DETERMINATION OF Be, Cr, Co, Ni, As, Se, Cd, Hg, Pb IN TOBACCO AND TOBACCO PRODUCTS BY ICP-MS

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ABSTRACT

The ICP-MS combines a high temperature heat source with a mass spectrometer to convert atoms of elements to ions, which are separated and detected according to their atomic masses. This presentation describes a method for determining the elemental content of tobacco and tobacco products such as cigarettes as well as smokeless products by ICP-MS. This method is capable of determining most of the Periodic Table for elements with a first ionization potential below argon. The method is used to determine chromium, nickel, arsenic, cadmium, lead, selenium, mercury, cobalt, and beryllium. Validation of the standard test method has been completed resulting in determination of optimal internal standards for each element as well as establishing LOQs, MLOQs, method precision, accuracy and other Figures of Merit for both the NexION and ELAN ICPMS instruments. Results of the validation also demonstrated successful removal of common polyatomic overlaps present in tobacco on the ^{60}Ni, ^{62}Ni and ^{75}As isotopes using the NexION instrument in KED mode. The method ensures accurate results using calibration standards, sample blanks, SRMs, ICV, and bracketing samples with a midrange and calibration blank to monitor carry-over and instrument drift.

INTRODUCTION

The method determines the elemental content of tobacco and tobacco products (including smokeless) through ICP-MS analysis. While ICP-MS is a common technique, certain mid-mass elements, such as nickel, chromium, arsenic, and selenium have polyatomic overlaps on the major isotope or carry-over (such as Hg). The validation data results have shown successful removal these inaccuracies to achieve optimum metals testing. The carryover due to mercury's vapor pressure was resolved by complexing the mercury with gold, thereby reducing the free mercury in the introduction system. Internal standards used for the analysis were ^{71}Ga, ^{74}Ge, ^{115}Cd, and ^{209}Bi.

METHODS & MATERIALS

Samples were digested utilizing nitric acid and then heated to high temperature in a closed vessel microwave oven, followed by analysis using both a Perkin Elmer NexION 300S ICPMS as well as a Perkin Elmer ELAN DRC Plus ICPMS.

Mars Xpress Microwave Digestion System

ELAN DRC ICP-MS

NexION 300 ICP-MS

METHOD PRECISION /ACCURACY RESULTS

Method Precision/Accuracy for Nickel and Arsenic in Oriental Tobacco Leaves, CTA-OTL-1 (NexION ICPMS, KED Mode)

	^{60}Ni (µg/g)	% Rec	^{62}Ni (µg/g)	% Rec	^{75}As (µg/g)	% Rec
Mean	4.99	79.0	4.98	78.7	0.617	114.4
%RSD	2.4	2.4	2.1	2.1	4.6	4.6

Method Precision/Accuracy for Cobalt and Cadmium in Oriental Tobacco Leaves, CTA-OTL-1 (NexION ICPMS)

	Mode		Mode		Mode		Mode	
	Normal		Normal		Normal		KED	
	^{59}Co (µg/g)	% Rec	^{111}Cd (µg/g)	% Rec	^{114}Cd (µg/g)	% Rec	^{59}Co (µg/g)	% Rec
Mean	0.883	100.5	1.17	104.4	1.15	102.6	0.816	92.8
%RSD	0.8	0.8	2.9	2.9	2.4	2.4	1.5	1.5

Method Precision/Accuracy for Lead, Mercury, and Chromium in Oriental Tobacco Leaves, CTA-OTL-1 (NexION ICPMS)

	Mode		Mode		Mode	
	Normal		Normal		NH_3	
Rep	^{202}Hg (µg/g)	% Rec	^{208}Pb (µg/g)	% Rec	^{52}Cr (µg/g)	% Rec
Mean	0.035	81	4.19	85.4	1.79	69.0
%RSD	2.9	2.9	1.0	1.0	6.5	6.5

SPECIFICITY

Specificity was evaluated by comparing an alternate method, Graphite Furnace Atomic Absorption Spectrometry (GFAAS), to the ICP-MS data for arsenic, selenium and nickel. Because lead, mercury, and cadmium have higher mass isotopes, they do not suffer from the same interferences that nickel, arsenic or selenium do on ICP-MS and the polyatomic overlap from the various combinations of ClO on chromium are completely removed in NH_3 reaction mode.

Arsenic results were compared between GFAAS and the NexION ICPMS in KED mode to remove the interference from the $^{40}Ar^{35}Cl^{+}$ polyatomic overlap. In all cases the GFAAS results were higher than the KED mode arsenic values, with the GFAAS values having positive bias. ICP-MS has better sensitivity as well as being more specific for arsenic. The KED mode appears to remove the interferences on arsenic, regardless of the matrix studied.

Nickel results were compared between GFAAS and the NexION ICPMS in KED mode. KED mode removed interferences from polyatomic overlaps from $^{44}Ca^{16}O$, $^{46}Ca^{16}O$, $^{23}Na^{37}Cl$, $^{25}Mg^{37}Cl$, $^{25}Na^{35}Cl$ and many other polyatomic overlaps common in digested botanical matrices, which often contain high levels of calcium, magnesium, sodium, potassium, and chloride in addition to the normal high levels of oxygen, argon, nitrogen and carbon found in the entrained gases in the plasma. The reaction gases NH_3 and CH_4 removed many of these interferences, however it sometimes did not remove all of them. The KED mode removed spectral interferences, although at some cost to sensitivity. Improved technology incorporated in the NexION ICPMS, such as bending low mass rather than passing it around a photon stop, as is used in the ELAN ICPMS, yielded improved resolution in KED mode without a reduction in sensitivity when compared to the ELAN ICPMS in reaction mode. The results of the KED mode on nickel yielded results that matched GFAAS in specificity in all matrices, while providing better sensitivity than GFAAS. Both the 60 and 62 isotopes and the GFAAS results matched across the matrices studied (smokeless products).

SPECIFICITY RESULTS

Arsenic ICP-MS (KED Mode) vs. GFAAS

Matrix	ID	GFAAS (µg/g)	KED ^{75}As (µg/g)	GFAAS % Rec	KED ^{75}As % Rec
O1	A1	3.91	2.57	145.1	107.6
O2	A2	3.82	2.57	138.9	108.0
S1	A7	3.22	2.44	127.4	110.3
S2	A8	3.34	2.38	136.8	110.0
Tobacco	A13	3.63	3.07	130.3	117.8
Tobacco	A14	3.24	2.58	127.4	112.5
ST1	A19	3.02	2.73	126.9	117.2
ST2	A20	3.13	2.77	133.1	117.9

Nickel ICP-MS (KED Mode) vs. GFAAS

Matrix	ID	GFAAS (µg/g)	KED ^{60}Ni (µg/g)	KED ^{62}Ni (µg/g)	GFAAS % Rec	KED ^{60}Ni % Rec	KED ^{62}Ni % Rec
O1	A1	3.97	3.80	3.81	96.5	91.8	92.6
O2	A2	3.94	3.82	3.89	98.5	93.0	95.6
S1	A7	4.17	4.36	4.37	106.2	97.4	96.9
S2	A8	4.18	4.39	4.58	115.7	100.8	105.9
Tobacco	A13	5.17	4.98	5.06	96.2	90.4	93.0
Tobacco	A14	4.67	4.30	4.30	90.0	82.2	82.6
ST1	A19	3.93	3.77	3.79	103.1	94.1	92.5
ST2	A20	4.08	3.84	3.88	106.7	95.1	94.5

CONCLUSIONS

The method gave very good results for all matrices studied with good precision (within the sample homogeneity of the tobacco) and good accuracy for all elements. The polyatomic interferences on nickel and arsenic have been resolved for all matrices with good comparison between both isotopes for nickel and when compared to GFAAS. Chromium remains resolved using NH_3 mode and selenium yields good results using the 78 isotope in KED mode. The other isotopes used to quantitate in the various matrices were ^{9}Be in normal mode, ^{59}Co in normal or KED mode, ^{75}As in KED mode, ^{60}Ni in KED mode, ^{114}Cd in normal mode, ^{52}Cr in NH_3 mode, ^{202}Hg and ^{208}Pb in normal mode.

ICPMS using a combination of normal mode for low masses,^{9}Be, and for high mass ^{111}Cd and up with a combination of KED and NH_3 reaction mode for mid-mass elements, 59 to 80 Daltons, yielded a technique that is superior to other available techniques, such as GFAAS in sensitivity, specificity as well as speed of analysis. Method Limit of Quantification (MLOQ) were less than 1 µg/L range in solution for all elements. Using 0.5 grams of sample, dilution to 100 mL yielded sample MLOQ values of less than 1 µg/g.