Determination of Trace Metals in Typical Edible Oils by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS)

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Introduction

Edible oil is an essential part of our daily diet. Trace metals in edible oils are important to determine in terms of food safety, nutrition, and oil storability. Metals like As, Cd, Cr, Pb, and Hg are toxic and should be eliminated from edible oils. Other metals like Fe, Cu, Co and Mn can increase the rate of oil oxidation, and have deleterious effects on their shelf lives. Trace metals in edible oils might come from water, soil, environment, fertilizer, pesticide, or be introducing during the production process or by contamination from the metal processing equipment.

In this work, we explore and discuss the applicability of the Shimadzu inductively coupled plasma – mass spectrometer 2030 (Shimadzu ICPMS-2030) to the qualification and quantification of 17 different metals in typical edible oils.

Experimental

Sample Preparation

- Method was developed for 17 target elements.

Aluminum (Al)	**Arsenic (As)**	**Barium (Ba)**	**Calcium (Ca)**	**Cadmium (Cd)**	**Cobalt (Co)**
Chromium (Cr)	**Copper (Cu)**	**Iron (Fe)**	**Mercury (Hg)**	**Potassium (K)**	**Magnesium (Mg)**
Manganese (Mn)	**Lead (Pb)**	**Antimony (Sb)**	**Vanadium (V)**	**Zinc (Zn)**	

- Nine oils were selected as representative of edible oil product, including vegetable oil, olive oil, canola oil, corn oil, avocado oil, almond oil, sesame oil, sunflower oil and peanut oil.
- Approximately 500 mg of each sample was weighted into a sealed Teflon™ reaction vessel that contained 5 mL of 70% HNO_3 and 2 mL of ultrapure water. The sample was then digested with a Multiwave GO microwave digestion system (Anton Par Inc.) using Organic A method: ramp time of 20 min to 180 °C and hold time of 10 min before cooling down. A blank sample consisting only of the reagents was also prepared for quality control.
- Fortified samples were prepared by spiking 0.2 mL stock standard solution into the reaction vessels before digestion to confirm the quantitative recovery of the analytes. Because the matrices usually have high amounts of common mineral elements like Al, Cu, Zn, Fe, Ca, K and Mg, and low amounts of other target elements, stock standard solution was prepared to contain elements at different levels of concentrations such that different elements can be calibrated and spiked at different ranges. The stock standard solution contains 50 ppm of K and Mg, 10 ppm of Fe and Ca, 2 ppm of Al, Cu and Zn as well as 1 ppm of other target elements.
- Digested samples were diluted to contain 5% HNO_3 before measurements. Calibration standards also contained 5% HNO_3 for matrix match.

Instrumentation

- Digested diluted samples were analyzed with a Shimadzu inductively coupled plasma – mass spectrometer 2030 coupled with a CETAC ASX-280 and a *ASXPress Plus* rapid sample introduction accessory.
- The ICPMS system was configured with the standard sample introduction system consisting of a coaxial glass nebulizer, a cyclone spray chamber, and a mini-torch. The interface consists of a copper sampling cone and a copper skimmer cone. The ICPMS is equipped with a collision cell that uses helium (He) to discriminate polyatomic interferences based on kinetic energy. Data were collected with He gas on to minimize the polyatomic interferences. Table 1 lists the operating conditions used for the ICPMS-2030. Analytical elements and their corresponding measurement parameters are listed in Table 2.
- The *ASXpress plus* rapid sample introduction accessory reduces time required for autosampler movement, sample uptake, stabilization, and rinse operations, thereby reducing sample run times significantly. In the current study, the total analysis time was reduced by 30%, greatly improving sample throughput.
- The ICPMS-2030 was automatically tuned to adjust torch position, lens voltage and mass resolution to optimize the signal intensity. The LabSolutions ICPMS software also collects screening data across the entire mass range from 5-260 m/z, referred to as Total Mass Scan. The function of Total Mass Scan can provide mass spectra in the entire mass range to help identify possible interference when post-processing the measurement data.
- Scandium (Sc), indium (In) and bismuth (Bi) were selected as internal standard elements to cover the entire mass range. The internal standard solution was added to the calibration standards and samples using an internal standard automatic addition kit, which utilizes a T-shaped glass tube and a peristatic pump for mixing the analysis sample with the internal standard sample and introducing the mixture to the nebulizer.

Table 1. Operating conditions of Shimadzu ICPMS-2030

Parameter	Setting	Parameter	Setting
Radio Freq. Power	1.20 kW	Mix Gas	0.00 L/min
Sampling Depth	5.0 mm	Cell Gas	6.0 mL/min
Plasma Gas	8.0 L/min	Cell Voltage	-21 V
Auxiliary Gas	1.10 L/min	Energy Filter	7.0 V
Carrier Gas	0.70 L/min	Chamber Temp.	5 °C

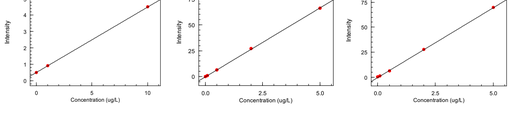
Table 2. Analytical elements and their corresponding measurement parameters

Element[a]	Mass	Internal Standard	Calibration Range (µg/L)	Correction coefficient R^2	Instrument Detection limit (µg/L)	Instrument LOQ (µg/L)	Spiked Concentration (µg/L)[b]	RSD[c]
Al	27	Sc (45)	0.2 - 10	0.9976	0.417	1.39	4	4.25
As	75	Sc (45)	0.1 - 5	0.9999	0.007	0.023	2	4.52
Ba	138	In (115)	0.1 - 5	0.9999	0.006	0.020	2	2.46
Ca	44	Sc (45)	1 - 50	0.9962	7.96	26.5	20	6.73
Cd	116	In (115)	0.1 - 5	0.9932	0.352	1.175	2	0.67
Co	59	Sc (45)	0.1 - 5	0.9999	0.001	0.002	2	4.89
Cr	52	Sc (45)	0.1 - 5	0.9999	0.021	0.070	2	4.29
Cu	65	Sc (45)	0.2 - 10	0.9960	3.86	12.9	4	3.93
Fe	56	Sc (45)	1 - 50	0.9999	0.286	0.953	20	2.97
Hg	202	Bi (209)	0.1 - 5	0.9981	0.0637	0.212	2	1.10
K	39	Sc (45)	5 - 250	0.9983	14.0	46.7	100	4.88
Mg	24	Sc (45)	5 - 250	0.9999	0.248	0.827	100	4.45
Mn	55	Sc (45)	0.1 - 5	0.9999	0.005	0.017	2	3.51
Pb	208	Bi (209)	0.1 - 5	0.9999	0.006	0.021	2	1.13
Sb	121	In (115)	0.1 - 5	0.9995	0.009	0.032	2	1.16
V	51	Sc (45)	0.1 - 5	0.9999	0.001	0.005	2	1.77
Zn	68	Sc (45)	0.2 - 10	0.9998	0.497	1.66	4	3.55

a. For all elements, integration time is 4 sec, No. of Scan 10, Repeat No. 3, helium cell gas on;
b. Spiked concentration is the spiked concentrations of different elements in the final measurement solutions after dilution;
c. Relative standard deviation for the highest calibration standard used.

Calibration

- Calibration curves for the target elements are shown in Figure 1. All of the calibration curves show excellent linearity across the respective calibration range.



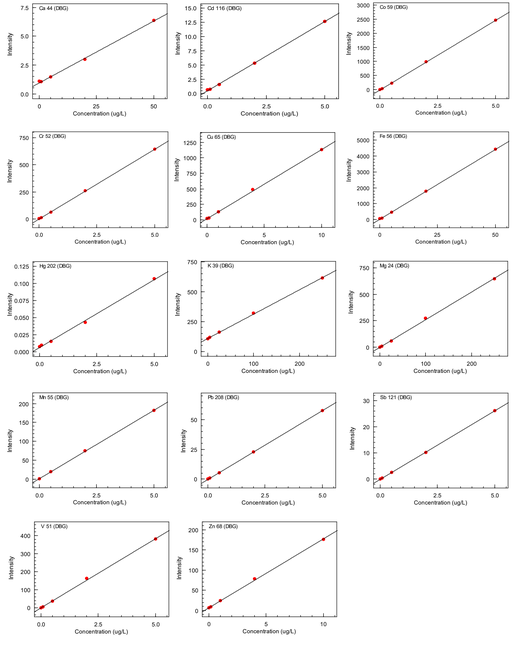


Figure 1. Calibration curves for 17 target elements.

Results and Discussion

- All of the nine different edible oils were completely decomposed, leaving clear solutions after digestion.
- Table 3 shows the concentrations of elements in ppb in digested solutions of original and fortified samples for nine different edible oils as well as blank sample. All of the target elements are below the detection limit for the blank sample.
- Most of relative standard deviations (RSD) are below 5, except the one highlighted in red in Table 2, indicating the high precision of the Shimadzu ICPMS-2030. All spiked recoveries were within ±10% of the added amounts, further validating the methodology and the accuracy of the Shimadzu ICPMS-2030.
- Table 4 shows concentrations of target elements in raw materials. All edible oils contain high amounts of Al, low level of As, and negligible amounts of Cd, Co, Cr, Cu, Hg, and Sb. High level of Ca also presents in most of edible oils, indicating edible oil is a good source of Ca.

Table 3. Concentrations of elements in ppb in digested solutions of original and fortified samples as well as recovery yields in percent

	^{27}Al	^{75}As	^{138}Ba	^{44}Ca	^{116}Cd	^{59}Co	^{52}Cr	^{65}Cu	^{56}Fe	^{202}Hg	^{39}K	^{24}Mg	^{55}Mn	^{208}Pb	^{121}Sb	^{51}V	^{68}Zn
Blank	n.d.	0.0099	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fortified blank	3.84	1.88	1.96	21.0	1.87	1.94	1.88	3.62	18.7	1.81	101	99.9	1.86	1.97	1.96	1.94	3.83
Recovery (%)	96	94	98	105	94	97	94	91	94	91	101	100	93	99	98	97	96
Almond oil	1.29	0.0153	0.132	10.2	n.d.	n.d.	n.d.	n.d.	4.38	n.d.	n.d.	n.d.	0.0717	n.d.	n.d.	n.d.	n.d.
Fortified almond oil	5.09	2.07	2.04	30.0	1.99	2.00	2.02	4.17	25.9	2.19	97.6	103	2.08	1.94	2.16	2.05	4.37
Recovery (%)	95	103	95	99	100	100	101	104	108	110	98	103	100	97	108	103	109
Avocado oil	0.508	0.0132	n.d.	6.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.0489	0.0122	n.d.	n.d.	n.d.
Fortified avocado oil	4.48	2.01	1.87	26.9	1.95	2.09	2.03	3.73	20.5	2.19	102	107	2.01	1.93	2.12	2.07	4.39
Recovery (%)	99	100	94	104	98	105	102	93	103	110	102	107	98	96	106	104	110
Canola oil	1.67	0.0203	n.d.	11.1	n.d.	n.d.	n.d.	n.d.	1.13	n.d.	n.d.	n.d.	0.057	0.0166	n.d.	n.d.	n.d.
Fortified canola oil	5.93	2.09	1.85	29.6	1.81	1.99	1.93	3.61	20.1	2.11	100	102	1.99	1.98	2.01	1.99	3.94
Recovery (%)	107	103	93	93	91	100	97	90	95	106	100	102	97	98	101	100	99
Corn oil	0.459	0.0117	n.d.	5.74	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fortified corn oil	4.59	2.01	1.93	24.3	1.96	2.01	2.04	3.77	20.6	2.01	97	105	2.03	2.00	2.03	2.02	4.39
Recovery (%)	103	100	97	93	98	101	102	94	103	101	97	105	102	100	102	101	110
Peanut oil	0.977	0.0123	n.d.	4.78	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.025	n.d.
Fortified peanut oil	5.34	2.18	1.93	26.8	1.98	2.17	2.13	4.05	21.7	1.83	109	110	2.15	1.99	2.04	2.19	4.39
Recovery (%)	109	108	97	110	99	109	107	101	109	92	109	110	108	100	102	108	110
Vegetable oil	0.332	0.0119	n.d.	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	2.12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fortified vegetable oil	3.95	2.1	1.98	29.8	1.94	1.96	1.89	3.89	18.9	1.83	98.1	111	1.89	2.06	2.14	1.96	4.23
Recovery (%)	90	104	99	99	97	98	95	97	95	92	98	109	95	103	107	98	106
Sesame oil	1.20	0.0114	0.261	15.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.06	n.d.	0.0358	n.d.	n.d.	n.d.
Fortified sesame oil	5.53	2.15	2.24	34.2	2.09	2.02	2	4.11	19.6	2.09	93.0	115	2.19	2.09	2.18	2.07	4.32
Recovery (%)	108	107	99	92	105	101	100	103	98	105	93	109	110	103	109	104	108
Sunflower oil	0.689	0.0106	0.47	34.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.60	0.327	n.d.	n.d.	n.d.	n.d.
Fortified sunflower oil	4.28	2.16	2.65	54.8	2.18	2.04	2.07	4.26	18.4	2.05	105	110	2.43	2.16	2.14	2.13	4.32
Recovery (%)	90	107	109	102	109	102	104	107	92	103	105	105	105	108	107	107	108
Olive oil	1.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.165	0.573	10.4	n.d.	n.d.	n.d.	n.d.	n.d.	0.147
Fortified olive oil	5.26	1.98	2.05	21.5	2.07	1.99	1.96	4	19.7	2.41	110	97.6	1.85	2.05	2.16	1.91	4.21
Recovery (%)	106	99	103	108	104	100	98	100	98	92	100	98	93	103	108	96	102

Table 4. Concentrations of elements (in µg/kg matrix) for raw materials, back-calculated for dilution and ~500 mg initial mass of matrices

	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn	Pb	Sb	V	Zn
Almond oil	256	3.04	26.2	2.03E+3	n.d.	n.d.	n.d.	n.d.	871	n.d.	n.d.	n.d.	14.3	n.d.	n.d.	n.d.	n.d.
Avocado oil	98.8	2.57	n.d.	1.18E+3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.51	2.37	n.d.	n.d.	n.d.
Canola oil	330	4.01	n.d.	2.19E+3	n.d.	n.d.	n.d.	n.d.	223	n.d.	n.d.	n.d.	11.3	3.28	n.d.	n.d.	n.d.
Corn oil	91.6	2.33	n.d.	1.15E+3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Peanut oil	189	2.38	n.d.	924	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.83	n.d.
Vegetable oil	66.3	2.38	n.d.	2.00E+3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	424	n.d.	n.d.	n.d.	n.d.	n.d.
Sesame oil	241	2.29	52.4	3.17E+3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.22E+3	n.d.	7.19	n.d.	n.d.	n.d.
Sunflower oil	138	2.12	94.2	6.91E+3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	922	65.5	n.d.	n.d.	n.d.	n.d.
Olive oil	203	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	32.6	113	2.05E+3	n.d.	n.d.	n.d.	n.d.	n.d.	29.0

Conclusions

- Complex matrices of edible oil products can be digested with microwave digestion system, and analyzed with the Shimadzu ICPMS-2030 to assess the levels of metals.
- Shimadzu ICPMS-2030 coupled with CETAX ASX-280 autosampler and *ASXPress Plus* rapid sample introduction accessory provides excellent sensitivity, precision, accuracy, tolerance, fast time response and high sample throughput for determination of multiple elements in complex matrices.

References

- "Practical Guide to ICP-MS", Robert Thomas , Marcel Dekker, Inc.