mass spectrometry was used for measurements of the elements contents.

2. Material and methods

2.1. Standards and reagents

The standards for ICP-MS were prepared from multielement stock solution (Periodic table Mix 1 for ICP, 10 mg/L, Sigma Aldrich, Munich, Germany) containing 33 elements (Al, As, Ba, Be, Bi, B, Cd, Ca, Cs, Cr, Co, Cu, Ga, In, Fe, Pb, Li, Mg, Mn, Ni, P, K, Rb, Se, Si, Ag, Na, Sr, S, Te, Tl, V, and Zn). Single-element standards were used for the construction of the calibration curves for Ti, Ge, Sb, Sn, and Mo (10 ppm in 10 % HNO_3 trace select, Sigma Aldrich, Munich, Germany). Spiked solutions were prepared from the stock solution as necessary. Ultrapure nitric acid, HNO_3 (69.0 %, *w/w*, trace select, Sigma Aldrich, Munich, Germany) and hydrogen peroxide H_2O_2 (69.0 %, *w/w*, trace select, Sigma Aldrich, Munich, Germany) were used in a mixture for total digestion of samples. Rhodium standard solution (1 mg/L, Sigma Aldrich, Munich, Germany) was used as an internal standard for correction of the drifts for external calibration curves. Ultrapure water was used (0.065 µS/cm), obtained from water purification system TKA Microlab, ASTM Type II water (Thermo Electron LED GmbH, Germany).

2.2. Microwave-assisted digestion for sample preparation

In this study, five step set or combination of power, pressure, and time conditions for microwave-assisted digestion (Table 1) was tested using two CRMs representing edible oil (CRM-TMSO, soybean oil, High purity standards, Charleston, South Carolina, USA) and aquatic plant (*Lagarosiphon major*) to determine the optimum set of conditions. This method was described for use with 12 microwave vessels simultaneously.

Microwave-assisted digestion conditions involved the digestion of 0.5 g of the CRM with 5 mL HNO_3 and 2 mL of H_2O_2 in the microwave oven. After digestion, the vessels were allowed to cool until the pressure of the vessel was reduced to below 50 psi and temperature was below 40 °C. The caps of each vessel were then carefully removed and the contents were filtered using 2 µm filter paper, diluted to 25 mL in a volumetric flask using deionized water, and stored in polyethylene vial prior to the final determination of the elements' concentration.

Table 1. Microwave digestion program for digestion of oil and wine samples

Step	**Initial *T* (°C)**	**Final *T* (°C)**	**Power (W)**	**Time (min.)**
1	25	150	800	15
2	150	150	800	10
3	150	180	1600	5
4	180	200	1600	10
5	200	200	800	5

2.3. ICP-MS measurements

A standard Agilent 7500cx ICP-MS system with a glass concentric nebulizer was used for all analyses. The instrument was tuned for standard robust plasma conditions (Table 2) and the ORS was operated in helium mode only. This means that all elements were measured under identical helium mode collision conditions and no mode switching was necessary. Furthermore, the helium mode conditions used are generic and do not have to be set up or modified for specific sample matrices. Method parameters are shown in Table 2. In this work an extended sequence of samples simulating the workload in a typical environmental laboratory was analysed repeatedly for more than 10 hours. The samples included high dissolved organic matrix and spikes, dissolved CRM's, and duplicates.

Table 2. Instrument (ICP-MS) tune and acquisition conditions used

Instrument		
Sampler cone	Ni (standard)	
Skimmer cone	Ni (standard)	
Nebulizer	MicroMist (standard)	
Plasma torch	Quartz, 2.5 mm (standard)	
Tune Parameters	**Normal mode**	**He mode**
RF power	1500 W	Same
Sample depth	7.6 mm	Same
Carrier gas	1.00 L/min	Same
Makeup gas	0.25 L/min	Same
Spray chamber temperature	2°C	Same
Extract 1	+6 V	Same
Extract 2	–145 V	Same
Omega bias	-24V	Same
Omega lens	-0.6 V	Same
Cell entrance	-30 V	Same
Energy discrimination	3 V	Same
Cell exit	-30 V	-44 V
Octopole bias	-7 V	-18 V
QP bias	-3.5 V	-14.5 V
Reaction gas	0	4.5 mL/min He
CeO/Ce	0.55%	0.45%
Ce++/Ce	2.08%	1.95%

2.4. Validation procedures

Using calibration solutions calibration curves: $y = ax + b$, were determined, where y is the signal intensity and x is the know concentration of the given analyte in the calibration solution. The *linearity* of the calibration curve was considered acceptable with correlation factor $R > 0.999$.

The *limit of detection* (LOD) is the lowest concentration or quantity of analyte which can be measured with reasonable statistical certainty. To determine the limit of detection 3SD method was used. Ultra-pure water was aspired and signal intensities for blank were recorded. A solution of 10 μg/L multi-element solution was aspired and the signal intensities for the analytes were recorded. The analysis of the blank solution (2 mL H_2O_2 and 5 mL HNO_3, diluted to final volume of 25 mL) for all target elements for 10 times with three repetitions at each measurement was conducted.

The limit of quantification (LOQ) is the lowest concentration that can be quantitatively determined with an acceptable level of repeatability accuracy. The quantification limit is generally considered to be approximately ten times the minimum detection limit. The maximum measurement limit is conditioned by the dynamics of the spectrometer detectors and limited by the requirement that the total amount of the dissolved solid must not exceed 0.2% in the sample solution (unless clogging of the nebulizer nozzels would lead to instabilities and loss of sensitivity). To test the maximum detection limit, a multielement sample of 10 mg/L was used.

The *validated range* is the interval of analyte concentration within which the method can be regarded as validated. While the calibration may cover a wide concentration range, the remainder of the validation (and usually much more important part in terms of uncertainty) will cover a more restricted range. In practice, most methods will be validated at only one or two levels of concentration. The validated range may be taken as a reasonable extrapolation from these points on the concentration scale [1].

Precision was defined as relative standard deviation (RSD) which was calculated as a percentage using the standard deviation divided by the mean of replicated samples.

Repeatability concerns the test results obtained with the same method, on the same sample in the same laboratory, with the same equipment, by the same operator, in short intervals of time.

Reproducibility was expressed as the closeness of agreement between test results obtained with the same method on identical test material analysed from two analysts. *T*-test was used as a statistical parameter for the reproducibility testing [1].

Accuracy was determined by comparing the measured concentration with the certified values and was expressed as percentage recovery R (%). To determine the accuracy, the concentration of elements in the certificate materials described earlier was determined. Also spikes were analysed for the same purpose.

Uncertainty estimation. A laboratory has to demonstrate the quality of the results produced and their fitness to the purpose, by giving an estimate of the confidence that can be associated with the result. All the possible sources of uncertainty have to be carefully identified and taken into account. While measuring the concentrations by ICP-MS with external standard, fluctuations in the measurement of ionic currents occurring as a result of the electrical noise in the detector, instabilities in plasma discharge, instabilities of the electrical parameters of the analyser, lead to uncertainties in the determination of the parameters of the calibration line. Possible errors in the preparation of the calibration solutions increase these uncertainties [1].

3. Results and discussion

All microwave-assisted digestions were performed using CEM model MARS 5 (CEM Corporation, Matthews, NC, USA). The Microwave Accelerated Reaction System (MARS) is designed for laboratory use of digesting, dissolving, hydrolysing, extracting or drying a wide range of materials. Its primary purpose is the rapid preparation of samples for analysis with atomic and mass spectroscopy. This system was designed to hold 12 polytetrafluoroethylene (PTFE) digestion vessels. The digestion vessels had rupture membranes for safe operation under 200 psi. At full power, the MARS delivers approximately 1600 watts of microwave energy at the frequency of 2450MHz.

The elemental analyses were conducted using an Agilent 7500ce inductively coupled plasma mass spectrometer (ICP/MS) AgilentTechnologies, USA). Optimization of the instrument was done as outlined in the Agilent 7500cx user’s manual. This type of ICP-MS is fitted with an octopole reaction-collision cell, operated in collision mode that will minimize the isobaric interferences from polyatomic ions such as oxides (MO^+) that may occur from either the matrix or the plasma through kinetic energy bias [7]. Additionally, this instrument is extremely sensitive, with a very large dynamic range that can measure analytes from the very low ng/L (ppt) level to the upper mg/L range (1000 mg/L) in one run.

3.1. Method validation

The ICP-MS system was optimized under typical tuning conditions for high and variable sample matrices. Table 3 shows the instrumental conditions used for the analyses, including preferred isotope, the tune mode (normal or helium collision) integration time, calibration range and approximate detection limit. The linearity of the calibration curve was acceptable for all of the analysed elements (R>0.999).

Table 3. Limits of detection (LOD), limits of quantifications (LOQ) and linearity of the calibration curves

Element	Isotope	ORS mode	Integration time (*s*)	Linear range (*μ*g/L)	Slope	Intercept	*R*	LOD (*μ*g/L)	LOQ (*μ*g/L)
Li	7	Normal	0.1	0.5-50	0.045	0.023	0.9997	0.042	0.140
Be	9	Normal	0.1	0.5-50	0.010	0.166	0.9960	0.012	0.040
B	11	Normal	0.1	10-1000	0.295	-7.648	0.9989	0.98	3.273
Na	23	Normal	0.1	1000-10000	2.125	391.2	0.9992	8.12	27.12
Mg	24	Normal	0.1	1000-10000	1240	13785	0.9995	5.77	19.27
Al	27	Normal	0.1	10-1000	0.882	19.36	0.9990	1.22	4.075
P	31	Helium	0.5	1000-10000	13455	12963	0.9991	5.96	19.91
K	39	Normal	0.1	1000-10000	35964	40552	0.9995	10.2	34.07
Ca	42	Normal	0.1	1000-10000	1796	3995	0.9991	2.34	7.816
Ti	48	Helium	0.5	1-100	1.36	5.998	0.9996	0.12	0.401
V	51	Normal	0.1	1-50	0.022	0.799	0.9999	0.096	0.321
Cr	53	Helium	0.5	0.5-50	0.024	-0.051	0.9991	0.0063	0.021
Mn	55	Normal	0.1	1-100	1.754	-9.321	0.9993	0.074	0.247
Fe	56	Helium	0.5	1-100	0.55	1.90	1.0000	0.017	0.057
Fe	57	Helium	0.5	1-100	1.25	15.6	1.0000	0.214	0.715
Co	59	Normal	0.1	0.5-50	1.528	-0.724	0.9996	0.0031	0.010
Ni	60	Normal	0.1	0.5-50	0.042	1.33	0.9993	0.0044	0.015
Cu	63	Helium	0.5	1-100	0.66	10.24	0.9991	0.199	0.665
Zn	64	Helium	0.5	1-100	0.322	7.82	0.9995	0.0017	0.006
Ga	69	Normal	0.1	0.5-10	0.037	-0.0059	0.9994	0.013	0.043
Ge	72	Normal	0.1	0.5-10	0.0014	0.0055	0.9990	0.0046	0.015
As	75	Helium	0.5	0.5-50	0.010	0.0022	0.9993	0.0011	0.004
Se	77	Helium	0.5	0.5-50	0.0069	-0.0037	0.9997	0.0019	0.006
Rb	85	Normal	0.1	1-100	1.150	2.483	1.0000	0.10	0.334
Sr	88	Normal	0.1	10-1000	1.680	10.27	0.9995	0.77	2.572
Mo	95	Normal	0.1	0.5-10	0.0079	0.0022	0.9991	0.0033	0.011
Ag	107	Normal	0.1	0.5-50	0.0037	-0.0059	0.9995	0.012	0.040
Cd	111	Normal	0.1	0.5-50	0.021	0.0025	1.0000	0.0044	0.015
Sn	118	Normal	0.1	0.5-10	0.0011	0.00069	0.9994	0.0012	0.004
Sb	121	Helium	0.5	0.5-10	0.038	10.47	0.9998	0.054	0.180
Cs	133	Normal	0.1	0.5-50	0.144	18.59	0.9991	0.13	0.434
Ba	137	Normal	0.1	1-100	0.058	-0.0063	0.9994	0.29	0.969
Hg	202	Helium	0.5	0.5-10	0.617	-0.55	0.9991	0.077	0.257
Tl	205	Normal	0.1	0.5-50	2.019	-5.94	1.0000	0.062	0.207
Pb	206	Normal	0.1	0.5-50	0.023	0.0647	0.9991	0.019	0.063
Pb	207	Normal	0.1	0.5-50	0.019	0.0565	0.9991	0.022	0.073
Pb	208	Normal	0.1	0.5-50	0.048	0.1333	0.9995	0.014	0.047
Bi	209	Helium	0.5	1-100	0.0092	-0.1046	0.9992	0.54	1.804

The precision explains the closeness of agreement between independent test results obtained under prescribed conditions. Precision depends only on the distribution of the random errors and has no relation with the true or specified value. The value of precision (explained through Variation of 10 replica) means that in 95% of the cases, the difference between two values obtained by the method, under the conditions defined, will be lower than or equal to Var-value. For none of the elements the RSD was above 10%. Repeatability was determined with the standard deviation, ranged between 0.029 μg/L for Be and 0.764 3.94 μg/L for Sr and between 0.050 mg/L for Mg and 0.419 mg/L for Ca (Table 4).

Table 4. Precision and repeatability of the measurements (1ppb, 10 ppb and 1 ppm standard solution), N=10

	Unit	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**X**	**Var**	**SD**	***RSD* (%)**
Li	μg/L	1.01	1.11	1.15	1.06	1.01	1.02	1.05	1.10	1.164	1.23	1.09	0.005	0.073	6.65
Be	μg/L	0.98	1.00	0.95	0.97	0.99	1.002	1.01	0.95	0.99	1.05	0.99	0.001	0.029	2.93
B	μg/L	10.1	10.2	10.1	10.5	10.4	10.5	10.1	10.5	10.2	10.5	10.3	0.038	0.196	1.89
Na	mg/L	1.24	1.23	1.07	1.45	1.22	1.09	1.04	1.23	1.14	1.23	1.19	0.014	0.118	9.87
Mg	mg/L	1.05	1.12	0.98	0.99	0.99	1.02	1.01	1.10	0.98	0.99	1.03	0.002	0.050	4.84
Al	mg/L	1.2	1.05	0.99	0.98	1.06	1.10	1.07	0.99	1.02	1.10	1.06	0.004	0.066	6.21
P	mg/L	1.22	0.98	1.11	1.25	1.08	1.15	1.07	1.05	1.11	0.99	1.10	0.007	0.085	7.74
K	mg/L	10.1	10.2	10.2	9.84	9.97	9.85	9.85	10.24	10.1	10.5	10.1	0.051	0.226	2.24
Ca	mg/L	9.57	10.2	10.4	9.88	9.65	10.2	10.6	10.7	9.85	9.87	10.12	0.17	0.419	4.14
Ti	μg/L	10.5	10.2	10.4	10.5	10.9	9.89	10.3	10.4	10.2	10.4	10.4	0.08	0.283	2.72
V	μg/L	10.1	9.79	9.58	10.2	10.4	9.74	9.85	9.52	10.2	10.1	9.97	0.09	0.311	3.12
Cr	μg/L	10.5	10.7	10.9	10.3	9.75	10.3	9.55	9.68	10.2	9.88	10.19	0.22	0.476	4.67
Mn	μg/L	9.63	9.55	10.5	10.6	11.3	9.85	11.2	10.7	10.9	9.68	10.4	0.45	0.674	6.47
^{56}Fe	μg/L	10.2	11.2	11.2	10.5	10.9	10.2	10.7	11.4	10.6	9.95	10.7	0.24	0.491	4.58
^{57}Fe	μg/L	9.87	10.1	10.2	10.4	10.7	11.1	10.8	10.4	10.2	10.4	10.4	0.14	0.376	3.59
Co	μg/L	1.14	0.98	1.14	1.17	1.26	1.08	1.11	1.02	1.06	1.04	1.10	0.007	0.082	7.44
Ni	μg/L	9.87	10.3	10.4	11.4	10.2	10.7	10.2	10.2	11.2	10.4	10.5	0.23	0.480	4.56
Cu	μg/L	10.1	10.5	11.2	9.86	9.74	9.56	9.58	10.2	10.4	11.2	10.2	0.37	0.610	5.95
Zn	μg/L	10.4	11.4	10.5	10.8	9.87	9.85	10.2	10.1	11.2	11.2	10.5	0.33	0.582	5.50
Ga	μg/L	1.11	1.03	1.25	1.09	1.12	1.26	1.01	1.25	1.14	0.99	1.13	0.01	0.100	8.90
Ge	μg/L	0.98	0.95	0.97	1.01	1.08	1.05	1.11	1.12	1.15	0.97	1.04	0.005	0.070	6.71
As	μg/L	1.25	0.97	0.95	1.08	1.07	0.96	0.97	0.97	1.11	1.2	1.06	0.011	0.106	10.0
Se	μg/L	10.4	11.2	10.5	9.58	9.67	9.84	10.54	10.8	10.7	11.1	10.4	0.34	0.589	5.63
Rb	μg/L	11.2	10.5	10.2	10.8	10.4	11.2	11.4	11.4	11.2	10.5	10.9	0.19	0.443	4.05
Sr	μg/L	10.7	11.2	9.87	9.65	10.2	10.1	10.4	11.8	11.7	10.5	10.6	0.58	0.764	7.17
Mo	μg/L	1.45	1.27	1.15	1.1	1.11	1.31	1.16	1.35	1.22	1.25	1.24	0.01	0.112	9.07
Ag	μg/L	0.97	1.05	0.95	0.89	0.94	1.11	1.07	1.06	0.97	0.96	1.00	0.005	0.070	7.06
Cd	μg/L	1.22	1.07	1.05	1.07	1.12	1.19	1.15	1.04	1.09	1.12	1.11	0.004	0.060	5.39
Sn	μg/L	0.95	0.94	0.98	1.04	1.10	1.11	1.05	0.87	0.85	0.9	0.98	0.009	0.093	9.49
Sb	μg/L	1.16	1.23	0.97	1.04	0.96	0.95	1.14	1.2	0.97	0.98	1.06	0.012	0.110	10.3
Cs	μg/L	10.1	10.4	9.58	9.36	10.4	11.2	10.7	10.5	10.9	9.88	10.3	0.34	0.589	5.70
Ba	μg/L	9.45	10.5	10.3	10.74	10.2	9.58	9.75	9.61	9.58	10.4	10.0	0.23	0.479	4.78
Hg	μg/L	1.33	1.25	1.47	1.37	1.24	1.6	1.55	1.24	1.26	1.33	1.36	0.018	0.133	9.73
Tl	μg/L	10.2	10.4	10.3	9.67	9.54	9.36	11.2	10.7	9.84	9.55	10.0	0.36	0.603	5.98
^{206}Pb	μg/L	1.55	1.24	1.32	1.24	1.27	1.44	1.25	1.36	1.1	1.2	1.30	0.016	0.128	9.84
^{207}Pb	μg/L	1.36	1.23	1.25	1.44	1.13	1.1	1.14	1.25	1.13	1.44	1.25	0.016	0.128	10.2
^{208}Pb	μg/L	1.22	1.24	1.25	1.36	1.17	1.28	1.26	1.1	1.23	1.33	1.24	0.005	0.07	5.96
Bi	μg/L	10.2	10.4	10.3	11.6	10.3	11.2	10.2	10.5	10.3	10.4	10.5	0.23	0.48	4.53

N-number of samples measurements, with 3 repetition for each measurement; **X** - mean value; **Var** – Variation; **SD** – standard deviation; ***RSD*** - relative standard deviation.

Reproducibility of the applied method was proved with measurements of the three levels of standard solution with known concentration of elements, independently from two analysts. Not significant differences were assumed between the measurements from both analysts.

Table 5. Reproducibility of the measurements (1 ppb, 10 ppb and 1ppm standard solution), significant differences at p<0.05, N=10

Element	**Unit**	**X_1**	***RSD* (%)**	**X_2**	***RSD* (%)**	***p***	**T**
Li	μg/L	1.07	3.15	1.11	0.58	0.44	-0.85
Be	μg/L	0.98	2.12	1.01	1.22	0.09	-2.19
B	μg/L	10.3	1.05	10.4	1.5	0.47	-0.80
Na	mg/L	1.24	1.14	1.15	2.15	0.31	1.17
Mg	mg/L	1.03	0.44	1.02	3.22	0.88	0.16
Al	mg/L	1.06	5.33	1.06	0.69	0.95	-0.07
P	mg/L	1.13	4.21	1.08	0.78	0.20	1.52
K	mg/L	10.1	1.25	10.1	4.3	0.88	-0.16
Ca	mg/L	10.1	3.45	10.3	3.9	0.06	-2.61
Ti	μg/L	10.6	2.35	10.3	1.7	0.08	2.32
V	μg/L	10.0	1.47	9.89	1.55	0.19	1.59
Cr	μg/L	10.5	1.25	9.92	2.36	0.15	1.75
Mn	μg/L	10.3	2.22	10.5	2.0	0.74	-0.35
^{56}Fe	μg/L	10.8	7.14	10.6	1.1	0.30	1.18
^{57}Fe	μg/L	10.3	1.36	10.6	3.5	0.31	-1.15
Co	μg/L	1.14	5.26	1.06	5.10	0.26	1.32
Ni	μg/L	10.5	3.36	10.6	2.5	0.67	-0.46
Cu	μg/L	10.3	2.25	10.2	6.1	0.86	0.18
Zn	μg/L	10.6	5.69	10.5	2.2	0.88	0.16
Ga	μg/L	1.12	3.61	1.13	4.25	0.82	-0.24
Ge	μg/L	1.00	2.44	1.08	2.11	0.17	-1.68
As	μg/L	1.07	5.77	1.05	1.09	0.77	0.31
Se	μg/L	10.31	5.14	10.6	1.2	0.53	-0.68
Rb	μg/L	10.7	3.26	11.2	1.6	0.10	-2.17
Sr	μg/L	10.3	2.49	11.0	0.8	0.39	-0.96
Mo	μg/L	1.22	1.05	1.26	1.25	0.58	-0.60
Ag	μg/L	0.99	0.84	1.03	0.89	0.25	-1.34
Cd	μg/L	1.11	0.95	1.12	2.65	0.56	-0.64
Sn	μg/L	1.00	1.25	0.96	1.23	0.58	0.61
Sb	μg/L	1.07	4.36	1.05	4.11	0.76	0.32
Cs	μg/L	9.99	1.25	10.7	0.9	0.14	-1.82
Ba	μg/L	10.3	2.77	9.79	1.23	0.15	1.76
Hg	μg/L	1.33	3.04	1.40	4.33	0.57	-0.62
Tl	μg/L	10.0	2.98	10.1	1.6	0.73	-0.37
^{206}Pb	μg/L	1.32	1.25	1.27	2.35	0.19	1.57
^{207}Pb	μg/L	1.28	3.64	1.21	6.23	0.56	0.63
^{208}Pb	μg/L	1.25	3.77	1.24	3.05	0.90	0.14
Bi	μg/L	10.6	1.08	10.6	0.7	0.97	0.04

N-number of samples measurements, with 3 repetition for each measurement; **X_1**-mean value from the first analyst; **X_2**-mean value from the second analyst; ***RSD*** – relative standard deviation; ***p*** - probability value (significant differences at $p<0.05$); **T**- value (T-test for dependent samples).

To confirm the accuracy of the method, two certified reference samples were analyzed repeatedly (BCR-060: Aquatic plant (*Lagarosiphon major*) and CRM-TMSO (soybean oil). Each sample was measured multiple times over the sequence and the mean concentration, percent relative standard deviation (*% RSD*), and mean recovery were calculated for each analyte (Table 6).

Table 6. Determined accuracy using certified reference materials, N=10

Element	**BCR-060 ^{a}** (mg/kg)	**BCR-060 ^{b}** (mg/kg)	***RSD*** (%)	***R*** (%)	**CRM-TMSO ^{a}** (mg/kg)	**CRM-TMSO ^{b}** (mg/kg)	***RSD*** (%)	***R*** (%)
B	25	24.3	1.2	97	/	/	/	/
Na*	9	9.81	1.7	109	/	/	/	/
Mg*	10	11.3	0.7	113	100	92.3	1.5	92
Al	4180	4057	2.6	97	/	/	/	/
P*	11.8	10.6	2.2	90	100	88.9	2.8	89
K*	13.7	14.2	0.6	104	/	/	/	/
Ca*	43.3	45.1	1.5	104	100	94.5	1.4	95
V	6	5.32	0.8	88	/	/	/	/
Cr	26	27.3	1.3	105	/	/	/	/
Mn	1760	1675	1.5	95	/	/	/	/
$^{56/57}$Fe	/	/	/	/	100	107.8	2.3	108
Co	4	3.70	1.3	93	/	/	/	/
Ni	40	38.6	1.1	97	100	109.3	1.4	109
Cu	51.2	52.4	2.7	102	100	89.6	0.9	90
Zn	313	317.8	1.5	102	100	92.3	1.1	92
As	8	9.34	1.9	116	/	/	/	/
Se	0.7	0.59	0.7	84	/	/	/	/
Rb	23	22.7	2.6	99	/	/	/	/
Mo	2	2.31	2.1	115	/	/	/	/
Ag	0.2	0.22	1.8	110	100	90.7	2.7	91
Cd	2.2	2.27	0.6	103	/	/	/	/
Sn	6	5.60	1.3	93	/	/	/	/
Sb	0.4	0.34	1.9	85	/	/	/	/
Cs	0.4	0.42	1.2	105	/	/	/	/
Hg	0.34	0.31	2.5	91	/	/	/	/
Tl	0.24	0.25	0.7	104	/	/	/	/
$^{206/207/208}$Pb	64	66.1	1.3	103	100	101.2	4.1	101

N-number of samples measurements, with 3 repetition for each measurement; **a –** certified value; **b** – measured value with the applied method; ***R*** – mean recovery; ***RSD*** – relative standard deviation; ***** - data are given for mass fraction of elements oxides: CaO, MgO, Na_2O, P_2O_5, K_2O in g/kg.

Along with the above CRMs, Matrix Spike (MS) CRMs and Matrix Spike Duplicates (MSD) CRMs spiked at the calibration midpoint (10 ppb for trace elements, 1 ppm and 10 ppm for mineral elements (Na, Mg, K, P, Ca, Al and Fe), and 1 ppb for Hg) were analyzed periodically, interspersed with the other samples throughout the sequence. No matrix matching of the calibration standards and blanks to these samples was required, as the octopole collision cell effectively eliminates matrix suppression by ensuring very high temperature robust plasma conditions (around 0.2% CeO/Ce ratio in He mode). All elements met the limits of 80% to 120% recovery for matrix spikes with satisfactory accuracy.

Optimized and validated method was applied on analysis of various matrixes: edible oil (sunflower cold-pressed oil), vegetables (tomato), fruits (apple) and alcoholic beverages (brandy). Results are presented in Tables 7, 8, 9 and 10, respectively.

Table 7. Spike recoveries and matrix spike (MS)/matrix spike duplicate (MSD) for oil samples (sunflower cold- pressed oil), N=25

Element	**Unit**	**Matrix mean**	***RSD*** **(%)**	**Matrix spike (MS) mean**	***RSD*** **(%)**	**Spike**	***R*** **(%)**
Li	μg/kg	<LOD	2.19	10.2	1.02	10	102
Be	μg/kg	<LOD	1.23	9.89	3.25	10	98.9
B	μg/kg	0.89	1.15	12.6	1.14	10	117
Na	mg/kg	1.025	0.88	2.01	0.75	1	99.0
Mg	mg/kg	2.85	1.28	3.79	1.25	1	94.2
Al	mg/kg	0.78	1.00	1.82	3.12	1	104
P	mg/kg	4.52	1.36	5.45	2.25	1	93.1
K	mg/kg	1.32	0.75	2.41	2.01	1	108
Ca	mg/kg	0.58	2.45	1.70	1.55	1	112
Ti	mg/kg	0.23	3.18	1.35	1.26	1	112
V	μg/kg	4.9	0.66	15.6	1.12	10	107
Cr	μg/kg	73.2	0.95	82.3	1.1	10	91.5
Mn	μg/kg	62.3	1.12	73.5	1.07	10	112
Fe	mg/kg	0.87	1.55	2.01	0.88	1	114
Co	μg/kg	2.3	1.36	13.5	0.75	10	112
Ni	μg/kg	78	1.75	88.7	0.45	10	107
Cu	μg/kg	140	1.78	149	0.9	10	95.1
Zn	μg/kg	35.4	1.05	44.2	1.02	10	88.5
Ga	μg/kg	15.2	0.88	25.3	1.07	10	101
Ge	μg/kg	9.25	2.16	20.1	1.44	10	108
As	μg/kg	<LOD	4.36	9.21	1.52	10	92.1
Se	μg/kg	<LOD	1.25	8.87	1.58	10	88.7
Rb	μg/kg	8.75	2.15	20.1	2.54	10	113
Sr	μg/kg	124	3.78	133	1.33	10	93.6
Mo	μg/kg	7.42	2.41	18.5	1.44	10	110
Ag	μg/kg	<LOD	0.55	8.75	1.65	10	87.5
Cd	μg/kg	<LOD	1.06	10.4	2.28	10	104
Sn	μg/kg	27.3	1.15	36.6	1.33	10	93.3
Sb	μg/kg	<LOD	1.89	9.15	2.14	10	91.5
Cs	μg/kg	35.7	1.24	45.5	2.25	10	98.3
Ba	μg/kg	88.1	0.55	96.8	1.47	10	87.5
Hg	μg/kg	<LOD	0.7	0.88	2.22	1	87.7
Tl	μg/kg	49.3	1.66	60.1	2.32	10	108
Pb	μg/kg	<LOD	1.78	8.69	2.25	10	86.9
Bi	μg/kg	<LOD	0.99	9.11	1.06	10	91.1

N-number of samples measurements, with 3 repetition for each measurement; ***R*** – mean recovery; ***RSD*** – relative standard deviation.

Table 8. Spike recoveries and matrix spike (MS)/matrix spike duplicate (MSD) for fruit sample (apple fruit), N=30

Element	**Unit**	**Matrix mean**	***RSD*** **(%)**	**Matrix spike (MS) mean**	***RSD*** **(%)**	**Spike**	***R*****(%)**
Li	μg/kg	<LOD	0.45	9.15	1.56	10	91.5
Be	μg/kg	<LOD	1.22	11.1	1.36	10	111
B	μg/kg	85.2	1.47	96.4	2.14	10	112
Na	mg/kg	5.78	1.69	15.2	1.08	10	94.5
Mg	mg/kg	35.9	2.77	44.7	1.16	10	88
Al	mg/kg	0.15	2.81	9.18	1.47	10	90.3
P	mg/kg	61.2	0.66	70.5	2.45	10	93.5
K	mg/kg	25.3	0.89	33.4	2.19	10	81
Ca	mg/kg	15.2	0.92	23.4	3.05	10	82
Ti	mg/kg	0.22	1.35	11.5	4.12	10	112
V	μg/kg	2.66	1.99	13.8	2.1	10	111
Cr	μg/kg	1.63	1.41	10.9	1.55	10	92.7
Mn	μg/kg	85	0.95	96.8	1.17	10	118
Fe	mg/kg	0.33	0.74	8.57	1.96	10	82.4
Co	μg/kg	8.9	0.66	19.6	2.05	10	107

Ni	μg/kg	1.35	1.25	10.8	3.47	10	95.2
Cu	μg/kg	105	0.91	114	1.01	10	92
Zn	μg/kg	5.1	0.55	15.5	1.55	10	104
Ga	μg/kg	1.15	3.45	9.87	1.06	10	87.2
Ge	μg/kg	2.45	2.18	11.2	0.89	10	87.5
As	μg/kg	<LOD	5.17	10.23	1.33	10	102
Se	μg/kg	<LOD	2.36	9.55	0.78	10	95.5
Rb	μg/kg	121	0.55	132	0.98	10	112
Sr	μg/kg	243	0.44	251	1.25	10	81
Mo	μg/kg	6.59	1.9	15.6	3.29	10	90.1
Ag	μg/kg	<LOD	3.22	8.62	1.99	10	86.2
Cd	μg/kg	<LOD	4.19	9.11	2.67	10	91.1
Sn	μg/kg	<LOD	2.45	10.3	5.14	10	103
Sb	μg/kg	<LOD	1.36	11.2	2.15	10	112
Cs	μg/kg	10.5	0.88	20.3	3.12	10	98
Ba	μg/kg	244	0.95	255	1.88	10	113
Hg	μg/kg	<LOD	1.56	0.92	1.65	1	92.3
Tl	μg/kg	<LOD	2.45	8.77	0.87	10	87.7
Pb	μg/kg	<LOD	3.17	9.15	0.55	10	91.5
Bi	μg/kg	1.2	1.02	10.6	1.33	10	94

N-number of samples measurements, with 3 repetition for each measurement; ***R*** – mean recovery; ***RSD*** – relative standard deviation.

Table 9. Spike recoveries and matrix spike (MS)/matrix spike duplicate (MSD) for vegetable sample (tomato) N=22

Element	**Unit**	**Matrix mean**	***RSD*** **(%)**	**Matrix spike (MS) mean**	***RSD*** **(%)**	**Spike**	***R*****(%)**
Li	μg/kg	0.8	2.55	10.7	3.21	10	99
Be	μg/kg	<LOD	1.62	9.85	1.55	10	98.5
B	μg/kg	46.3	1.08	55.2	1.56	10	89
Na	mg/kg	79.5	1.44	87.9	1.12	10	84
Mg	mg/kg	450	0.78	461	0.95	10	112
Al	mg/kg	150	0.96	158.9	1.7	10	89
P	mg/kg	648	3.45	656	2.26	10	85
K	mg/kg	552	3.66	562	1.44	10	103
Ca	mg/kg	89.3	2.78	97.4	1.23	10	81
Ti	μg/kg	10.2	2.22	19.6	0.47	10	93.8
V	μg/kg	<LOD	1.05	11.5	0.99	10	115
Cr	μg/kg	0.8	1.19	9.8	4.2	10	90.2
Mn	μg/kg	89.6	0.55	98.66	1.61	10	90.6
Fe	mg/kg	0.582	1.49	9.66	2.14	10	90.7
Co	μg/kg	1.12	3.26	12.3	1.06	10	112
Ni	μg/kg	<LOD	4.25	8.78	4.11	10	87.8
Cu	μg/kg	13.5	2.09	24.5	2.55	10	110
Zn	μg/kg	124	1.34	133.1	3.08	10	91.3
Ga	μg/kg	<LOD	1.1	9.12	3.11	10	91.2
Ge	μg/kg	<LOD	0.85	10.5	1.02	10	105
As	μg/kg	<LOD	2.64	8.66	1.11	10	86.6
Se	μg/kg	0.2	1.25	10.7	1.47	10	105
Rb	μg/kg	122	1.46	134	0.88	10	120
Sr	μg/kg	184	1.92	195.2	0.65	10	112
Mo	μg/kg	19.0	0.86	27.8	0.78	10	88.1
Ag	μg/kg	<LOD	4.55	9.05	1.02	10	90.5
Cd	μg/kg	0.04	2.73	10.2	1.55	10	101
Sn	μg/kg	<LOD	1.26	8.65	1.36	10	86.5
Sb	μg/kg	<LOD	0.85	9.34	1.11	10	93.4
Cs	μg/kg	1.23	0.69	12.3	1.28	10	110
Ba	μg/kg	62.3	1.1	73.5	0.96	10	115
Hg	μg/kg	<LOD	1.45	0.853	1.25	1	85.3
Tl	μg/kg	<LOD	136	11.2	2.36	10	112
Pb	μg/kg	0.056	0.77	9.63	3.55	10	95.7
Bi	μg/kg	0.87	3.44	12.5	1.28	10	116.3

N-number of samples measurements, with 3 repetition for each measurement; **R** – mean recovery; **RSD** – relative standard deviation.

Table 10. Spike recoveries and matrix spike (MS)/matrix spike duplicate (MSD) for grape brandy, N=10

Element	Unit	Matrix mean	*RSD* (%)	Matrix spike (MS) mean	*RSD* (%)	Spike	*R* (%)
Li	μg/L	0.16	2.33	10.2	1.69	10	100
Be	μg/L	<LOD	3.15	8.67	2.03	10	86.7
B	μg/L	36.3	1.29	45.5	2.66	10	92
Na	mg/L	6.08	0.78	7.24	0.59	1	116
Mg	mg/L	1.15	0.56	2.33	1.23	1	118
Al	mg/L	0.21	2.13	1.15	1.04	1	94
P	mg/L	9.63	1.00	10.48	2.13	1	85
K	mg/L	22.7	1.25	23.57	2.22	1	87
Ca	mg/L	5.66	1.63	6.58	0.78	1	92
Ti	μg/L	55.4	1.04	63.7	0.59	10	83
V	μg/L	0.33	2.44	10.17	0.63	10	98.4
Cr	μg/L	1.25	3.58	10.5	1.54	10	92.5
Mn	μg/L	56.4	3.66	64.8	1.96	10	84
Fe	mg/L	0.34	2.14	9.48	1.58	10	91.4
Co	μg/L	0.28	0.77	8.75	1.30	10	84.7
Ni	μg/L	5.17	1.99	16.3	0.55	10	111
Cu	mg/L	1.28	2.68	10.65	1.47	10	93.7
Zn	μg/L	10.2	3.45	19.34	3.55	10	91.1
Ga	μg/L	0.24	4.11	9.25	4.23	10	90.1
Ge	μg/L	<LOD	2.96	8.75	1.28	10	87.5
As	μg/L	0.078	1.08	9.12	1.46	10	90.4
Se	μg/L	<LOD	2.33	11.08	0.96	10	111
Rb	μg/L	4.87	1.14	15.2	0.88	10	103
Sr	μg/L	25.6	1.57	33.87	1.35	10	82.4
Mo	μg/L	1.44	0.86	10.27	2.45	10	88.3
Ag	μg/L	0.16	0.77	9.66	1.32	10	95
Cd	μg/L	0.057	1.65	9.04	1.14	10	89.8
Sn	μg/L	<LOD	3.58	10.24	3.55	10	102
Sb	μg/L	<LOD	2.65	9.25	2.60	10	92.5
Cs	μg/L	1.72	3.46	11.24	1.29	10	95.2
Ba	μg/L	105	2.55	117	1.11	10	120
Hg	μg/L	<LOD	1.02	1.17	0.58	1	117
Tl	μg/L	0.14	1.11	9.17	1.44	10	90.3
Pb	μg/L	1.12	1.37	12.3	2.55	10	112
Bi	μg/L	1.95	2.65	10.32	1.24	10	83.7

N-number of samples measurements, with 3 repetition for each measurement; ***R*** – mean recovery; ***RSD*** – relative standard deviation.

4. Concluding remarks

Multi-element determination method for sample preparation followed with ICP-MS for analysis of edible oils, vegetables, fruits and alcoholic beverages was optimized and developed. The method presented satisfactory linearly, LOD, LOQ, accuracy, repeatability, and reproducibility for total 35 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, Ti, V and Zn).

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