P5

ACCURACY MEASUREMENT OF TOXIC AND NUTRIENT ELEMENTS IN VEGETAL TISSUE AND SOIL SAMPLES BY USING ISOTOPIC DILUTION ICP-SFMS

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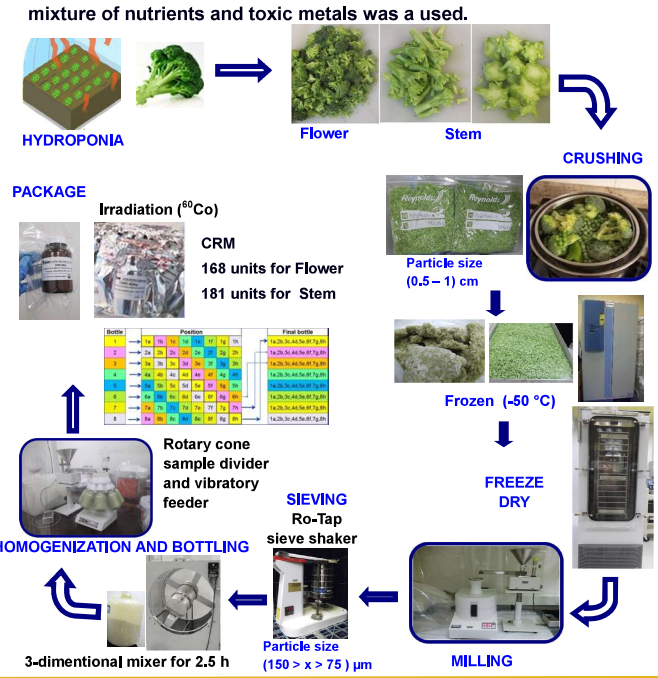
PREPARATION OF REFERENCE MATERIAL

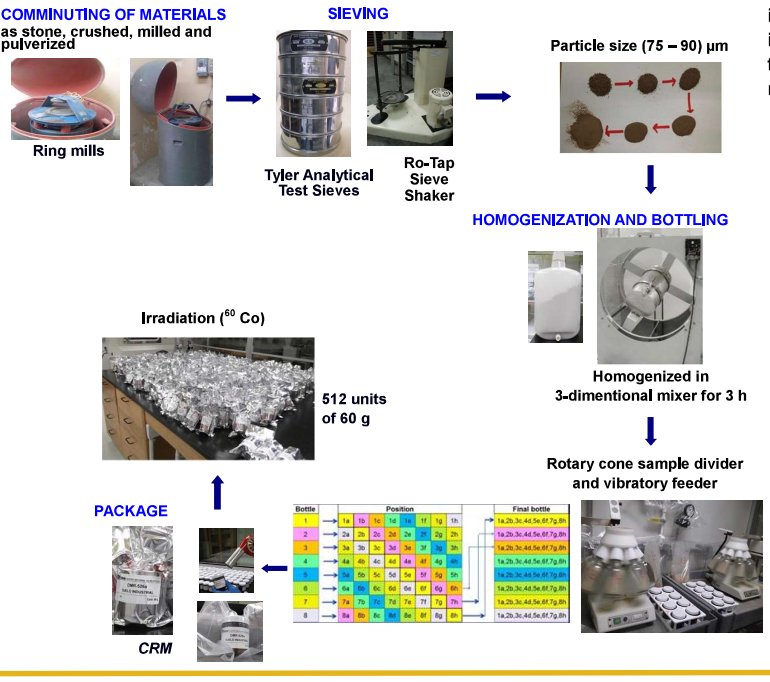
Broccoli

Broccoli was grown by hydroponia, a solution with a mixture of nutrients and toxic metals was a used.



Contaminated soil

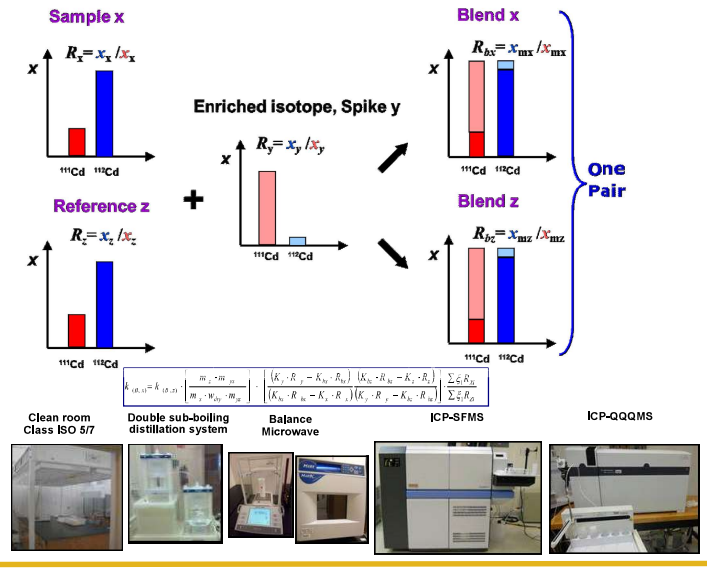
Sandy soil of rhyolitic origin, from a contaminated site in a mining region of Mexico



PRINCIPLE OF MEASUREMENT

ID-ICPMS Two Steps and Exact Matching Method

The isotope dilution is based on the addition of known amount of an enriched isotope to sample and primary standard. After equilibration of the enriched isotope with natural isotopes, in the sample and in primary standard, the altered isotopic ratios (R_{bx} *and* R_{bz}), are measured using inductively couple plasma mass spectrometry.



METHOD SEPARATION

Interferences

^{110}Cd	^{111}Cd	^{112}Cd	^{113}Cd	^{114}Cd
$^{94}Mo^{16}O$	$^{95}Mo^{16}O$	$^{96}Mo^{16}O$	$^{97}Mo^{16}O$	$^{98}Mo^{16}O$
$^{94}Zr^{16}O$	$^{93}Nb^{18}O$	$^{94}Mo^{18}O$	$^{95}Mo^{18}O$	$^{96}Mo^{18}O$
$^{92}Zr^{18}O$		$^{97}Mo^{15}N$		^{114}Sn
$^{93}Nb^{17}O$		$^{98}Mo^{14}N$		
$^{92}Mo^{18}O$		$^{97}Mo^{14}N^{1}H$		
		$^{96}Mo^{15}N^{1}H$		
		$^{96}Zr^{16}O$		
		$^{94}Zr^{18}O$		
		$^{93}Nb^{18}O^{1}H$		
		^{112}Sn		

^{54}Fe	^{56}Fe	^{57}Fe	^{58}Fe
^{54}Cr	$^{40}Ca^{16}O$	$^{40}Ar^{17}O$	^{58}Ni
$^{40}Ar^{14}N$	$^{40}Ar^{16}O$	$^{40}Ar^{16}O^{1}H$	$^{23}Na^{35}Cl$

^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb
$^{164}Er^{40}Ar$	$^{166}Er^{40}Ar$	$^{167}Er^{40}Ar$	$^{168}Er^{40}Ar$
$^{188}Os^{16}O$	$^{170}Yb^{36}Ar$	$^{171}Yb^{36}Ar$	$^{168}Yb^{40}Ar$
^{204}Hg	$^{190}Os^{16}O$	$^{191}Ir^{16}O$	$^{192}Pt^{16}O$
			$^{192}Os^{16}O$

^{64}Zn	^{66}Zn	^{67}Zn	^{68}Zn
^{64}Ni	$^{28}Si^{38}Ar$	$^{51}V^{16}O$	$^{52}Cr^{16}O$
$^{28}Si^{36}Ar$	$^{50}Cr^{16}O$	$^{28}Si^{38}Ar$	$^{28}Si^{40}Ar$
$^{24}Mg^{40}Ar$	$^{28}Mg^{40}Ar$	$^{31}P^{36}Ar$	$^{32}S^{36}Ar$
$^{48}Ca^{16}O$	$^{48}Ti^{18}O$	$^{27}Al^{40}Ar$	
$^{48}Ti^{16}O$	$^{36}Ar^{14}N^{16}O$	^{134}Ba ++	
$^{23}Na^{23}Na^{17}O^{1}H$			
$^{23}Na^{23}Na^{18}O^{2}H$			
$^{14}N^{18}O^{16}O^{16}O$			
$^{27}Al^{37}Cl$			

Mechanism of the ion-exchange separation method

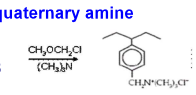
The Cd, Fe, Pb and Zn forms an anionic complexes with Cl^-, which are stable in HCl (aqueous solution) and the interfering elements do not form stable complexes.

Dowex resin 1X-8

Strong base anion resin, Type 1

Functional group: quaternary amine

Copolymer PS-DVB



The ion exchange chemical reaction is:

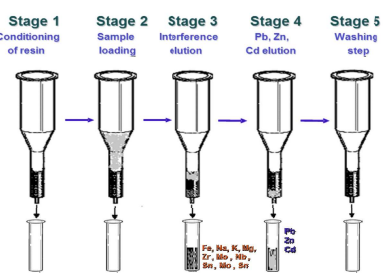
$2\ R\text{-}N{+}(R')_3\ Cl^- + [CdCl_4]^{2-} \longrightarrow [R\text{-}N{+}(R')_3]^2\ [CdCl_4]^{2-} + 2Cl^-$

$R\text{-}N{+}(R')_3\ Cl^- + [ZnCl_3]^- \longrightarrow [R\text{-}N{+}(R')_3]^2\ [ZnCl_3]^- + Cl^-$

$R\text{-}N{+}(R')_3\ Cl^- + [PbCl_3]^- \longrightarrow [R\text{-}N{+}(R')_3]^2\ [PbCl_3]^- + Cl^-$

$R\text{-}CH_2N^+(CH_3)_3\ Cl^- + [FeCl_4]^- \longrightarrow [R\text{-}CH_2\ N^+(CH_3)_3]\ [FeCl_4]^- + 2Cl^-$

Development



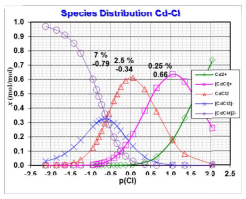
For Cd, Pb and Zn:

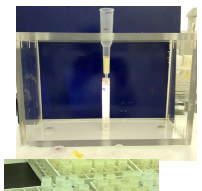
Stage 1	Stage 2	Stage 3	Stage 4
7 % HCl	7 % HCl	0,1 – 2,5 % HCl	1 % HNO_3
2,5 % HNO_3	7 % HCl + 3 % $HCLO_4$	0,5 – 2,5 % HNO_3 12% HCl+13% HF	2,5 % HNO_3
	7 % HCl + 0,5 % $HClO_4$		
10 - 25 mL	3 – 10 g	10 - 20 mL	10 - 15 mL

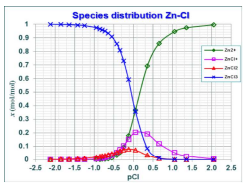
For Fe:

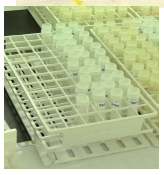
Stage 1	Stage 2	Stage 3	Stage 4
12 M HCl 6 M HCl	6 M HCl	0.5 M HCl	water

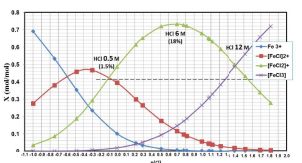
Diagram of species distribution



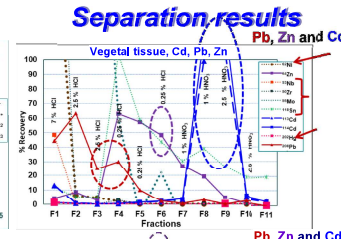


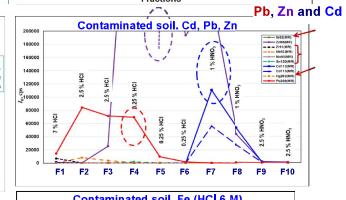


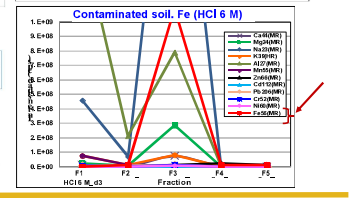




Separation results







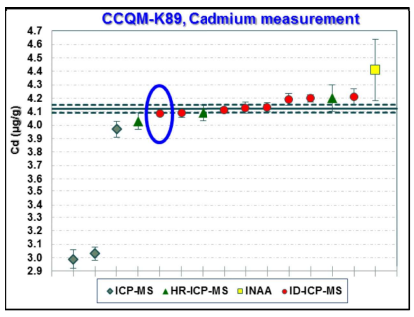
The ion exchange chromatography separation method has been developed for Cd, Fe, Pb and Zn in tissue and soil matrices. Elements as Ca, Na, K, Mg are separated in F1, then the total dissolved solids are reduced.

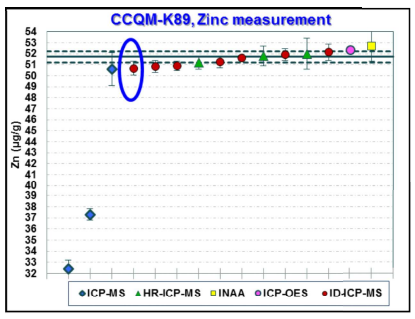
For vegetal tissue and soil, 11 fractions (F) of 4 mL were obtained. The Pb was obtained in F3 and F4, Zn in F6 and Cd in F8-soil, F7-soil.

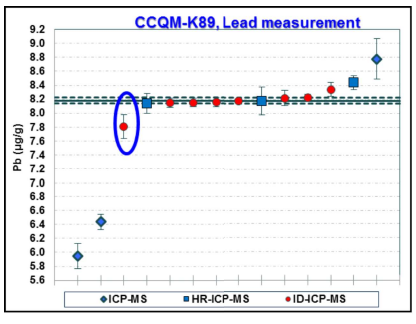
For Fe in soil, 5 fractions (F) of 2, 2, 4, 2 and 2 mL were obtained, the Fe was obtained in F3.

CCQM COMPARISONS

CCQM-K89 , Trace and essential elements in Herba Ecliptae



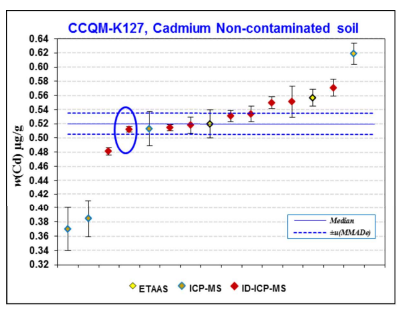


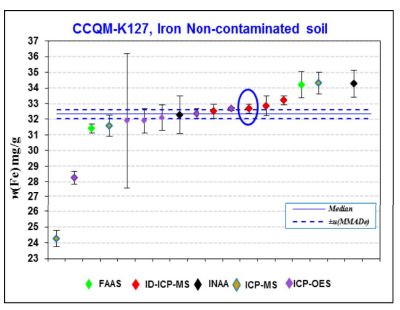


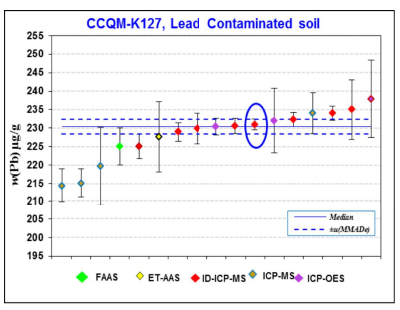
For ID-ICPMS two steps and exact matching method, the R_b measured:

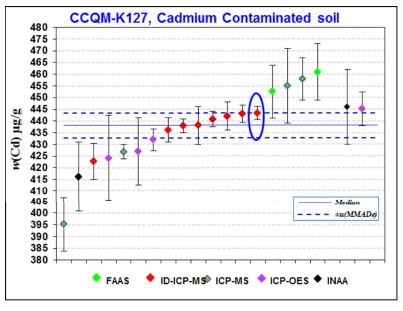
Cd: $^{111}Cd/^{114}Cd$
Fe: $^{57}Fe/^{56}Fe$
Pb: $^{206}Pb/^{208}Pb$
Zn: $^{66}Zn/^{64}Zn$

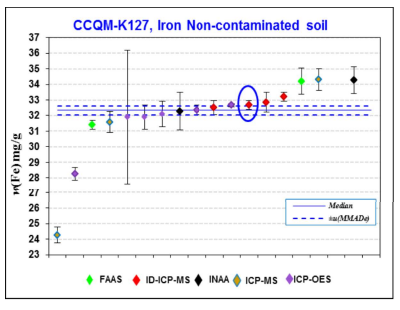
CCQM-K127 "Contaminant and other elements in soil"

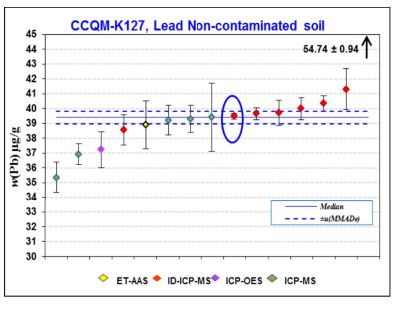












CMC CLAIMS

M. Service Cat. No.	Matrix	Measurand		Dissemination Range of Measurement Capability			Range of Expanded Uncertainties for Measurement Capability			Mechanism(s) for Meas Service Delivery	Source of Traceability	Measurement Technique(s)
		Analyte	Quantity	From	To	Unit	From	To	Unit			
11.1	Vegetal tissue	zinc	Mass fraction	10	80	µg/g	3	4	%	Traceable Reference Materials (MRTC)	CENAM	IC-ID-ICP-SFMS
11.1	Vegetal tissue	calcium	Mass fraction	10	50	mg/g	1.5	4	%	Traceable Reference Materials (MRTC)	CENAM	IC-ID-ICP-SFMS
11.2	Vegetal tissue	cadmium	Mass fraction	1	10	µg/g	1	3	%	Traceable Reference Materials (MRTC), DMR-494a and DMR-494b	CENAM	IC-ID-ICP-SFMS
11.2	Vegetal tissue	lead	Mass fraction	0.5	20	µg/g	5	7	%	Traceable Reference Materials (MRTC), DMR-494a and DMR-494b	CENAM	IC-ID-ICP-SFMS
13.1	Soil	lead	Mass fraction	25	300	µg/g	1.0	1.3	%	PT, DMR-526	CENAM	IC-ID-ICP-SFMS
13.1	soil	cadmium	Mass fraction	0.5	500	µg/g	1.6	1.3	%	PT, DMR-526	CENAM	IC-ID-ICP-SFMS
13.1	soil	Iron	Mass fraction	10	40	mg/g	2.7	1.7	%	PT, DMR-526	CENAM	IC-ID-ICP-SFMS

CONCLUSION

Accuracy measurement method of toxic elements as Cd, Pb and nutrient elements as Fe and Zn in vegetal tissue and soil samples were developed by using ion exchange chromatography separation methods with isotopic dilution ICP-SFMS.

The method were validated by CCQM comparisons CCQM-K89 for vegetal tissue and CCQM-K127 for soil. 7 CMCs has been claimed.

CENAM has been certified three reference materials: 2 batches of Broccoli (Stem and flower) one batch of Contaminated Soil. The range of relative uncertainties is between (1 to 4) %.

ACKNOWLEDGES

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