Direct Measurement of Trace Metals in Edible Oils by 7500cx ICP-MS with Octopole Reaction System

Application Note

Foods

Author

Glenn Woods
ICP-MS Specialist
Agilent Technologies UK Ltd.
Lakeside Business Park
Cheadle Royal Cheshire SK8 3GR
United Kingdom

Abstract

A simple methodology for the measurement of trace and ultratrace metals in edible oils is described. A selection of seed, olive, and nut oils were measured with a spike recovery being performed on a rapeseed oil – recoveries of between 94% (Ag) and 107% (Sn) were achieved. Each sample was analyzed directly using an Agilent 7500cx ICP-MS with Octopole Reaction System (ORS) technology following a simple 3x dilution in kerosene. The ORS is used to remove plasma- and matrix-based interferences within a single acquisition, greatly improving the detection limit performance for the interfered-with elements, such as Cr, Fe, and Mg. The detection limits (DLs) and background equivalent concentrations (BECs) were in the µg/kg (ppb) to ng/kg (ppt) range for all elements. An 8½-hour stability run on a spiked (~12 µg/kg) rapeseed oil was performed and precision was found to be approximately 2% RSD for all elements except Na (4%), which was partially influenced by contamination.

Agilent Technologies

Introduction

Edible oils form an essential part of our daily diet. They are used in their native form for high-temperature cooking (for example, frying); as an ingredient for texture, flavor, and nutritional improvers; and as flavor carriers for other ingredients. Edible oils also have very wide usage as a processed foodstuff, for example, in their hydrogenated form as nondairy spreads and food additives. In their processed form, they are also gaining increased usage as a renewable biofuel [1].

Although the overall quality of the product is generally defined by its culinary benefits, the inorganic content of these oils has a very important role in terms of food safety and general product longevity. The mechanisms whereby inorganic constituents are incorporated into the oil include the natural uptake and preconcentration of the element by the plant, contamination during harvesting/processing (for example, from foreign bodies during harvesting or wear metals in the press), and addition or adulteration at some point. As well as the obvious importance of monitoring these elements for safety or nutritional reasons, it has been reported [2] that some trace elements can act as autoxidation accelerators, altering the flavor and quality of the product over time.

Some traditional approaches to elemental analysis of these materials include inductively coupled plasma optical emission spectroscopy (ICP-OES), atomic absorption spectrometry (FAAS/GFAAS), and ion chromatography (IC). These techniques each suffer severe interferences from the organic matrix; for this reason it is usual to digest the sample or perform an aqueous extraction to eliminate the organic matrix. Whilst digestion/extraction procedures are generally well developed, they are time consuming, often require additional equipment, and can introduce potential errors (for example, analyte loss through incomplete extraction or elemental volatility and contamination from reagents/vessels). In addition, many of these techniques do not offer sufficient sensitivity or detection limits for the measurement of important toxic elements.

This procedure describes a simple dilution approach for sample preparation and analysis by ICP-mass spectrometry (ICP-MS). The plasma- and matrix-based interferences are efficiently attenuated using an Octopole Reaction System (ORS) operating in collision and reaction modes.

Experimental

Standards and internal standards were prepared by weight/weight dilution from ~1,000 mg/kg metallo-organic oils (Spex Certiprep, Metuchen, New Jersey, USA and Conostan, Conoco-Phillips, Bartlesville, OK, USA) and diluted in kerosene (Purum, Fluka Sigma-Aldrich, St. Louis, USA). Internal standards (Li, In, and Bi) were added to all samples and standards prior to analysis to compensate for viscosity differences and to allow nonmatrix-matched standards to be used; samples were prepared by simple 3x dilution in kerosene using weight/weight preparation. Three seed oils (rape, sunflower, and corn), four olive oils (Spanish, Greek, Italian, and Sicilian), and three nut oils (hazel, almond, and groundnut) were investigated.

An Agilent 7500cx ICP-MS fitted with an ORS for removal of polyatomic interferences was used for this study. The instrument was operated using hydrogen, helium, and no-gas cell modes. All modes were acquired sequentially during a single visit to the sample vial. Instrumental conditions are given in Table 1.

The ORS operating in He collision mode removes polyatomic interferences using a process known as kinetic energy discrimination (KED). The larger interfering species experience more collisions with He atoms and lose energy as they pass through the cell. An energy differential is applied to prevent the lower energy polyatomic ions from entering the mass filter. Optional reaction mode using H_2 gas was used to remove the intense plasma- and matrix-based species such as $^{14}N_2$ and $^{12}C^{16}O$ on ^{28}Si, $^{38}Ar^{40}Ar$ on ^{78}Se, ^{40}Ar on ^{40}Ca, and $^{40}Ar^{12}C$ on ^{52}Cr. The interference is neutralized or converted to another species by reaction. For interference-free analytes, the cell can be operated in either He collision or no-gas mode, that is, with no gas added to the ORS cell. Oxygen was added to the plasma (as a 50% O_2 blend in Ar) by an additional mass flow controller to prevent carbon from condensing on the interface and ion lenses; this was used in conjunction with the organic solvent introduction kit and 1.5 mm id injector torch. Note that, while a 50% O_2 in argon mix was used for this application, a 20% O_2 in argon mix is the preferred option, as this provides more precise control of the O_2 flow rate, which may be critical in certain applications, such as low-level S and P analysis.

Table 1. 7500cx ICP-MS Operating Conditions

Forward power	1550W
Plasma gas	15 L/min
Auxiliary gas	1 L/min
Sampling depth	8 mm
Carrier gas	0.9 L/min
Oxygen (50% O_2 in Ar)	0.12 L/min
ORS Cell Gas Flow Rates	
Helium (He)	5.7 mL/min
Hydrogen (H_2)	6.5 mL/min

Results and Discussion

Table 2 displays the detection limit (DL) and background equivalent concentration (BEC) for the kerosene standard blank. The BEC is an indication of the calibration offset expressed as a concentration (due to elemental contamination in the kerosene matrix). The DLs and BECs were in the µg/kg (ppb) or ng/kg (ppt) range for all elements measured.

Table 2. Detection Limits (3s) and Background Equivalent Concentrations for the Standard Blank Solution (Data reported as µg/kg [ppb].)

Element	Mass	Mode	DL	BEC
Be	9	No gas	0.0153	0.0234
B	10	No gas	0.344	4.63
Na	23	No gas	2.99	18.8
Mg	24	H_2	1.37	8.9
Si	28	H_2	5.17	53.3
P	31	He	10	52
K	39	H_2	0.649	1.34
Ca	40	H_2	0.568	2.95
Ti	47	He	0.125	0.0396
V	51	He	0.0198	0.0435
Cr	52	H_2	0.0935	0.0772
Mn	55	He	0.0249	0.0527
Fe	56	He	0.0447	0.129
Co	59	He	0.0113	0.0245
Ni	60	He	0.025	0.0367
Cu	63	He	0.0525	0.681
Cu	65	He	0.0723	0.675
Zn	66	He	0.0393	0.0685
As	75	He	0.0896	0.192
Sr	88	No gas	0.0335	0.121
Mo	95	No gas	0.5	0.411
Ag	107	No gas	0.0374	0.0832
Cd	111	No gas	0.121	0.138
Sn	118	No gas	0.0173	0.0901
Sb	121	No gas	0.0261	0.0827
Ba	137	No gas	0.0472	0.145
W	182	No gas	0.0111	0.0231
Hg	201	No gas	0.0147	0.107
Pb	208	No gas	0.00724	0.0595

In order to test the cell's performance in gas mode, several interfered elements were also measured with no gas in the cell. The effect of the $^{40}Ar^{12}C$ interference can be seen in Figures 1a and 1b (^{52}Cr determined in H_2 reaction mode and no-gas mode): the BEC has been reduced from over 80 ppb to less than 0.08 ppb. Figures 2a and 2b (Mn determined in He collision mode and no-gas mode) demonstrate the removal of the $^{38}Ar^{17}O$ (interference due to oxygen addition) and $^{40}Ar^{15}N$ (from air entrainment and residual nitrogen in the matrix) – both minor polyatomics but nevertheless present at mass 55. The BEC is reduced from > 1.2 ppb without cell gas to ~0.05 ppb in gas mode.

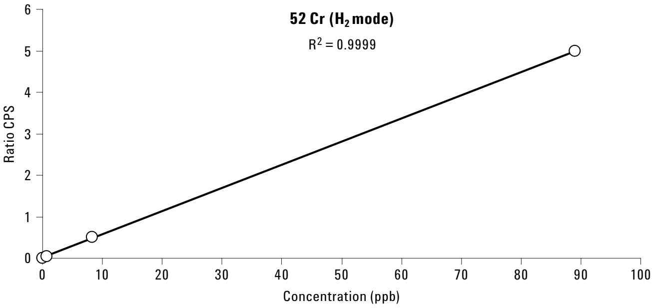

Figure 1a. Cr (H_2 reaction mode). Note excellent curve fit and minimal calibration offset (BEC = 0.077 ppb), indicating efficient interference (ArC) removal.

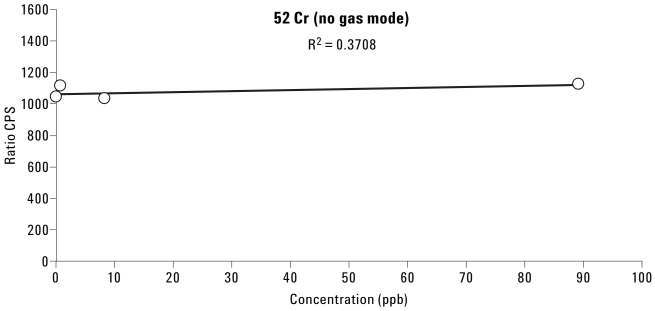

Figure 1b. Cr (no-gas mode). Note very poor curve fit due to extremely high calibration offset (approximate BEC ≥ 83 ppb) due to the intensity of the ArC interference.

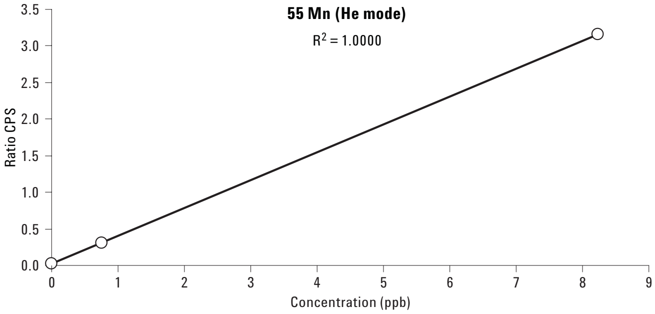

Figure 2a. Mn (He collision mode). Low BEC (0.053 ppb) indicates efficient interference (ArO, ArN) removal.

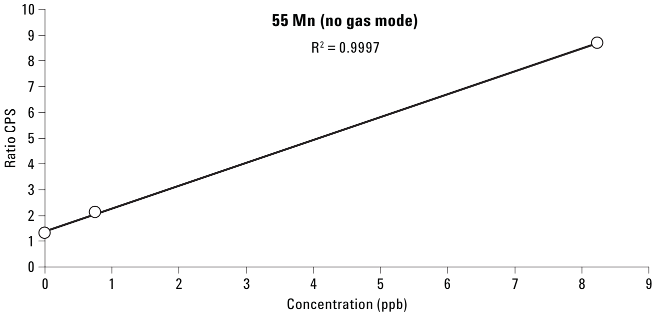

Figure 2b. Mn (no-gas mode). Small but significant offset most likely due to $^{38}Ar^{17}O$ and $^{40}Ar^{15}N$ interferences equivalent to 1.23 ppb BEC.

Table 3 displays the quantitative results obtained for the samples, including spike recovery data for the rapeseed sample. Recoveries for all elements ranged from a low of 93.7% for silver to a high of 107.1% for tin; generally, the recoveries for all elements were excellent, considering that the standards were not matched exactly for viscosity. Overall, the nut oils had higher elemental levels than the other oils studied, which is probably an indication of the different biological pathways of the plants rather than any specific contamination during production.

Instrumental stability was tested over a period of 8.5 hours using a spiked (~12 µg/kg) rapeseed oil. Figure 3 displays the normalized stability plot. Precision was found to be around 2% for most elements (Na RSD was higher at 4%, most likely due to some airborne contamination occurring during the run), which clearly demonstrates the applicability of the technique to routine analysis of this organic matrix.

Table 3. Quantitative Results for the Oil Materials (Corrected for Dilution) (All results presented as µg/kg. spike recoveries are presented for the rapeseed material.)

			Seed oil			Olive oil				Nut oil			Rapeseed spike recovery		
			Sunflower	**Rape**	**Corn**	**Spanish**	**Greek**	**Italian**	**Sicilian**	**Groundnut**	**Hazel**	**Almond**	Spk amt	Measured	**% Rec**
Be	9	No gas	0.0675	1.2	0.4549	0.4394	0.115	0.0591	0.0747	0.0994	0.0089	0.0734	16.3	17.84	102.1
B	10	No gas	15.36	1.123	N/D	N/D	N/D	N/D	2.829	N/D	41.53	32.53	12.4	14.33	106.5
Na	23	No gas	131.1	168.2	488.2	199.2	441.6	213.6	304.9	1620	723.9	938	Spike too low		
Mg	24	H_2	N/D	N/D	74.58	N/D	N/D	43.43	N/D	298.9	1740	8133	12.4	12.07	97.3
Si	28	H_2	45.9	N/D	43.98	1.486	356.7	404.7	481.7	251.9	327.6	129.8	12.4	12.78	103.1
P	31	He	382.4	2910	545.4	164.8	251.2	231.3	115.4	9196	11410	60860	Spike too low		
K	39	He	53.25	155.03	139.5	100.4	144.1	186.6	208.3	1031	2415	15540	Spike too low		
Ca	43	He	16.49	10.423	52.54	27.88	29.14	25.31	28.57	62.46	628.7	1785	12.4	22.81	99.9
Ti	47	He	0.6974	0.4051	0.9066	0.3111	1.12	0.1628	1.681	0.9585	80.1	3.568	12.4	12.62	98.5
V	51	He	0.1162	0.0383	0.068	N/D	N/D	N/D	N/D	0.0034	1.072	0.1468	12.4	13.01	104.6
Cr	52	H_2	1.671	1.295	1.515	1.043	2.918	2.043	3.048	1.206	5.029	2.681	12.4	13.69	100.0
Mn	55	He	0.7513	2.905	2.225	1.513	1.069	0.8085	0.3445	9.736	341.5	170.9	12.4	15.67	102.9
Fe	56	He	16.81	20.03	123.3	18.79	12.9	14.36	1.024	62.47	83.09	358.2	12.4	32.64	101.7
Co	59	He	0.462	0.8684	13.89	4.869	3.185	1.355	0.5555	1.275	0.0679	1.427	14.8	15.38	98.1
Ni	60	He	0.4023	2.841	2.823	0.398	0.3685	0.132	0.1193	0.9994	1.129	0.6101	12.4	16.01	106.2
Cu	63	He	5.602	22.03	5.351	1.562	10.3	6.393	4.11	2.137	2.538	5.084	12.4	34.26	98.6
Zn	66	He	1.229	2.164	4.415	2.867	3.934	4.035	0.5509	12.73	25.54	119.9	12.4	15.06	104.0
As	75	He	0.7322	0.4324	4.467	2.325	0.6854	0.1878	0.3433	5.952	0.6574	1.42	17.4	18.4	103.3
Se	78	H_2	1.187	0.85852	3.0902	0.584	1.8861	N/D	3.2414	0.528	2.305	1.8362	12.4	13.54	102.27
Sr	88	No gas	0.4056	0.688	2.44	1.584	0.5329	0.6583	0.2142	1.417	10.54	119.9	15.4	16.57	103.1
Ag	107	No gas	0.2432	0.3273	0.2934	0.3644	0.0758	0.1772	0.0922	0.0482	N/D	0.6216	12.4	11.95	93.7
Cd	111	No gas	0.6787	2.054	0.6848	1.502	0.3816	0.2396	0.2795	N/D	N/D	N/D	12.4	14.58	101.0
Sn	118	No gas	N/D	N/D	0.9429	N/D	N/D	0.1151	N/D	N/D	77.1	0.2331	12.4	13.28	107.1
Ba	137	No gas	0.2509	0.4626	1.121	0.5088	0.0928	0.1067	N/D	3.019	29.43	76.7	12.4	13.54	105.5
W	182	No gas	N/D	N/D	4.366	2.314	0.3513	N/D	N/D	0.3609	N/D	0.2165	12.4	12.93	104.3
Hg	201	No gas	0.5693	0.4652	0.5729	0.3813	0.6913	0.5076	0.7274	0.3244	0.3807	0.3391	Not in spike mix		
Pb	208	No gas	0.11	0.6082	0.5475	0.425	0.1735	0.1308	0.3311	0.6437	0.4816	1.261	12.4	13.46	103.6

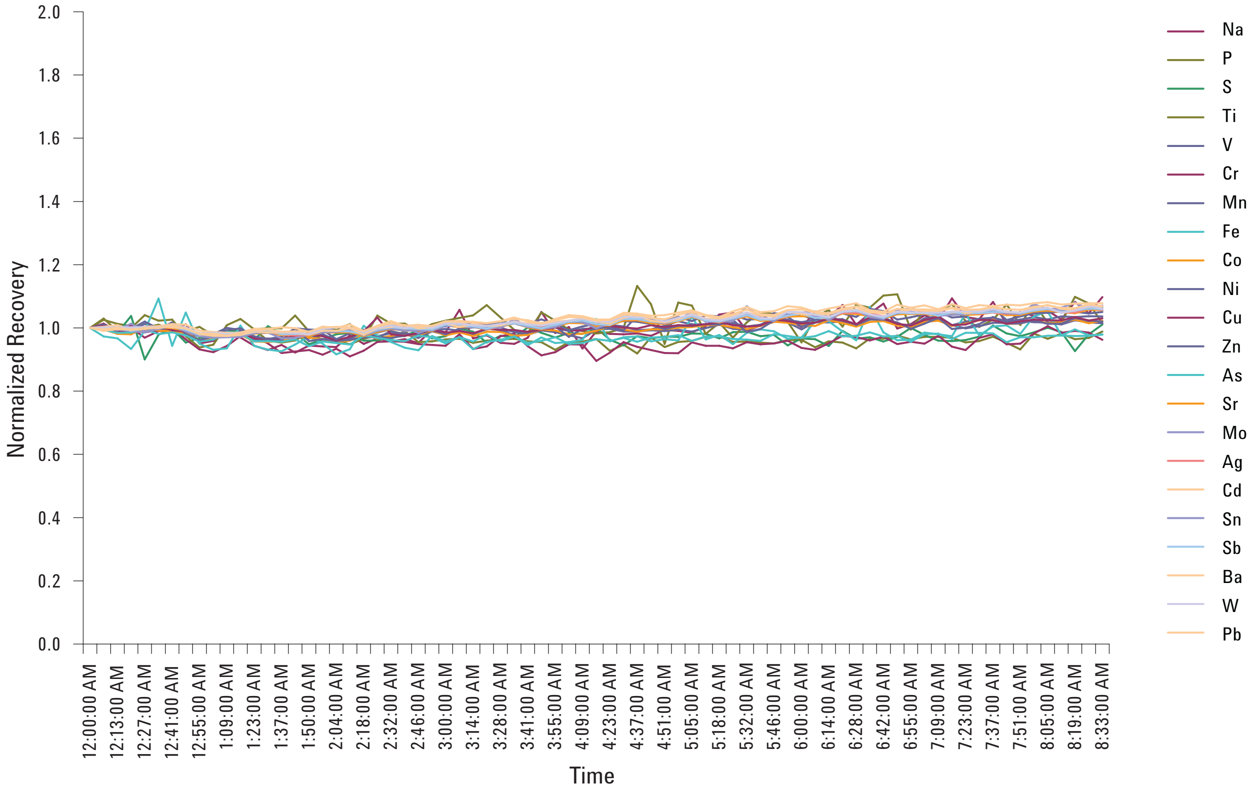

Figure 3. Normalized stability plot for a spiked (~12 µg/kg) rapeseed oil. Repeat measurements were taken over a period of 8 hours 33 minutes.

Conclusions

The measurement of trace and ultratrace elements in edible oils by 7500cx (ORS) ICP-MS is routine, sensitive, and selective. The ORS efficiently attenuates matrix- and plasma-based interferences to concentrations below background contamination, providing ppt-level detection performance for almost all elements. Furthermore, the simplicity of the method setup and sample preparation lends itself to a routine environment, as very little sample workup or instrument optimization is required. The result is improved productivity and a reduced likelihood of preparation errors.

References

1. Agilent Technologies publication, "Direct Elemental Analysis of Biodiesel by 7500cx ICP-MS with ORS," 5989-7649EN, April 17, 2008
2. Eunok Choe and David Min, "Mechanisms and Factors for Edible Oil Oxidation," *Comprehensive Reviews in Food Science and Food Safety*, 5, p. 169–186, 2006

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Published in the USA
December 9, 2008
5989-9888EN

Agilent Technologies