Robust Plasma Conditions for the Analysis of Trace Metals in Organic Samples

Featuring the Agilent Technologies 7500s ICP-MS

What are Organic Samples?

- "Organic" refers here to non water-soluble organic solvents, rather than just a high carbon level
    - Diluted/digested biological sample is not considered an "organic" matrix
    - A few 1000's ppm C content is not considered an "organic" matrix

- Many organic solvents are analyzed after simple dilution in water or dilute nitric acid - (only qualify as "organic" if run undiluted)
    - N-methyl pyrolidone (NMP)
    - Tetra-methyl ammonium hydroxide (TMAH)
    - Methanol, ethanol, butanol, etc
    - Acetonitrile, acetic acid, etc

- Many organic solvents cannot be diluted in an aqueous matrix and must be analyzed direct or digested/evaporated
    - Digestion/evaporation is not always suitable, due to potential for uncontrolled reactions, possibility of contamination and loss of volatile analytes

Myths and Rumors about Organic Sample Analysis by ICP-MS

"ICP-MS cannot routinely analyse organic solvents directly"
"ICP-MS ICP generators cannot handle organic solvents"

- **Not correct!** Organic solvents can be analysed easily and routinely, provided a few simple hardware and optimization rules are followed:

- Know your organic
    - compatibility with instrument hardware (tubing, o-rings, drain components)
    - consider volatility (greater volatility leads to higher vapor pressure and greater disruption of the plasma)
    - consider carbon content (long-chain, more complex, aromatic organic molecules take more energy to decompose in the plasma)
    - which elements are to be measured and at what levels

Practical Considerations (1)

- Many plastics will dissolve or degrade (swell or harden) on contact with organic solvents
    - sample uptake and drain tubing and connectors and spray chamber o-rings are replaced with organic resistant alternatives
    - peristaltic pump used only for spray chamber drain, to avoid degradation of and contamination from peripump uptake tubing
    - free-aspiration nebulizer used and sample flow rate controlled by nebulizer gas flow rate, sample uptake tubing length, sample uptake tubing internal diameter (ID)

- High vapor pressure of some volatile organic solvents at room-temperature will extinguish the plasma
    - Peltier-cooled spray chamber is operated at below ambient temperature to reduce vapor pressure
    - the higher heat transfer efficiency of a Peltier compared to a water jacket means -5°C is suitable for even the most volatile solvents

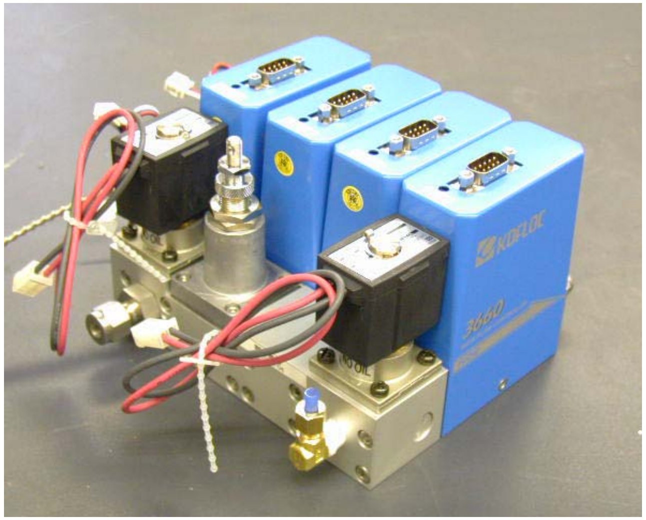
Practical Considerations (2)

- Carbon will deposit on the sample and skimmer cones, unless decomposed by addition of oxygen
  - with water-soluble organics, water matrix may provide enough oxygen
  - with non-water soluble organics, oxygen gas must be added
    - typically 20% oxygen in argon is used, for safe storage and handling
    - 20% O_2 mix is added to carrier gas, either in spray chamber or using T-connector before torch (optional 5th MFC)
    - minimum acceptable O_2 level will depend on the matrix

- Aggressive, O_2-rich plasma will degrade standard Ni cones
  - Ni cones replaced with Pt-tipped cones - more inert

- Aqueous calibration standards may not be suitable
  - organo-metallic standards used (e.g. Conostan S-21)

Sample Introduction for Organics



Mass Flow Control for all plasma gases - Cool, Auxiliary, Nebulizer, Blend and optional 5th gas supply for addition of option gas (oxygen)

Nebulizer must operate at low sample flow rates (between 25uL/min and 400uL/min), avoiding solvent overloading

Solvent resistant kit comprising uptake tubing, nebulizer and spray chamber o-rings, isoversinic pump tubing for drain, drain container (separate waste) and torch and T-connector if required

Range of narrow ID injector torches (1.0mm to 2.0mm) in place of standard 2.5mm ID torch

Optimization of Oxygen Level

- Oxygen is added to the carrier gas, to decompose the organic matrix

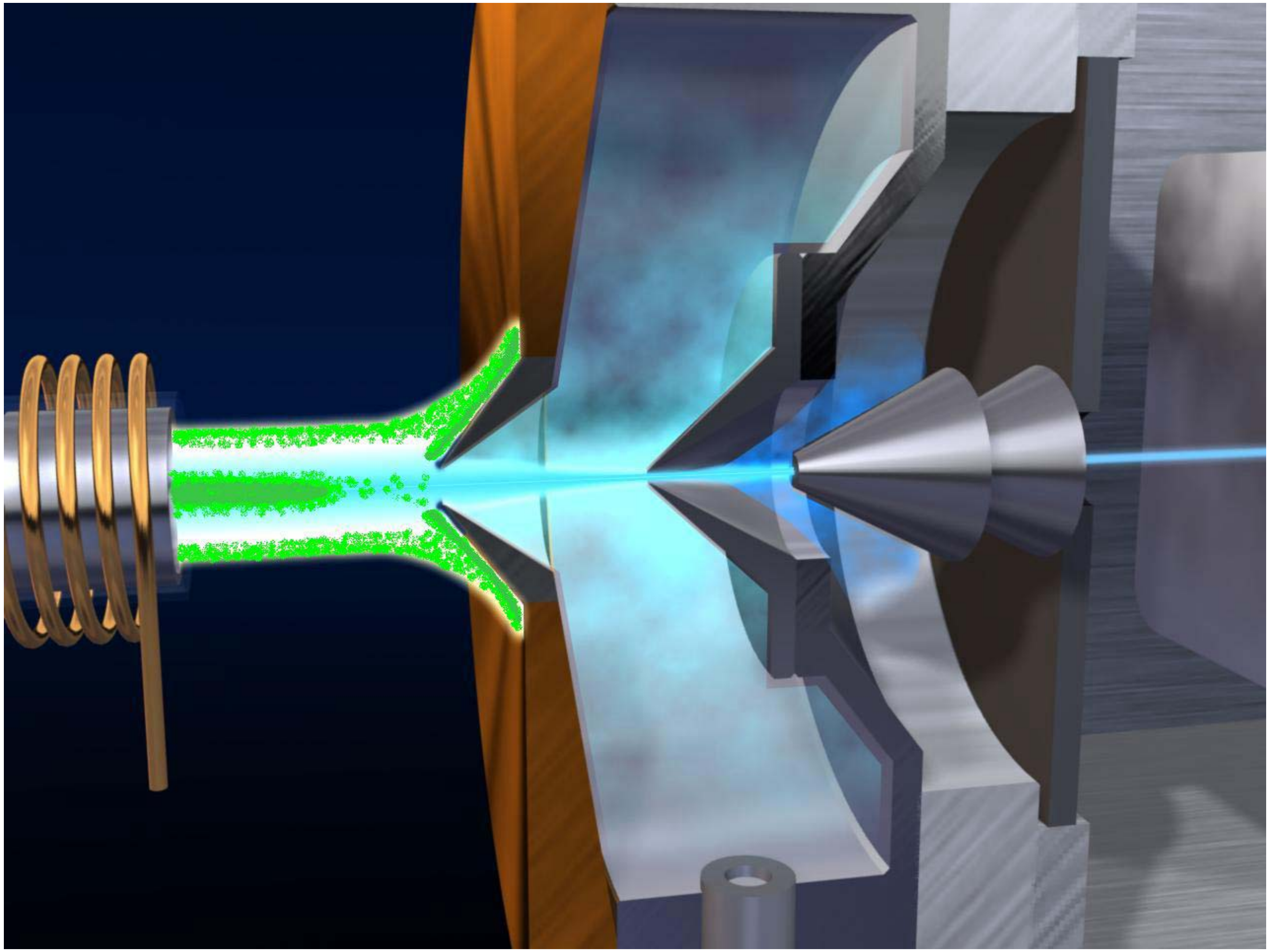
- Without oxygen, the matrix “condenses” as a sooty deposit on the sample cone, leading to rapid signal loss

- The correct oxygen level is easily determined for a particular organic solvent
  - default oxygen level is added on start-up (typically about 5% of total carrier flow)
  - if no sooty deposit forms, oxygen level can be decreased to find cut-off point
  - if sooty deposit begins to form, oxygen addition is increased

  - oxygen level is determined after other conditions (sample flow rate, etc)
  - small excess of oxygen is used, to ensure long-term resistance to soot build-up
  - if several different organic solvents are to be run, oxygen level can be set for the highest C matrix, giving an excess for the easier sample types

  - ***THAT’S IT!!***

Optimization of Oxygen Level



- For unknown solvents, oxygen addition is adjusted to give green C_2 emission “tongue” that stops well before sample cone orifice, indicating organic matrix has been decomposed
- Cooler regions of plasma (outer edge and in front of cone) also show C_2 emission
- Good view of plasma is essential for optimization

Typical Oxygen Levels

Organic solvent	*Sample tubing id (mm)	Torch injector id. (mm)	**Oxygen Flow (% of carrier gas)	**Oxygen Flow (mL/min)
ethyl alcohol (Ethanol)	0.3	1.5	3	35
propylene glycol mono-methyl acetate (PGMEA)	0.3	1.5	3	35
ethyl lactate	0.3	1.5	3	35
kerosene	0.3	1.5	5	60
methyl iso-butyl ketone (MIBK)	0.3	1.5	8	100
xylene	0.3	1.5	10	120
toluene	0.3	1.5	12	150
acetone	0.16	1	5	60

* Assumes a length of 50 to 70cm.

** 5x this amount of 20% oxygen in argon blend is added

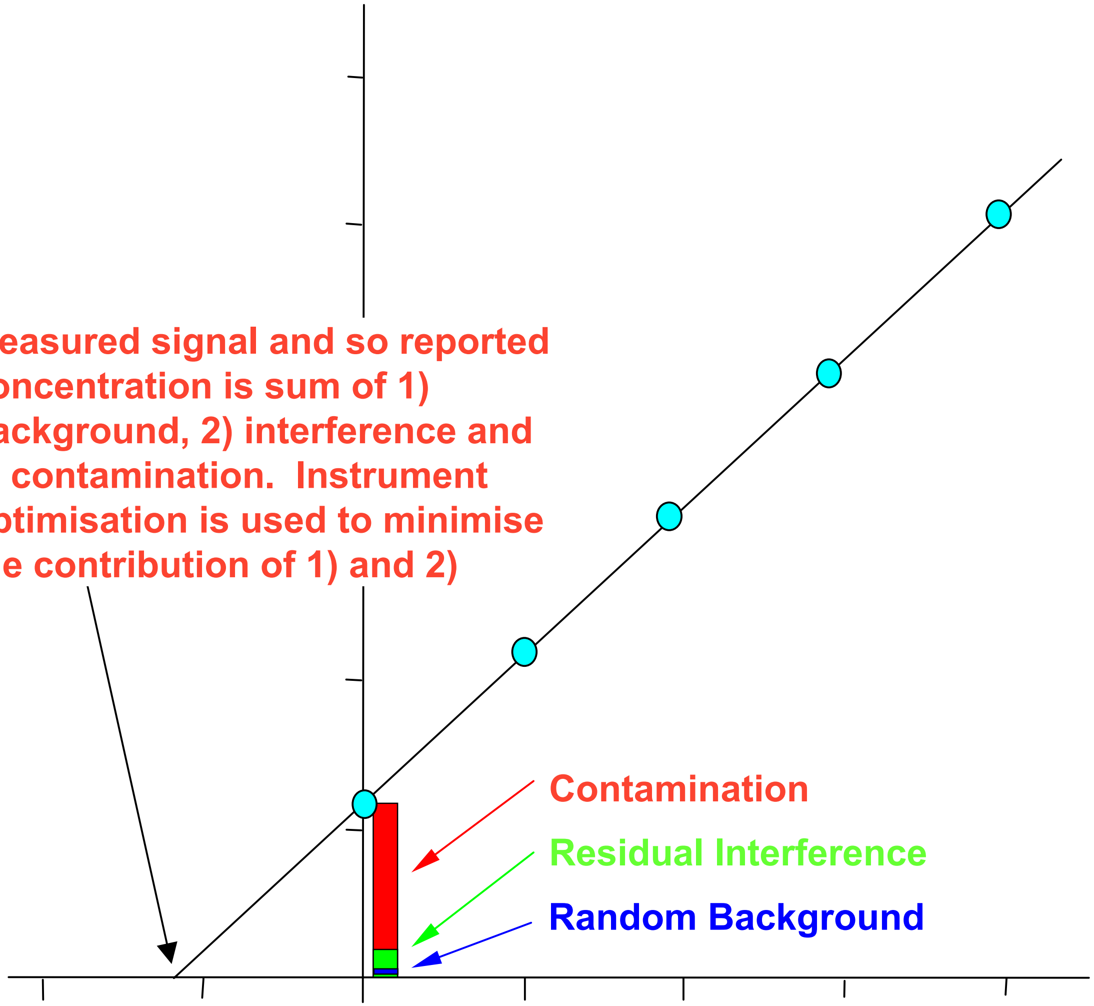
- Too much oxygen - green emission disappears from centre of plasma
- Too little oxygen - black carbon deposits build up on tip of sample cone. Carbon burns off as orange sparks when oxygen level is increased
- Once O_2 addition has been optimized for a new solvent, it does not require routine adjustment

System Optimization

	for Organics	for Aqueous
RF Forward Power	1400	1350
Sampling Depth	9	8
Carrier Gas	1.1	1.1
Spray Chamber Temperature	-5	2
Sensitivity (cps per ppb)	>30,000	>30,000
Background cps*	<5	<5
Oxide **	<0.3	<0.3
* Mean background counts, not SD of background		
** BaO/Ba ratio - Ba is used as it is present in S-21		

- Performance (sensitivity) can be improved approximately x10 by using ShieldTorch System to minimise ion energy spread

Use of MSA for High Purity Samples

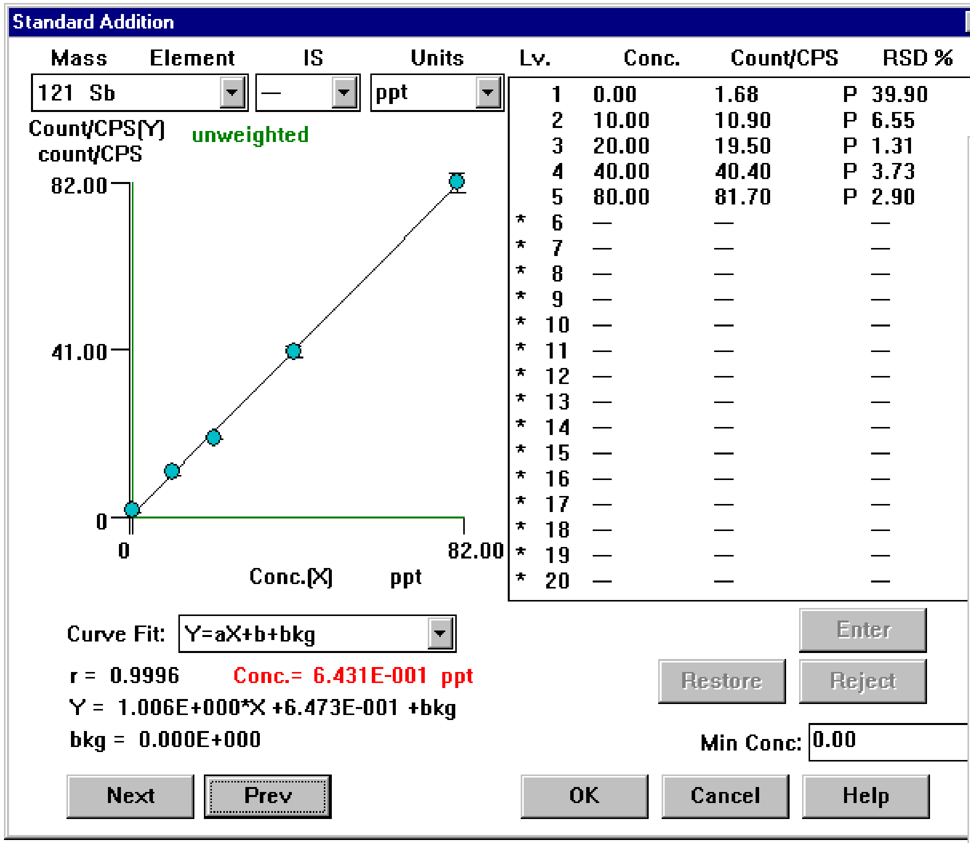


Measured signal and so reported concentration is sum of 1) background, 2) interference and 3) contamination. Instrument optimisation is used to minimise the contribution of 1) and 2)

MSA - often used for high purity matrices. MSA calibration on one sample can be applied to all samples of the same matrix type, so analysis time is not compromised

External calibration (with or without blank subtraction) can give under-reporting (reported value lower than true value), due to subtraction of too high a blank signal or signal changes due to sample transport and nebulization

Examples of Calibration in Simple Organic Matrix (Isopropyl Alcohol IPA)



Standard Addition

Mass Element: 121 Sb
IS: —
Units: ppt

Count/CPS(Y) unweighted
count/CPS

	Lv.	Conc.	Count/CPS		RSD %
	1	0.00	1.68	P	39.90
	2	10.00	10.90	P	6.55
	3	20.00	19.50	P	1.31
	4	40.00	40.40	P	3.73
	5	80.00	81.70	P	2.90
*	6	—	—		—
*	7	—	—		—
*	8	—	—		—
*	9	—	—		—
*	10	—	—		—
*	11	—	—		—
*	12	—	—		—
*	13	—	—		—
*	14	—	—		—
*	15	—	—		—
*	16	—	—		—
*	17	—	—		—
*	18	—	—		—
*	19	—	—		—
*	20	—	—		—

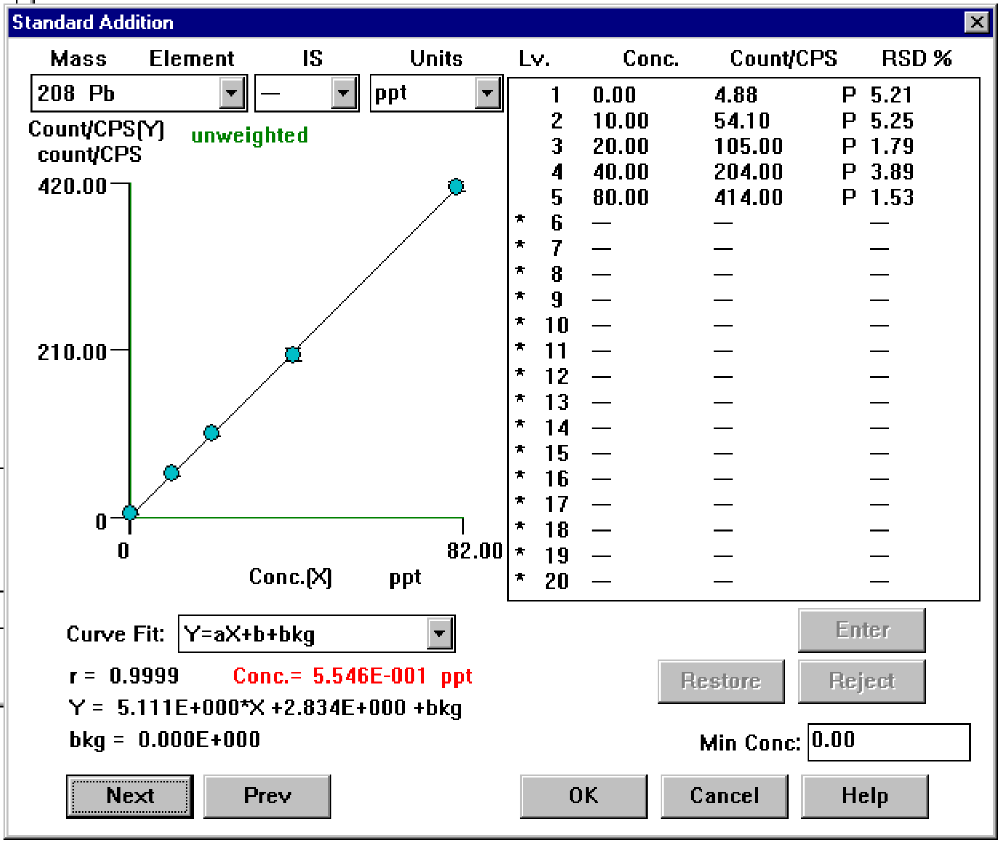
Curve Fit: Y=aX+b+bkg

r = 0.9996 Conc.= 6.431E-001 ppt

Y = 1.006E+000*X +6.473E-001 +bkg

bkg = 0.000E+000

Min Conc: 0.00



Standard Addition

Mass Element: 208 Pb
IS: —
Units: ppt

Count/CPS(Y) unweighted
count/CPS

	Lv.	Conc.	Count/CPS		RSD %
	1	0.00	4.88	P	5.21
	2	10.00	54.10	P	5.25
	3	20.00	105.00	P	1.79
	4	40.00	204.00	P	3.89
	5	80.00	414.00	P	1.53
*	6	—	—		—
*	7	—	—		—
*	8	—	—		—
*	9	—	—		—
*	10	—	—		—
*	11	—	—		—
*	12	—	—		—
*	13	—	—		—
*	14	—	—		—
*	15	—	—		—
*	16	—	—		—
*	17	—	—		—
*	18	—	—		—
*	19	—	—		—
*	20	—	—		—

Curve Fit: Y=aX+b+bkg

r = 0.9999 Conc.= 5.546E-001 ppt

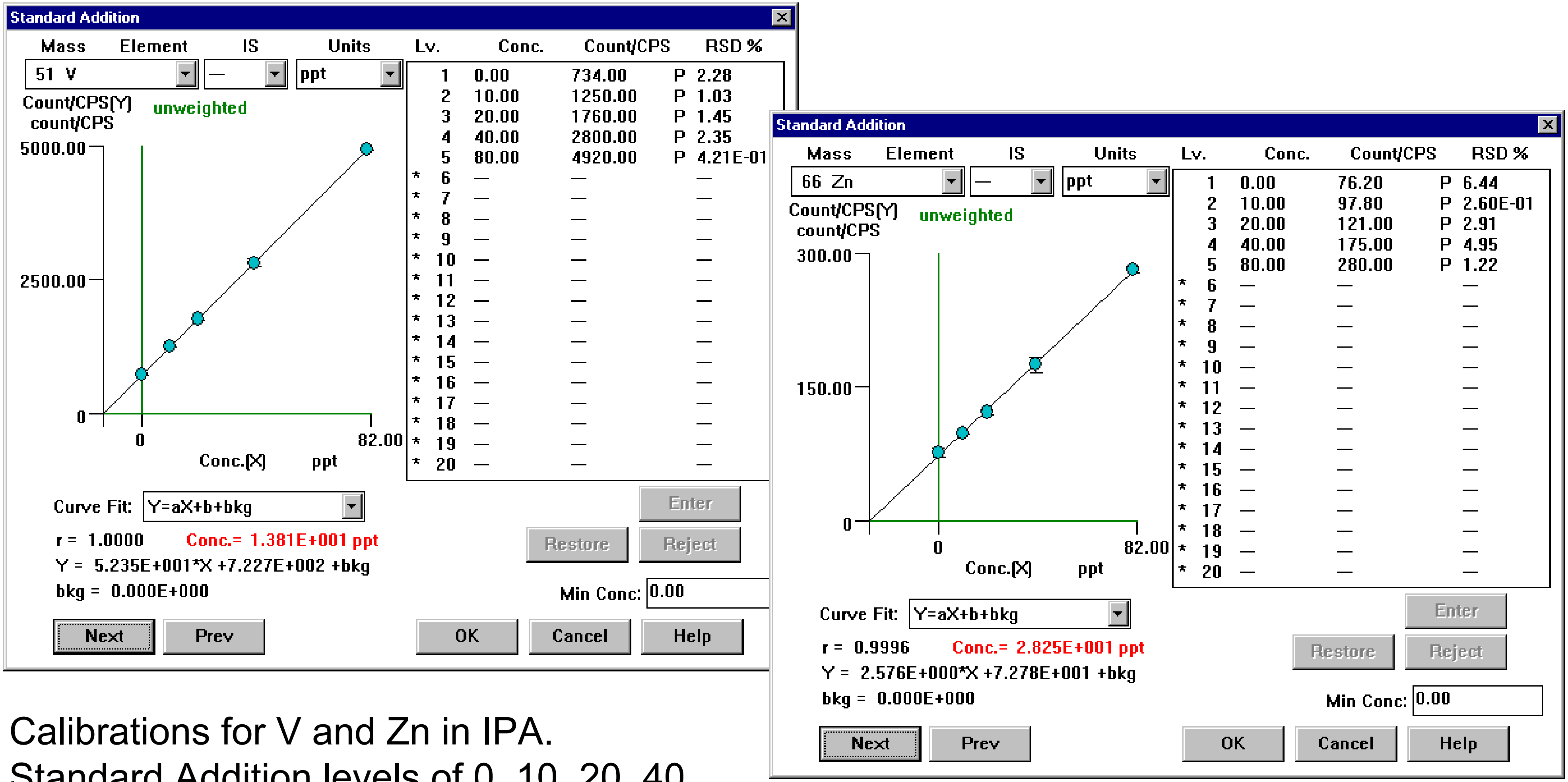
Y = 5.111E+000*X +2.834E+000 +bkg

bkg = 0.000E+000

Min Conc: 0.00

Calibrations for Sb and Pb in IPA. Standard Addition levels of 0, 10, 20, 40 and 80 ng/L (ppt)

Examples of Calibration in Simple Organic Matrix (Isopropyl Alcohol IPA)



Mass: 51 V Element IS: — Units: ppt

Count/CPS(Y) unweighted
count/CPS

Lv.	Conc.	Count/CPS	RSD %
1	0.00	734.00	P 2.28
2	10.00	1250.00	P 1.03
3	20.00	1760.00	P 1.45
4	40.00	2800.00	P 2.35
5	80.00	4920.00	P 4.21E-01
* 6	—	—	—
* 7	—	—	—
* 8	—	—	—
* 9	—	—	—
* 10	—	—	—
* 11	—	—	—
* 12	—	—	—
* 13	—	—	—
* 14	—	—	—
* 15	—	—	—
* 16	—	—	—
* 17	—	—	—
* 18	—	—	—
* 19	—	—	—
* 20	—	—	—

Curve Fit: Y=aX+b+bkg

r = 1.0000 Conc.= 1.381E+001 ppt

Y = 5.235E+001*X +7.227E+002 +bkg

bkg = 0.000E+000

Min Conc: 0.00

Mass: 66 Zn Element IS: — Units: ppt

Count/CPS(Y) unweighted
count/CPS

Lv.	Conc.	Count/CPS	RSD %
1	0.00	76.20	P 6.44
2	10.00	97.80	P 2.60E-01
3	20.00	121.00	P 2.91
4	40.00	175.00	P 4.95
5	80.00	280.00	P 1.22
* 6	—	—	—
* 7	—	—	—
* 8	—	—	—
* 9	—	—	—
* 10	—	—	—
* 11	—	—	—
* 12	—	—	—
* 13	—	—	—
* 14	—	—	—
* 15	—	—	—
* 16	—	—	—
* 17	—	—	—
* 18	—	—	—
* 19	—	—	—
* 20	—	—	—

Curve Fit: Y=aX+b+bkg

r = 0.9996 Conc.= 2.825E+001 ppt

Y = 2.576E+000*X +7.278E+001 +bkg

bkg = 0.000E+000

Min Conc: 0.00

Calibrations for V and Zn in IPA. Standard Addition levels of 0, 10, 20, 40 and 80 ng/L (ppt)

Potential Problem Elements in Organics

Argon-based Interferences

Element	Mass	Overlap
K	39	$^{38}Ar^{1}H$
Ca	40	^{40}Ar
Fe	56	$^{40}Ar^{16}O$

Well established method exists to remove these overlaps
Cool plasma ICP-MS - standard method in semiconductor labs

Organic matrix-based overlaps

Element	Mass	Overlap
Mg	24	$^{12}C_2$
Cr	52	$^{40}Ar^{12}C$

Do the same Cool Plasma conditions also work for organics?

Myths and Rumors about Cool Plasma

"Cool Plasmas are fragile and not robust enough to analyse high matrix samples"

- BUT - not all cool plasma configurations are "fragile"
  - high-matrix samples are analyzed routinely by cool plasma ICP-MS in semiconductor and other applications
    - high concentrations of mineral acids (e.g. 10% H_2SO_4)
    - 1000ppm high-purity metal digests (e.g. precious metals, Cu, Co, etc.)

- Same hardware technology and similar operating conditions can be applied to organic solvents, with similar benefits
    - reduction/removal of interfering species (Argon and Carbon-based)
    - MUCH easier setup and MUCH higher sensitivity than collision/reaction cell technology
      - single set of conditions for ALL cool plasma elements
    - lower detection limits than collision/reaction cell for key "difficult" elements - K, Ca & Fe - plus Mg and Cr in organics

Defining Organic Samples

- Organic materials used into five (5) distinct types, each requiring slightly differing analytical approach

1. Water soluble sample types
    - Tetra-Methyl Ammonium Hydroxide, water based strippers etc.

2. Non-volatile simple organics
    - N-Methyl Pyrrolidone, Ethyl Lactate etc

3. More volatile not necessarily water soluble
    - Methanol, Iso-propyl Alcohol (IPA),Toluene, Kerosene etc

4. Difficult volatile samples
    - Acetone
    - Methyl ethyl Ketone

5. Complex high-solids samples
    - Photoresist, LCD materials etc

Analytical Approaches (1)

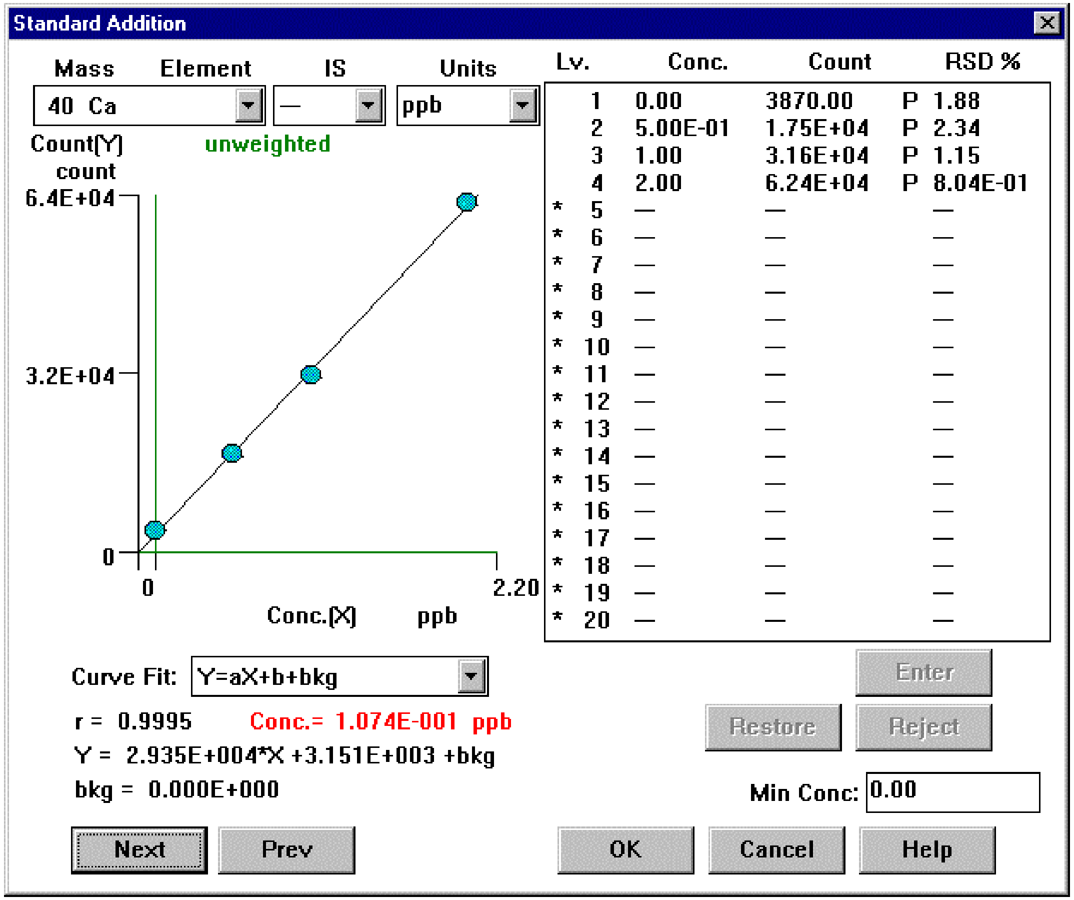
- Water soluble sample types which can be analyzed directly under normal aqueous conditions.
  - **No** oxygen addition is required as the water base provides oxygen for carbon combustion.
  - Analyzed at approximately normal flow rates for the Agilent 7500 (200-400 uL/min).

◆Tetra-Methyl Ammonium Hydroxide (TMAH) - normally supplied as 25% or 2% solutions in de-ionized water. Analyzed at 2% or 2.5% concentration

◆Tri-Methyl Ammonium Hydroxide (TMH) - analyzed as for TMAH

◆Water-based photoresist strippers, such as hydroxylamine/choline-based solvents - normally diluted 1:10 in de-ionized water.

Calibration for ^{40}Ca in Photoresist Stripper (hydroxylamine mixture)



Mass: 40 Ca
Element
IS: —
Units: ppb
unweighted

	Lv.	Conc.	Count		RSD %
	1	0.00	3870.00	P	1.88
	2	5.00E-01	1.75E+04	P	2.34
	3	1.00	3.16E+04	P	1.15
	4	2.00	6.24E+04	P	8.04E-01
*	5	—	—		—
*	6	—	—		—
*	7	—	—		—
*	8	—	—		—
*	9	—	—		—
*	10	—	—		—
*	11	—	—		—
*	12	—	—		—
*	13	—	—		—
*	14	—	—		—
*	15	—	—		—
*	16	—	—		—
*	17	—	—		—
*	18	—	—		—
*	19	—	—		—
*	20	—	—		—

Curve Fit: Y=aX+b+bkg

r = 0.9995 Conc.= 1.074E-001 ppb

Y = 2.935E+004*X +3.151E+003 +bkg

bkg = 0.000E+000

Min Conc: 0.00

Standard Addition Calibration at 0, 0.5, 1.0 and 2.0 ppb for Ca

Analyte measured at mass 40. ^{40}Ar background completely removed, even in complex solvent mixture

Sample run after simple 1:10 dilution in deionized water

Normal aqueous operating conditions

Analytical Approaches (2)

- Simple organic samples types which are not very volatile
- Can be analyzed directly and require no special conditions
  - Typically analyzed at normal flow rates for the Agilent 7500
    - 2 - 5% oxygen addition
    - Special Organics Torch.

◆N-Methyl Pyrrolidone (NMP) - water soluble, but can be analyzed undiluted as an organic sample

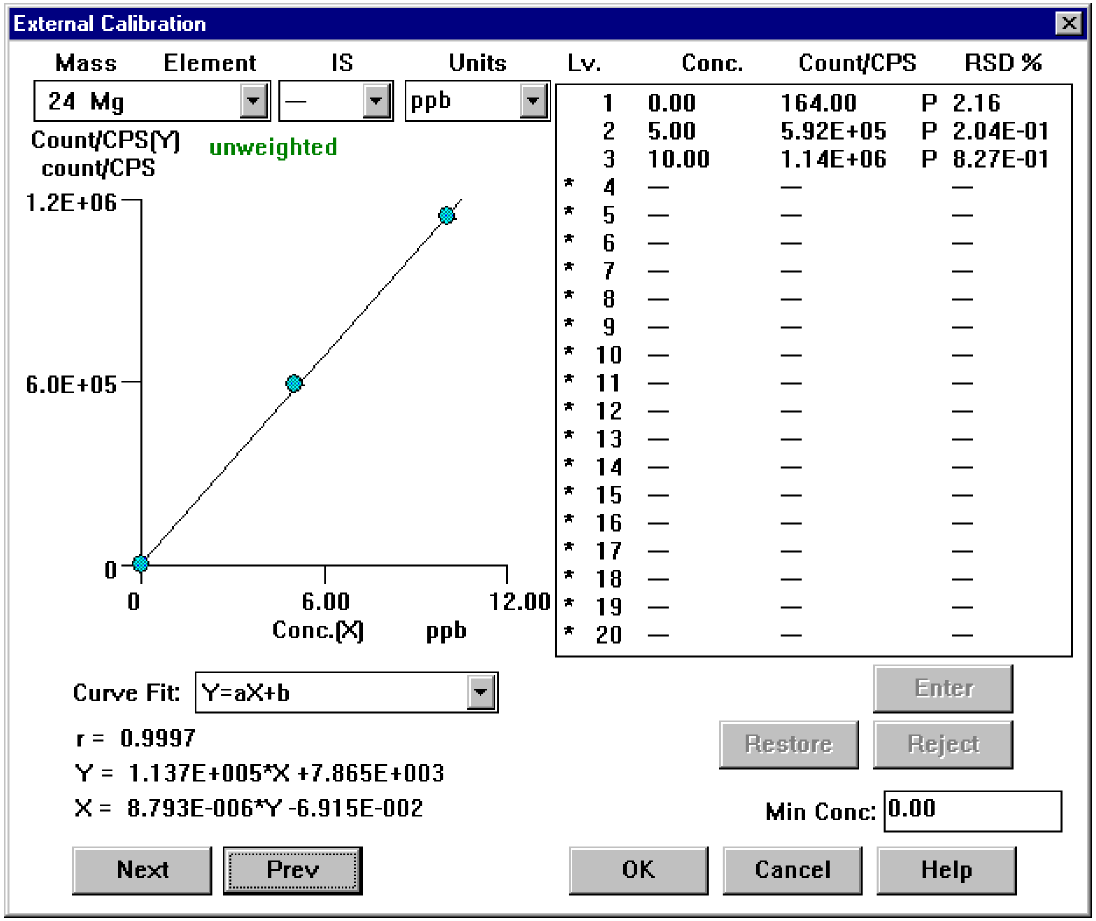
◆Ethyl Lactate - a typical solvent for photoresist

◆Propylene Glycol Monomethyl Ether (PGME)

◆Propylene Glycol Monomethyl Ether Acetate (PGMEA)

◆1:1 Methoxypropanol/butyl acetate (ZS-50)

Calibration for ^{24}Mg in PGMEA



Mass / Element: 24 Mg

IS: —

Units: ppb

unweighted

	Lv.	Conc.	Count/CPS		RSD %
	1	0.00	164.00	P	2.16
	2	5.00	5.92E+05	P	2.04E-01
	3	10.00	1.14E+06	P	8.27E-01
*	4	—	—		—
*	5	—	—		—
*	6	—	—		—
*	7	—	—		—
*	8	—	—		—
*	9	—	—		—
*	10	—	—		—
*	11	—	—		—
*	12	—	—		—
*	13	—	—		—
*	14	—	—		—
*	15	—	—		—
*	16	—	—		—
*	17	—	—		—
*	18	—	—		—
*	19	—	—		—
*	20	—	—		—

Curve Fit: Y=aX+b

r = 0.9997

Y = 1.137E+005*X +7.865E+003

X = 8.793E-006*Y -6.915E-002

Min Conc: 0.00

Standard Addition Calibration at 0, 5 and 10ppb for Mg

Analyte measured at mass 24. $^{12}C_2$ background completely removed

Sample is not highly volatile and can be analysed without requiring special operating conditions

Analytical Approaches (3)

- More difficult samples types which are more volatile
  - would disrupt the plasma more
- Analysed at a lower sample flow rate
  - oxygen addition at approx 5%
  - Special Organics Torch

◆Methanol

◆Ethanol

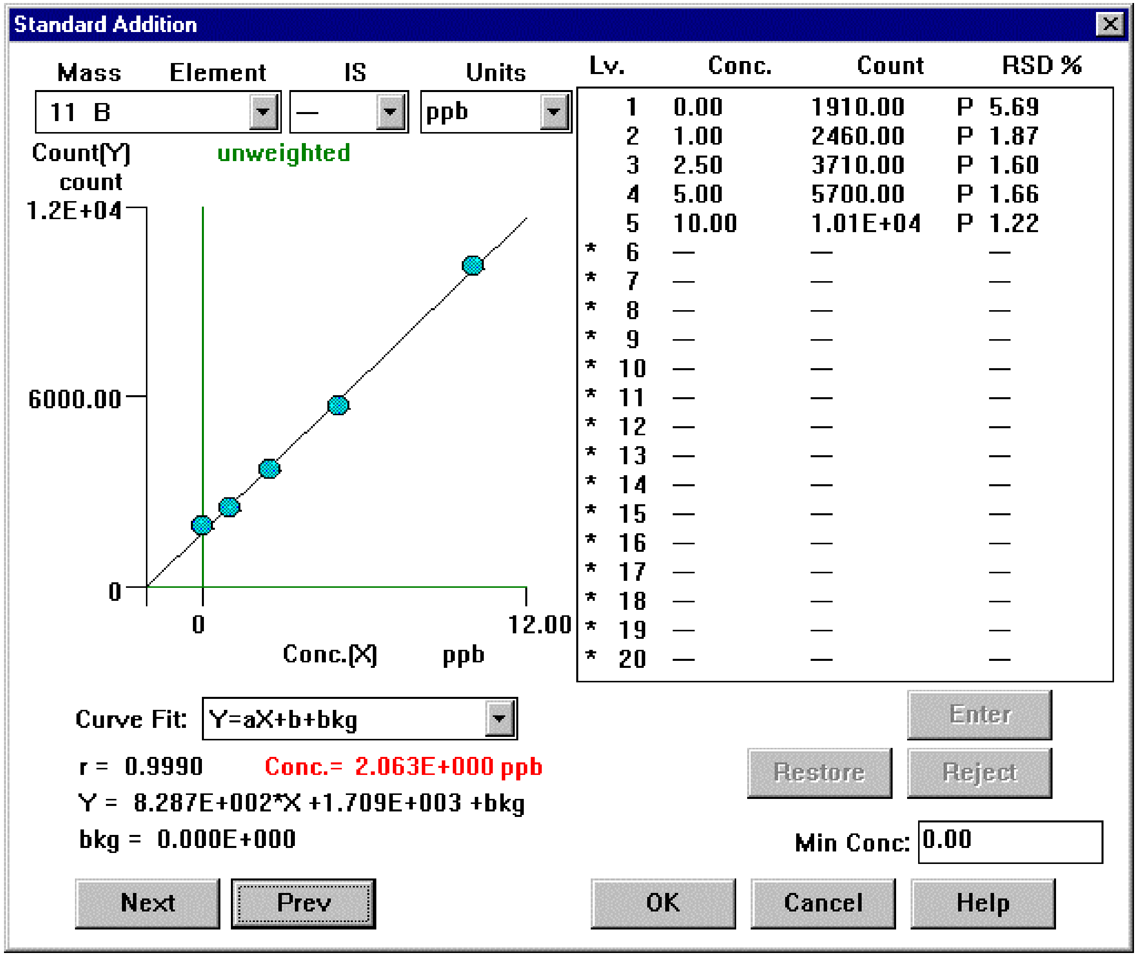
◆Iso-propyl Alcohol (IPA)

◆Toluene

◆Kerosene

◆Xylene

Calibration for ^{11}B in Methanol



Mass: 11
Element: B
IS: —
Units: ppb

	Lv.	Conc.	Count		RSD %
	1	0.00	1910.00	P	5.69
	2	1.00	2460.00	P	1.87
	3	2.50	3710.00	P	1.60
	4	5.00	5700.00	P	1.66
	5	10.00	1.01E+04	P	1.22
*	6	—	—		—
*	7	—	—		—
*	8	—	—		—
*	9	—	—		—
*	10	—	—		—
*	11	—	—		—
*	12	—	—		—
*	13	—	—		—
*	14	—	—		—
*	15	—	—		—
*	16	—	—		—
*	17	—	—		—
*	18	—	—		—
*	19	—	—		—
*	20	—	—		—

Curve Fit: Y=aX+b+bkg

r = 0.9990 Conc.= 2.063E+000 ppb

Y = 8.287E+002*X +1.709E+003 +bkg

bkg = 0.000E+000

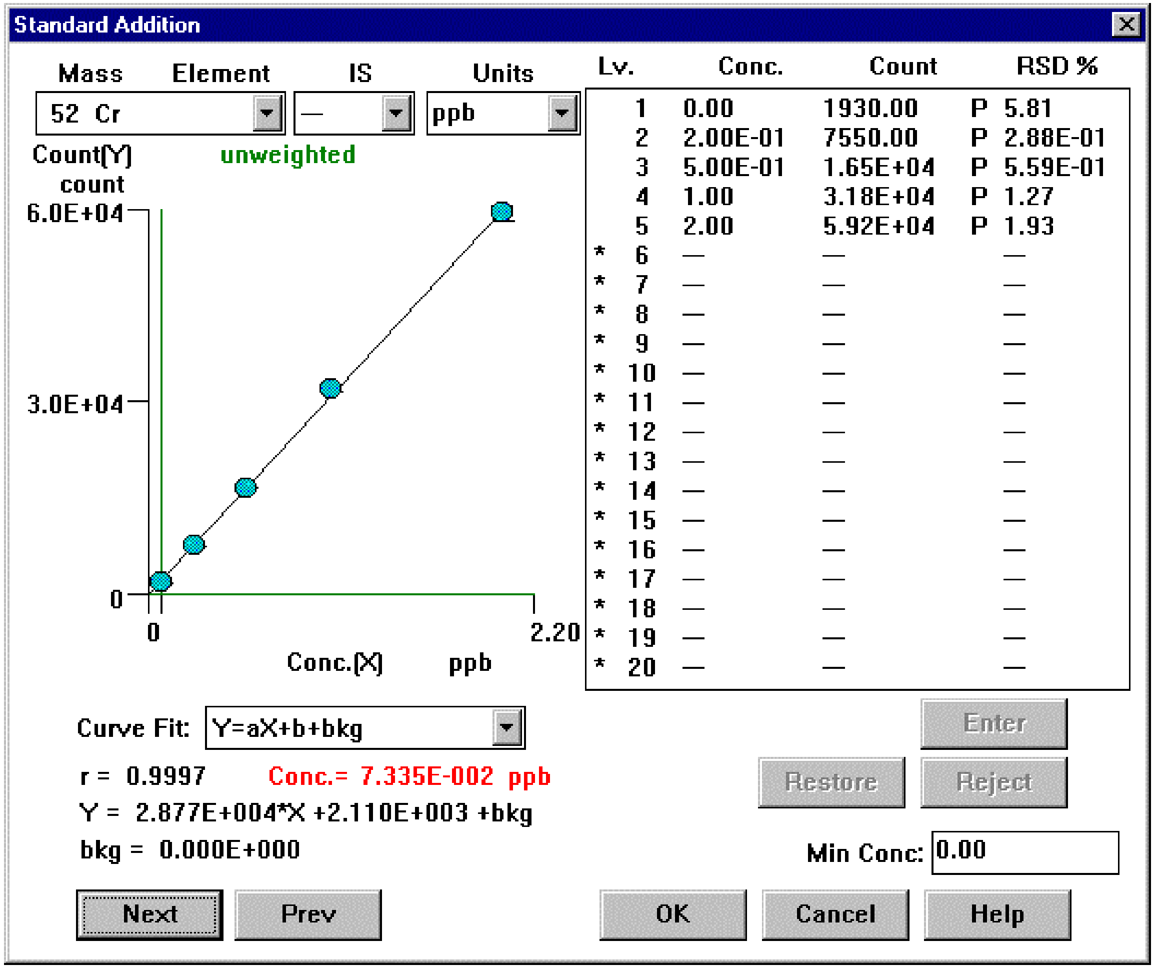
Min Conc: 0.00

Standard Addition Calibration at 0, 1, 2.5, 5 and 10ppb for B

Analyte measured at mass 11. ^{12}C signal intensity reduced and so no interference from adjacent peak

Sample is moderately volatile and can be analysed at a flow rate of 100 uL/min

Calibration for ^{52}Cr in Methanol



Mass	Element	IS	Units
52	Cr	—	ppb

	Lv.	Conc.	Count		RSD %
	1	0.00	1930.00	P	5.81
	2	2.00E-01	7550.00	P	2.88E-01
	3	5.00E-01	1.65E+04	P	5.59E-01
	4	1.00	3.18E+04	P	1.27
	5	2.00	5.92E+04	P	1.93
*	6	—	—		—
*	7	—	—		—
*	8	—	—		—
*	9	—	—		—
*	10	—	—		—
*	11	—	—		—
*	12	—	—		—
*	13	—	—		—
*	14	—	—		—
*	15	—	—		—
*	16	—	—		—
*	17	—	—		—
*	18	—	—		—
*	19	—	—		—
*	20	—	—		—

Curve Fit: Y=aX+b+bkg

r = 0.9997 Conc.= 7.335E-002 ppb

Y = 2.877E+004*X +2.110E+003 +bkg

bkg = 0.000E+000

Min Conc: 0.00

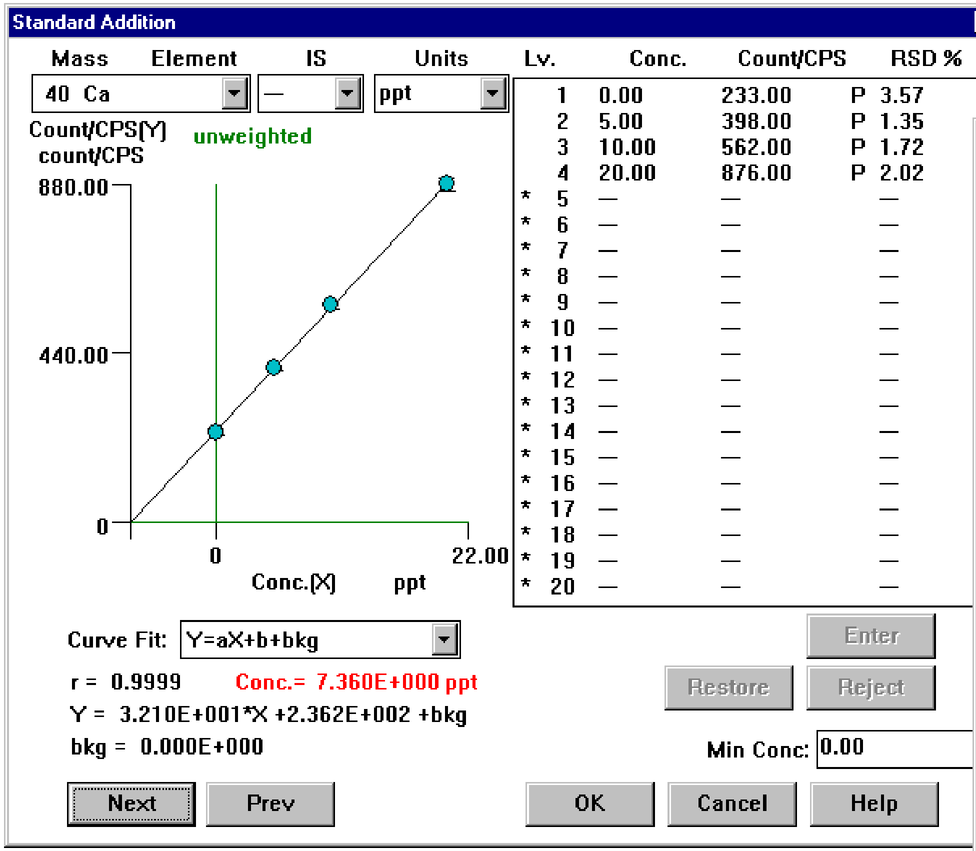
Standard Addition Calibration at 0, 0.2, 0.5, 1.0 and 2.0ppb for Cr

Analyte measured at mass 52. ^{40}Ar^{12}C interference removed.

Standard Addition result of 70ppt Cr in sample

Sample is moderately volatile and can be analysed at a flow rate of 100 uL/min

Cool Plasma Analysis of “Difficult” Elements in IPA - ^{40}Ca and ^{56}Fe



Mass Element: 40 Ca
IS: —
Units: ppt

	Lv.	Conc.	Count/CPS	RSD %
	1	0.00	233.00	P 3.57
	2	5.00	398.00	P 1.35
	3	10.00	562.00	P 1.72
	4	20.00	876.00	P 2.02
*	5	—	—	—
*	6	—	—	—
*	7	—	—	—
*	8	—	—	—
*	9	—	—	—
*	10	—	—	—
*	11	—	—	—
*	12	—	—	—
*	13	—	—	—
*	14	—	—	—
*	15	—	—	—
*	16	—	—	—
*	17	—	—	—
*	18	—	—	—
*	19	—	—	—
*	20	—	—	—

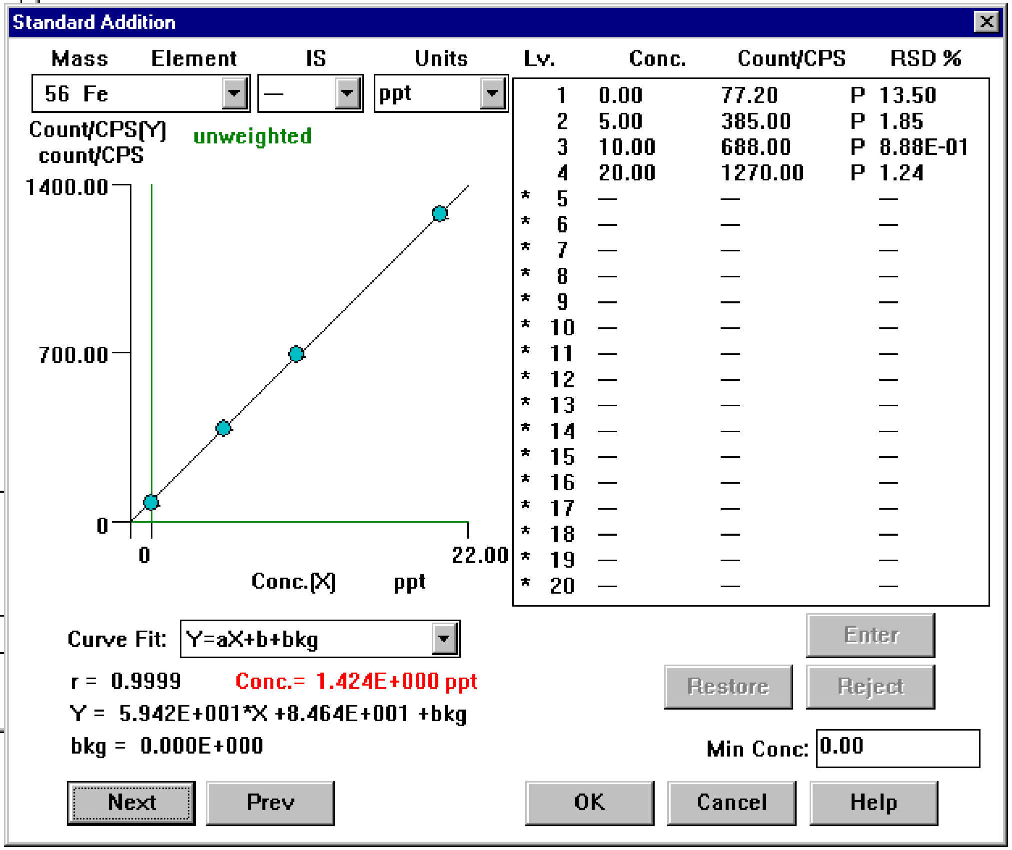
Curve Fit: Y=aX+b+bkg

r = 0.9999 Conc.= 7.360E+000 ppt

Y = 3.210E+001*X +2.362E+002 +bkg

bkg = 0.000E+000

Min Conc: 0.00



Mass Element: 56 Fe
IS: —
Units: ppt

	Lv.	Conc.	Count/CPS	RSD %
	1	0.00	77.20	P 13.50
	2	5.00	385.00	P 1.85
	3	10.00	688.00	P 8.88E-01
	4	20.00	1270.00	P 1.24
*	5	—	—	—
*	6	—	—	—
*	7	—	—	—
*	8	—	—	—
*	9	—	—	—
*	10	—	—	—
*	11	—	—	—
*	12	—	—	—
*	13	—	—	—
*	14	—	—	—
*	15	—	—	—
*	16	—	—	—
*	17	—	—	—
*	18	—	—	—
*	19	—	—	—
*	20	—	—	—

Curve Fit: Y=aX+b+bkg

r = 0.9999 Conc.= 1.424E+000 ppt

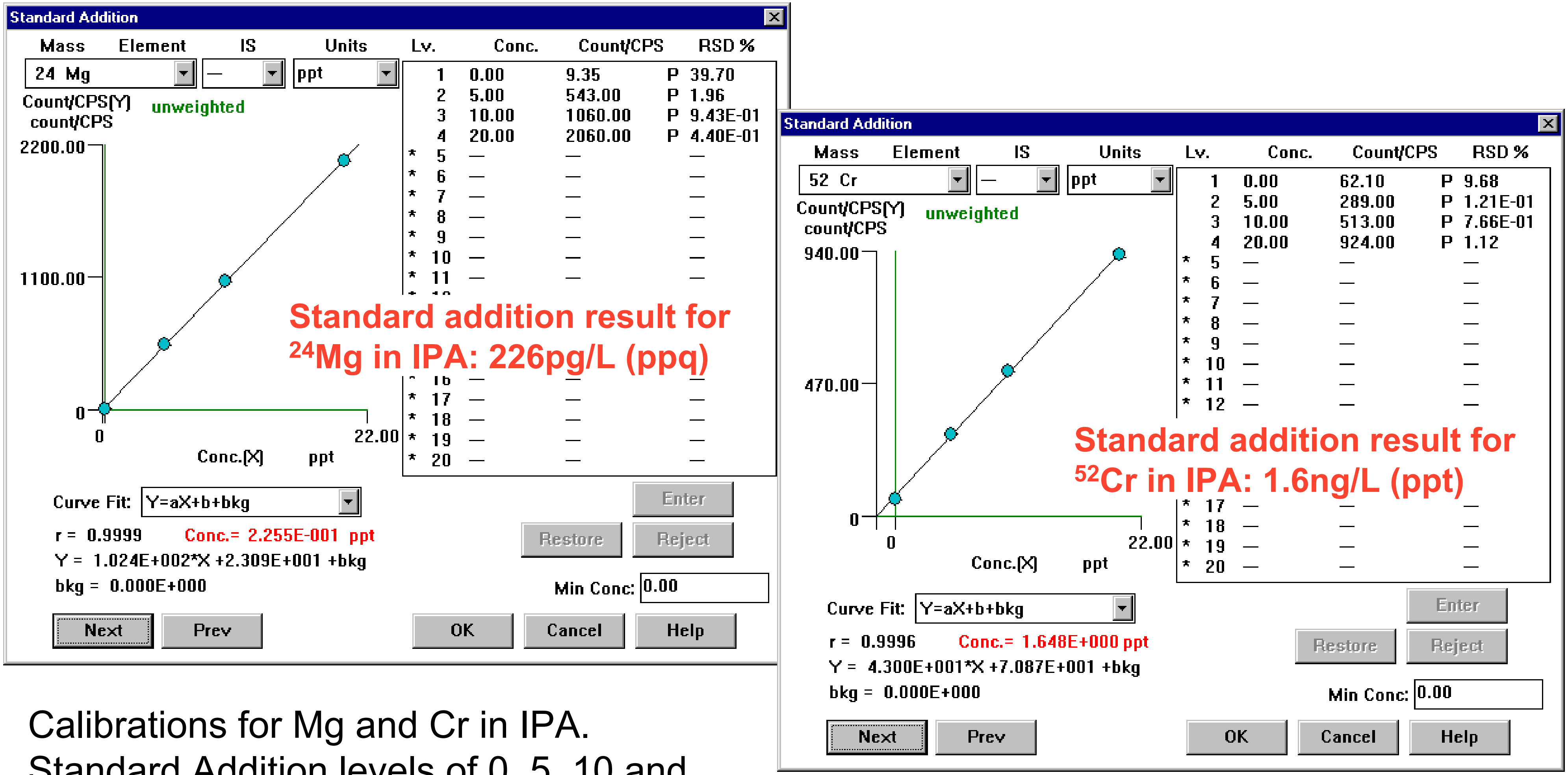
Y = 5.942E+001*X +8.464E+001 +bkg

bkg = 0.000E+000

Min Conc: 0.00

Calibrations for Ca and Fe in IPA. Standard Addition levels of 0, 5, 10 and 20 ng/L (ppt)

Cool Plasma Analysis of “Difficult” Elements in IPA - ^{24}Mg and ^{52}Cr



Standard Addition

Mass: 24 Mg
Element
IS: —
Units: ppt
Count/CPS(Y) unweighted
count/CPS

	Lv.	Conc.	Count/CPS	RSD %
	1	0.00	9.35	P 39.70
	2	5.00	543.00	P 1.96
	3	10.00	1060.00	P 9.43E-01
	4	20.00	2060.00	P 4.40E-01
*	5	—	—	—
*	6	—	—	—
*	7	—	—	—
*	8	—	—	—
*	9	—	—	—
*	10	—	—	—
*	11	—	—	—
	16	—	—	—
*	17	—	—	—
*	18	—	—	—
*	19	—	—	—
*	20	—	—	—

Curve Fit: Y=aX+b+bkg
r = 0.9999 Conc.= 2.255E-001 ppt
Y = 1.024E+002*X +2.309E+001 +bkg
bkg = 0.000E+000
Min Conc: 0.00

Standard addition result for ^{24}Mg in IPA: 226pg/L (ppq)

Standard Addition

Mass: 52 Cr
Element
IS: —
Units: ppt
Count/CPS(Y) unweighted
count/CPS

	Lv.	Conc.	Count/CPS	RSD %
	1	0.00	62.10	P 9.68
	2	5.00	289.00	P 1.21E-01
	3	10.00	513.00	P 7.66E-01
	4	20.00	924.00	P 1.12
*	5	—	—	—
*	6	—	—	—
*	7	—	—	—
*	8	—	—	—
*	9	—	—	—
*	10	—	—	—
*	11	—	—	—
*	12	—	—	—
*	17	—	—	—
*	18	—	—	—
*	19	—	—	—
*	20	—	—	—

Curve Fit: Y=aX+b+bkg
r = 0.9996 Conc.= 1.648E+000 ppt
Y = 4.300E+001*X +7.087E+001 +bkg
bkg = 0.000E+000
Min Conc: 0.00

Standard addition result for ^{52}Cr in IPA: 1.6ng/L (ppt)

Calibrations for Mg and Cr in IPA. Standard Addition levels of 0, 5, 10 and 20 ng/L (ppt)

Quantitative Results in IPA

Element	Mass	BEC (ppt)	3s LOD (ppt)	Mode
Li	7	0.256	0.035	Cool
Na	23	1.855	4.179	Cool
Mg	24	0.226	0.109	Cool
Al	27	1.639	1.018	Cool
K	39	2.795	3.795	Cool
Ca	40	7.36	0.779	Cool
Ti	48	74.14	1.670	Hot
V	51	13.81	0.961	Hot
Cr	52	1.648	0.419	Cool
Mn	55	0.168	0.011	Cool
Fe	56	1.424	0.526	Cool
Co	59	0.251	0.033	Cool
Ni	60	0.627	0.172	Cool
Cu	63	0.37	1.053	Cool
Zn	66	28.25	5.688	Hot
As	75	32.07	6.513	Hot
Sn	118	20.63	2.899	Hot
Sb	121	0.643	2.004	Hot
Ba	137	0.744	0.656	Hot
Pb	208	0.555	0.149	Hot

BEC and LOD figures taken from Standard Addition calibrations

Most elements have 3s LOD below 1ppt. “Difficult” elements Mg and Cr have LOD below 500 ppq

Simple automated switch between one set of hot plasma and one set of cool plasma conditions:

- No single element optimization
- No special conditions for specific interferences
- No corrosive or explosive gases required (oxygen at 20% in Ar)

Analysis of Kerosene

- Samples provided by ATOFINA Fina Research, Belgium
- High-purity kerosene
- Sample spiked with S-21 to give calibration standards from 100 ng/L (ppt) to 1000 ng/L
  - Method of Standard Additions (MSA) used
  - Automated switch between hot and cool plasma conditions within run is possible on 7500 (improved torchbox position precision and robustness compared to 4500)

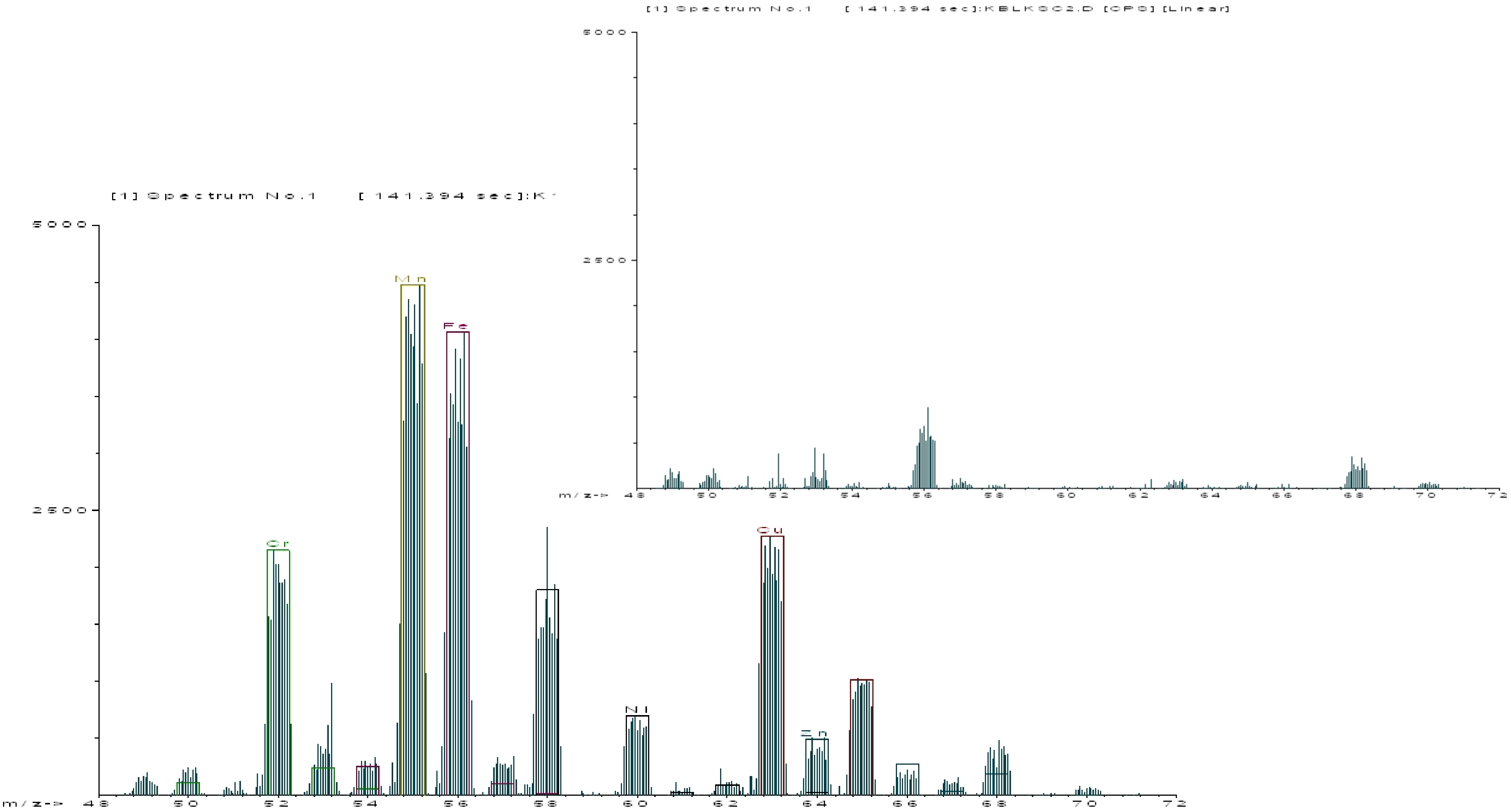
ATOFINA

FINA RESEARCH

Analyse

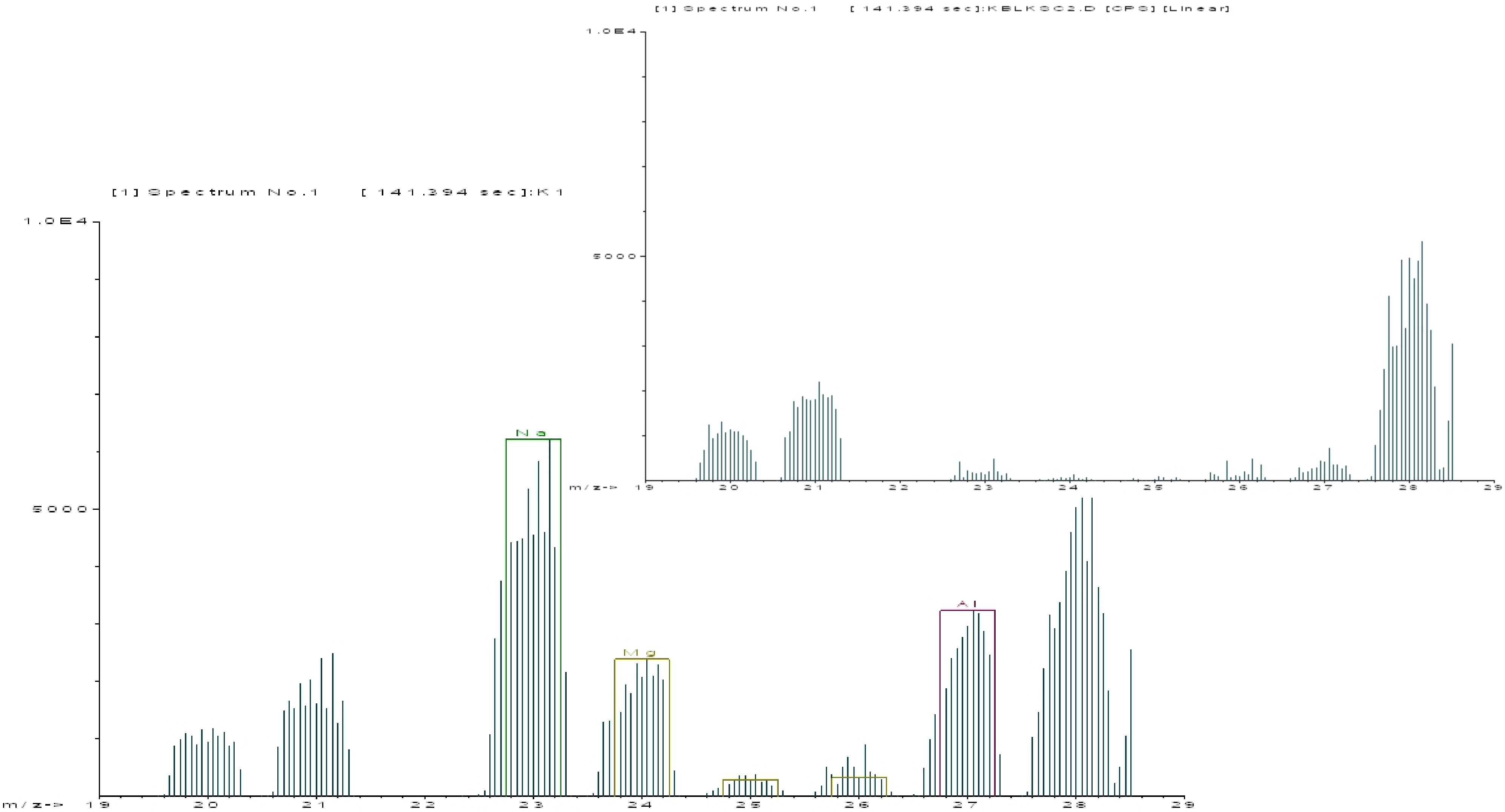
Analyses Elémentaires

Kerosene Blank and 1ppb Spike



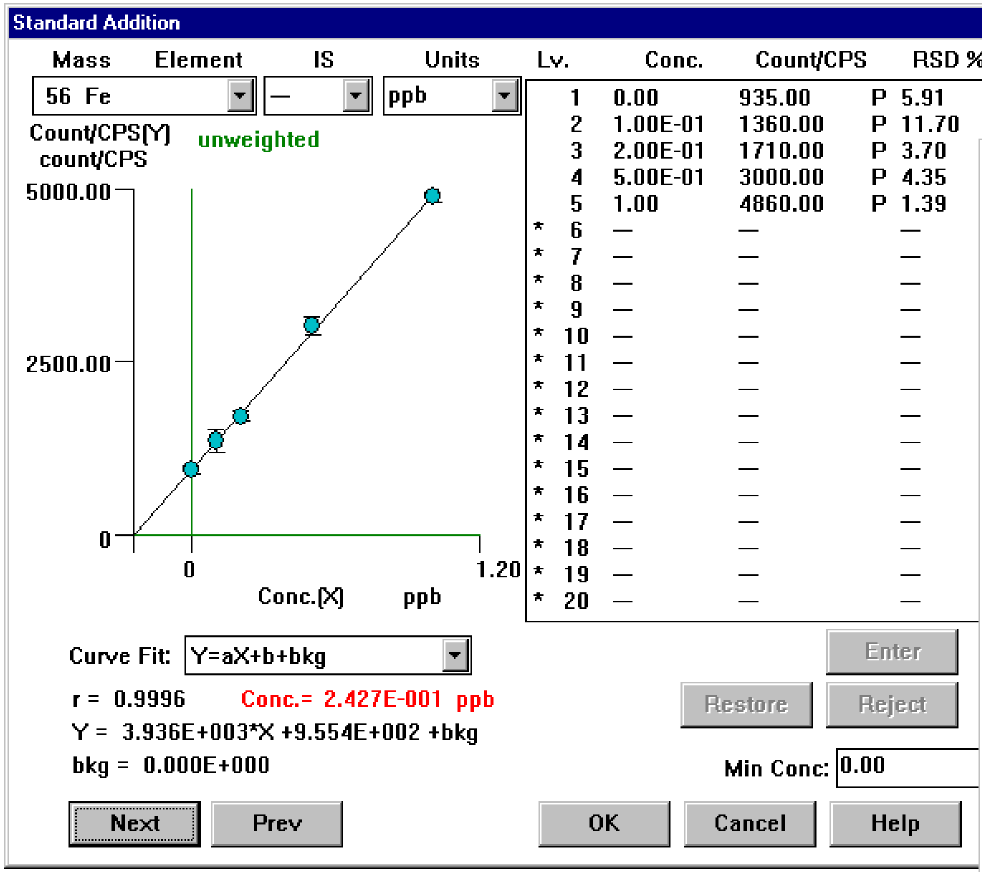
Scan of kerosene blank (top) and same sample spiked at 1 ug/L (ppb) for Cr, Mn, Fe, Ni, Cu and Zn (no background or blank subtraction)

Kerosene Blank and 1ppb Spike



Scan of kerosene blank and same sample spiked at 1 ug/L (ppb) for Na, Mg and Al (no background or blank subtraction)

Examples of Kerosene Calibrations under Cool Plasma Conditions



Mass: 56 Fe
Element
IS: —
Units: ppb

Count/CPS(Y) unweighted
count/CPS

Lv.	Conc.	Count/CPS	RSD %
1	0.00	935.00	P 5.91
2	1.00E-01	1360.00	P 11.70
3	2.00E-01	1710.00	P 3.70
4	5.00E-01	3000.00	P 4.35
5	1.00	4860.00	P 1.39
* 6	—	—	—
* 7	—	—	—
* 8	—	—	—
* 9	—	—	—
* 10	—	—	—
* 11	—	—	—
* 12	—	—	—
* 13	—	—	—
* 14	—	—	—
* 15	—	—	—
* 16	—	—	—
* 17	—	—	—
* 18	—	—	—
* 19	—	—	—
* 20	—	—	—

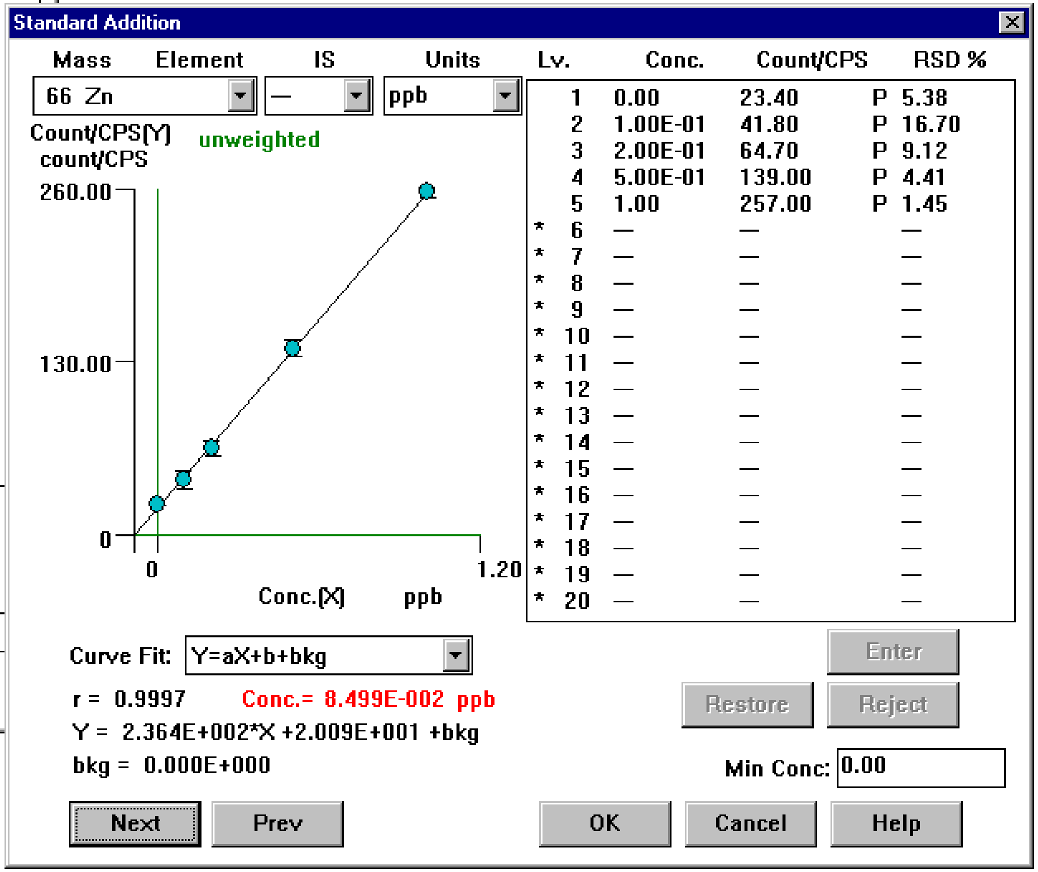
Curve Fit: Y=aX+b+bkg

r = 0.9996 Conc.= 2.427E-001 ppb

Y = 3.936E+003*X +9.554E+002 +bkg

bkg = 0.000E+000

Min Conc: 0.00



Mass: 66 Zn
Element
IS: —
Units: ppb

Count/CPS(Y) unweighted
count/CPS

Lv.	Conc.	Count/CPS	RSD %
1	0.00	23.40	P 5.38
2	1.00E-01	41.80	P 16.70
3	2.00E-01	64.70	P 9.12
4	5.00E-01	139.00	P 4.41
5	1.00	257.00	P 1.45
* 6	—	—	—
* 7	—	—	—
* 8	—	—	—
* 9	—	—	—
* 10	—	—	—
* 11	—	—	—
* 12	—	—	—
* 13	—	—	—
* 14	—	—	—
* 15	—	—	—
* 16	—	—	—
* 17	—	—	—
* 18	—	—	—
* 19	—	—	—
* 20	—	—	—

Curve Fit: Y=aX+b+bkg

r = 0.9997 Conc.= 8.499E-002 ppb

Y = 2.364E+002*X +2.009E+001 +bkg

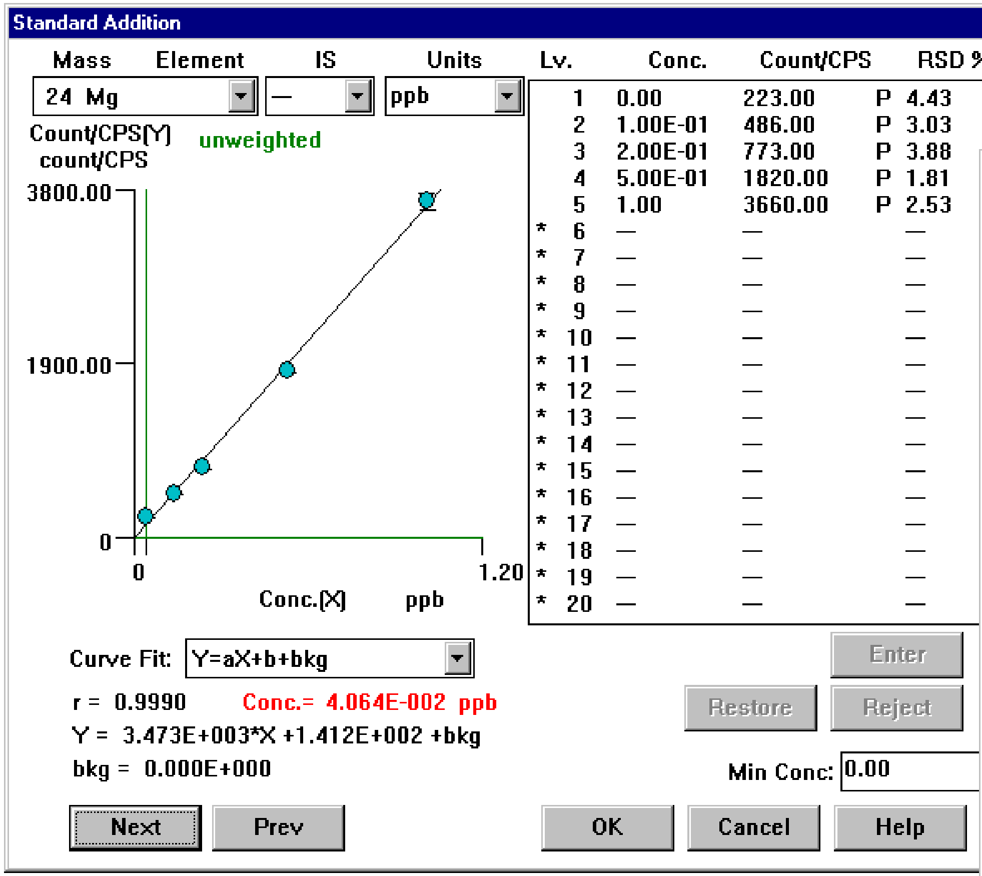
bkg = 0.000E+000

Min Conc: 0.00

Standard Addition Calibration levels for ^{56}Fe and ^{66}Zn at 0.1, 0.2, 0.5 and 1.0 ppb.

Note: Zn measured under cool plasma conditions

Examples of Kerosene Calibrations under Cool Plasma Conditions



Mass: 24 Mg
Element
IS: —
Units: ppb

Count/CPS[Y] unweighted
count/CPS

	Lv.	Conc.	Count/CPS	RSD %
	1	0.00	223.00	P 4.43
	2	1.00E-01	486.00	P 3.03
	3	2.00E-01	773.00	P 3.88
	4	5.00E-01	1820.00	P 1.81
	5	1.00	3660.00	P 2.53
*	6	—	—	—
*	7	—	—	—
*	8	—	—	—
*	9	—	—	—
*	10	—	—	—
*	11	—	—	—
*	12	—	—	—
*	13	—	—	—
*	14	—	—	—
*	15	—	—	—
*	16	—	—	—
*	17	—	—	—
*	18	—	—	—
*	19	—	—	—
*	20	—	—	—

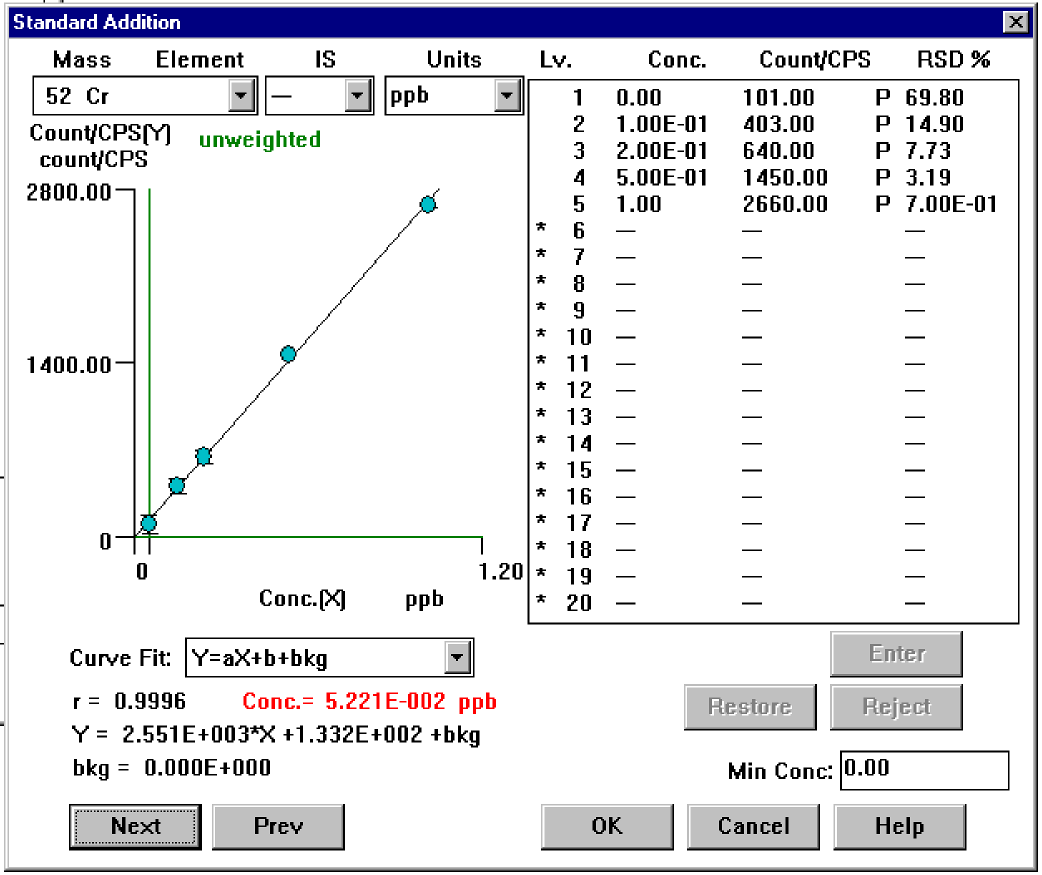
Curve Fit: Y=aX+b+bkg

r = 0.9990 Conc.= 4.064E-002 ppb

Y = 3.473E+003*X +1.412E+002 +bkg

bkg = 0.000E+000

Min Conc: 0.00



Mass: 52 Cr
Element
IS: —
Units: ppb

Count/CPS[Y] unweighted
count/CPS

	Lv.	Conc.	Count/CPS	RSD %
	1	0.00	101.00	P 69.80
	2	1.00E-01	403.00	P 14.90
	3	2.00E-01	640.00	P 7.73
	4	5.00E-01	1450.00	P 3.19
	5	1.00	2660.00	P 7.00E-01
*	6	—	—	—
*	7	—	—	—
*	8	—	—	—
*	9	—	—	—
*	10	—	—	—
*	11	—	—	—
*	12	—	—	—
*	13	—	—	—
*	14	—	—	—
*	15	—	—	—
*	16	—	—	—
*	17	—	—	—
*	18	—	—	—
*	19	—	—	—
*	20	—	—	—

Curve Fit: Y=aX+b+bkg

r = 0.9996 Conc.= 5.221E-002 ppb

Y = 2.551E+003*X +1.332E+002 +bkg

bkg = 0.000E+000

Min Conc: 0.00

Standard Addition Calibration levels for ^{24}Mg and ^{52}Cr at 0.1, 0.2, 0.5 and 1.0 ppb

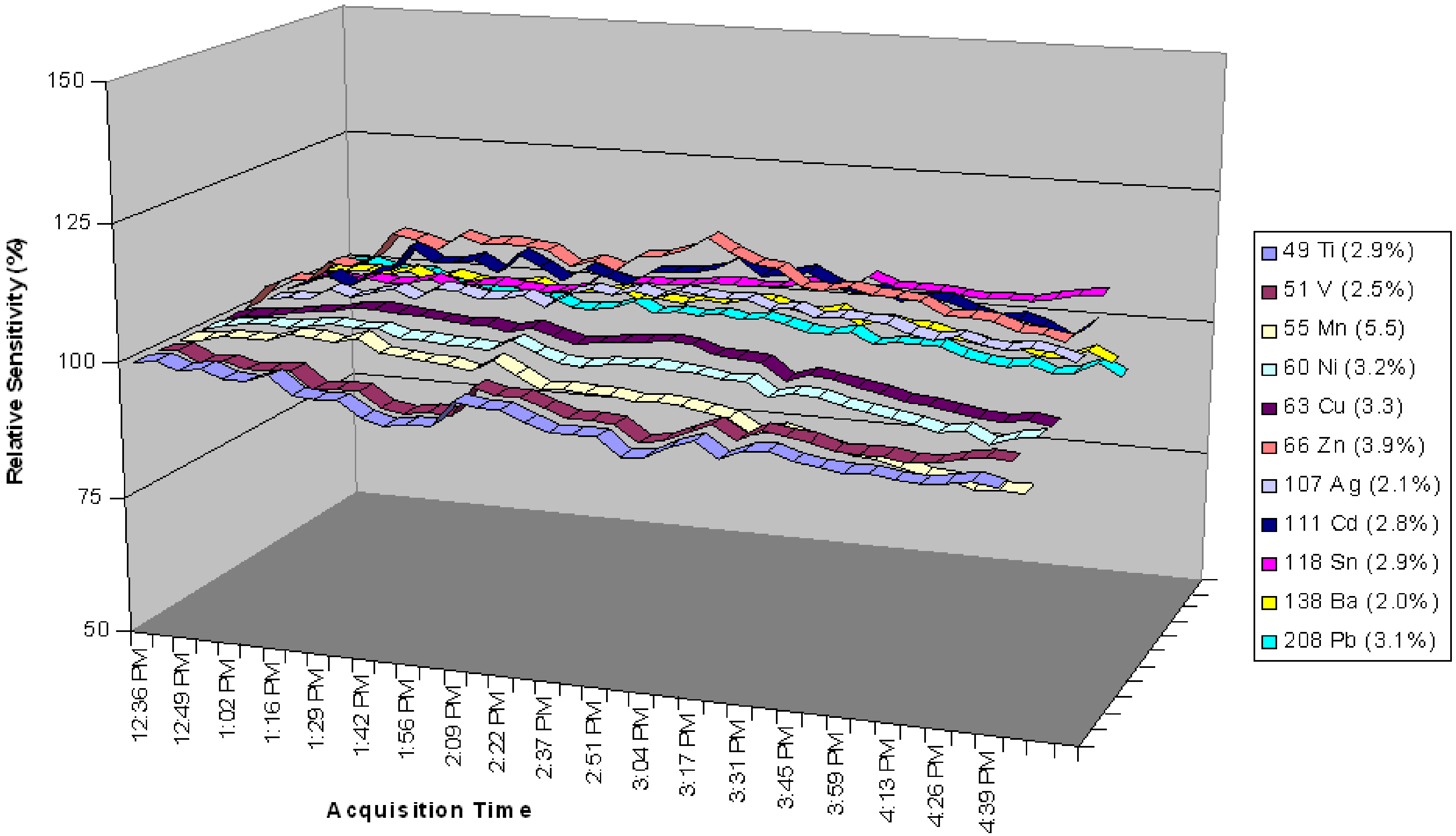
Agilent 7500 ICP-MS Performance for Analysis of Kerosene

Element	Isotope	BEC (ppt)*	3s LOD (ppt)	Plasma Conditions**
B	10	1631.0	381.9	Hot
Na	23	62.9	9.8	Hot
Na	23	136.0	28.9	Cool
Mg	24	64.1	8.5	Cool
Al	27	706.6	121.7	Hot
Ti	49	198.7	99.3	Hot
Cr	52	39.5	82.8	Cool
V	51	12.8	5.6	Hot
Mn	55	43.4	37.8	Hot
Mn	55	55.0	25.3	Cool
Fe	56	239.1	42.4	Cool
Ni	60	30.2	8.3	Hot
Ni	60	37.2	8.5	Cool
Cu	63	30.5	7.5	Hot
Cu	63	57.3	9.1	Cool
Zn	66	147.6	36.8	Hot
Zn	66	99.8	16.1	Cool
Mo	98	10.9	7.6	Hot
Ag	107	8.8	4.5	Hot
Ag	107	16.5	2.7	Cool
Cd	111	74.2	44.3	Hot
Sn	120	31.6	1.3	Hot
Ba	138	33.1	9.2	Hot
Pb	208	60.5	11.8	Hot

* BEC is sum of background and trace contamination

** Plasma conditions can be switched automatically during sequence

Trace Elements in Xylene -
4-Hour Stability at 2ug/L Level. No ISTD



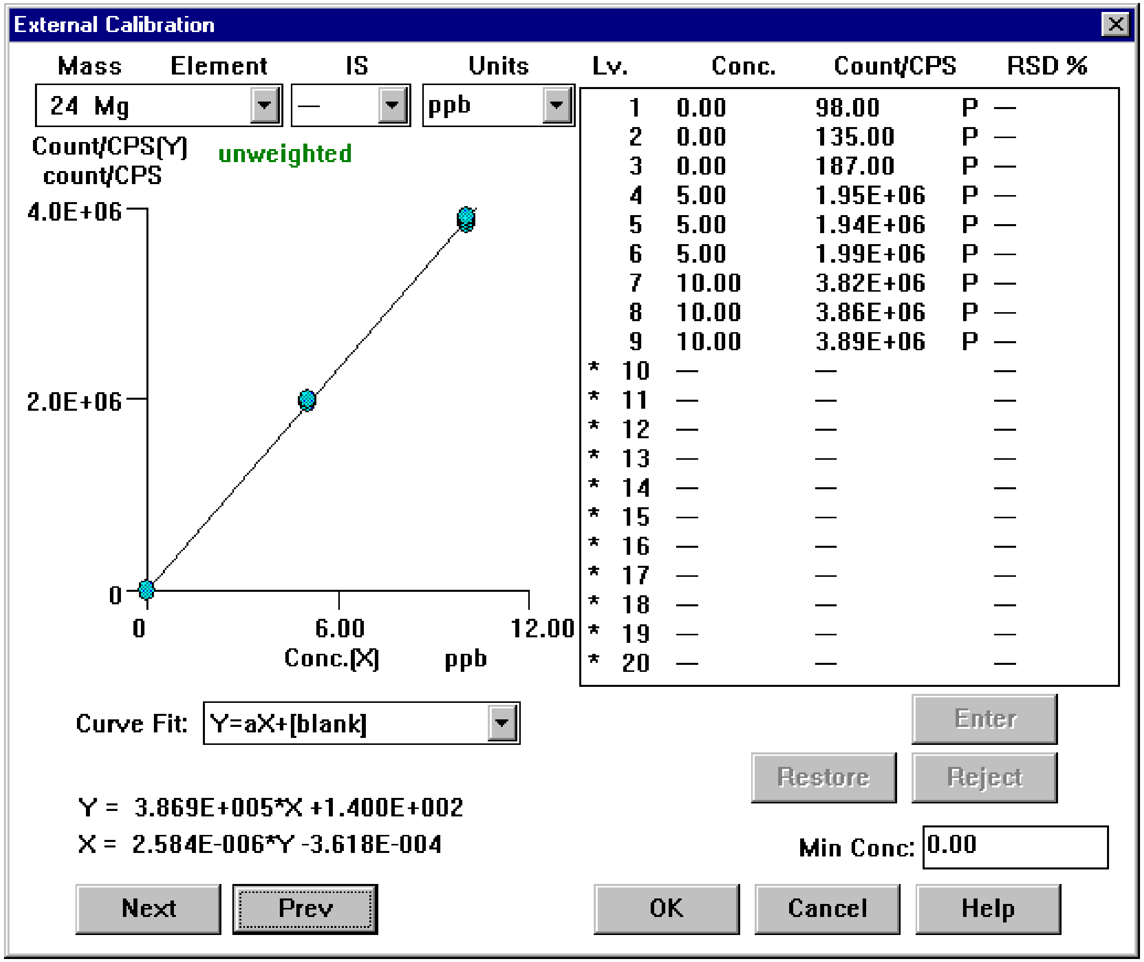
Analytical Approaches (4)

- Very difficult volatile samples types
- Special conditions required for successful analysis
- Analysed at a **very low flow rate**
  - Special Volatile Organics Torch
  - Spray chamber cooled to -5°C

    - Acetone

    - Methyl ethyl Ketone

Calibration for ^{24}Mg in Acetone



Mass: 24 Mg
Element:
IS: —
Units: ppb

unweighted

Lv.	Conc.	Count/CPS		RSD %
1	0.00	98.00	P	—
2	0.00	135.00	P	—
3	0.00	187.00	P	—
4	5.00	1.95E+06	P	—
5	5.00	1.94E+06	P	—
6	5.00	1.99E+06	P	—
7	10.00	3.82E+06	P	—
8	10.00	3.86E+06	P	—
9	10.00	3.89E+06	P	—
* 10	—	—		—
* 11	—	—		—
* 12	—	—		—
* 13	—	—		—
* 14	—	—		—
* 15	—	—		—
* 16	—	—		—
* 17	—	—		—
* 18	—	—		—
* 19	—	—		—
* 20	—	—		—

Curve Fit: Y=aX+[blank]

Y = 3.869E+005*X +1.400E+002
X = 2.584E-006*Y -3.618E-004

Min Conc: 0.00

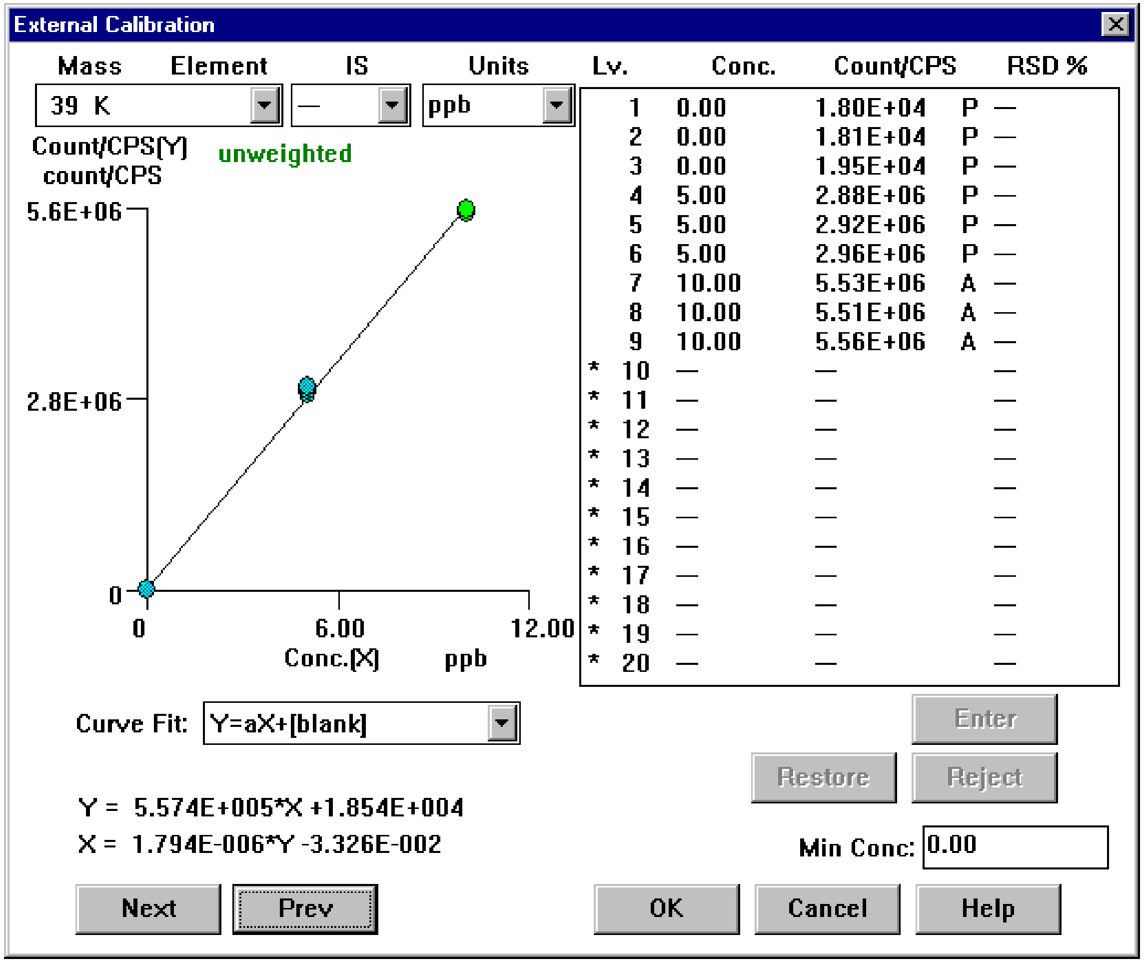
Standard Addition Calibration at 0, 5 and 10ppb for Mg

Analyte measured at mass 24. $^{12}C_2$ interference removed

Blank and standards each repeated 3 times, showing good reproducibility

Sample is very volatile and must be analysed at a flow rate of <50 uL/min. Special Volatile Organics Torch

Calibration for ^{39}K in Acetone



Mass: 39 K
Element: K
IS: —
Units: ppb

	Lv.	Conc.	Count/CPS		RSD %
	1	0.00	1.80E+04	P	—
	2	0.00	1.81E+04	P	—
	3	0.00	1.95E+04	P	—
	4	5.00	2.88E+06	P	—
	5	5.00	2.92E+06	P	—
	6	5.00	2.96E+06	P	—
	7	10.00	5.53E+06	A	—
	8	10.00	5.51E+06	A	—
	9	10.00	5.56E+06	A	—
*	10	—	—		—
*	11	—	—		—
*	12	—	—		—
*	13	—	—		—
*	14	—	—		—
*	15	—	—		—
*	16	—	—		—
*	17	—	—		—
*	18	—	—		—
*	19	—	—		—
*	20	—	—		—

Curve Fit: Y=aX+[blank]

Y = 5.574E+005*X +1.854E+004
X = 1.794E-006*Y -3.326E-002

Min Conc: 0.00

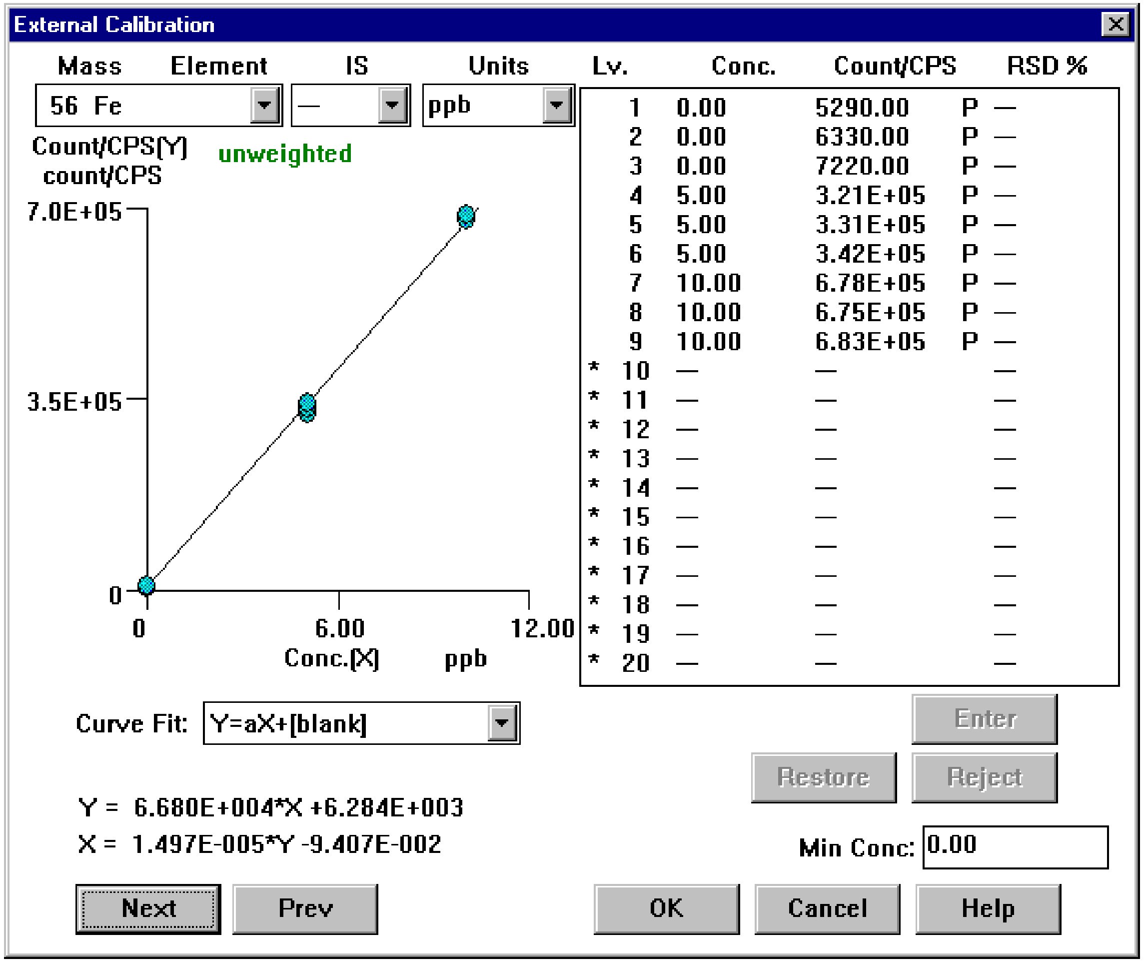
Standard Addition Calibration at 0, 5 and 10ppb for K

Analyte measured at mass 39. ^{38}Ar^{1}H interference removed

Blank and standards each repeated 3 times, showing good reproducibility

Sample is very volatile and must be analyzed at very low flow rate. Special Volatile Organics Torch

Calibration for ^{56}Fe in Acetone



Mass Element: 56 Fe

IS: —

Units: ppb

	Lv.	Conc.	Count/CPS		RSD %
	1	0.00	5290.00	P	—
	2	0.00	6330.00	P	—
	3	0.00	7220.00	P	—
	4	5.00	3.21E+05	P	—
	5	5.00	3.31E+05	P	—
	6	5.00	3.42E+05	P	—
	7	10.00	6.78E+05	P	—
	8	10.00	6.75E+05	P	—
	9	10.00	6.83E+05	P	—
*	10	—	—		—
*	11	—	—		—
*	12	—	—		—
*	13	—	—		—
*	14	—	—		—
*	15	—	—		—
*	16	—	—		—
*	17	—	—		—
*	18	—	—		—
*	19	—	—		—
*	20	—	—		—

Curve Fit: Y=aX+[blank]

Y = 6.680E+004*X +6.284E+003

X = 1.497E-005*Y -9.407E-002

Min Conc: 0.00

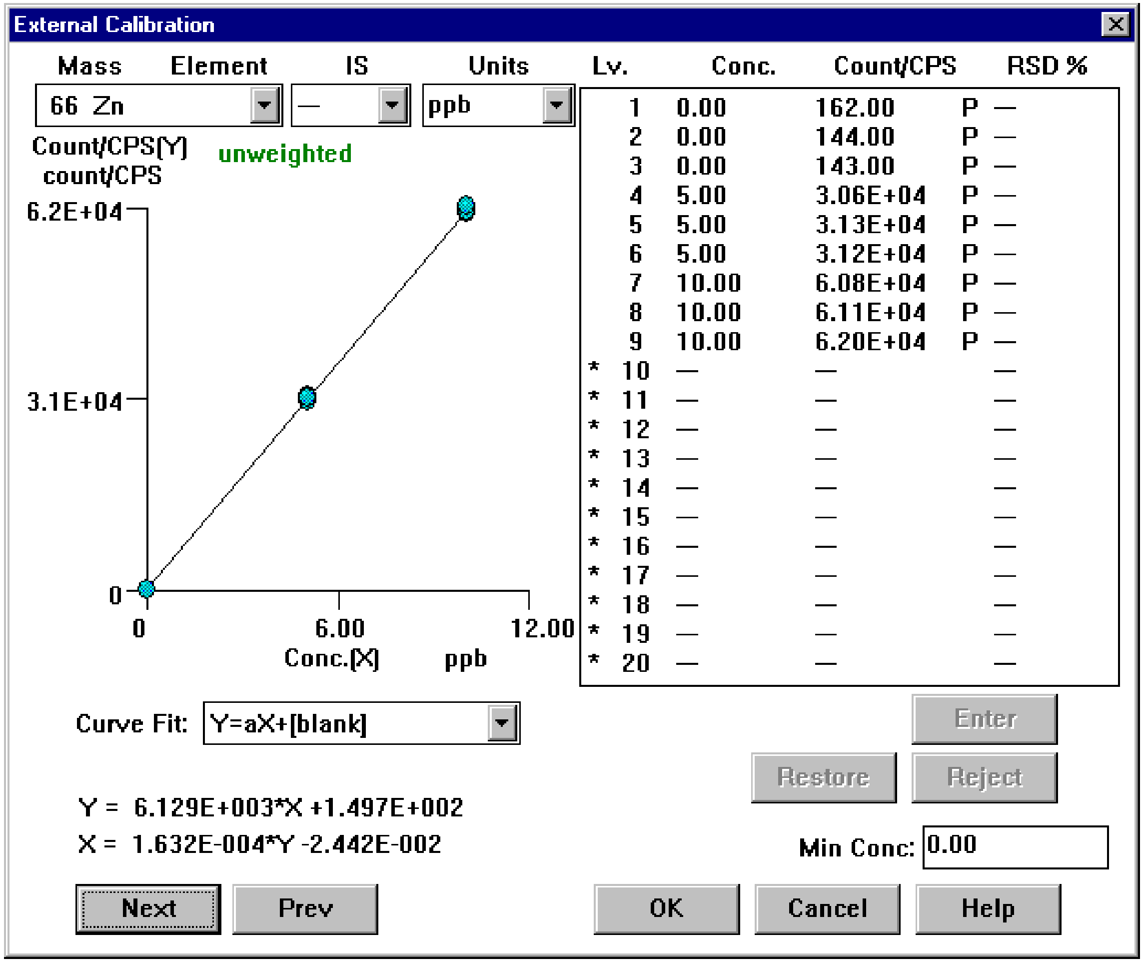
Standard Addition Calibration at 0, 5 and 10ppb for Fe

Analyte measured at mass 56. $^{40}Ar^{16}O$ interference removed

Blank and standards each repeated 3 times, showing good reproducibility

Sample is very volatile and must be analyzed at very low flow rate. Special Volatile Organics Torch

Calibration for ^{66}Zn in Acetone



Mass Element: 66 Zn

IS: —

Units: ppb

Count/CPS[Y] count/CPS unweighted

	Lv.	Conc.	Count/CPS		RSD %
	1	0.00	162.00	P	—
	2	0.00	144.00	P	—
	3	0.00	143.00	P	—
	4	5.00	3.06E+04	P	—
	5	5.00	3.13E+04	P	—
	6	5.00	3.12E+04	P	—
	7	10.00	6.08E+04	P	—
	8	10.00	6.11E+04	P	—
	9	10.00	6.20E+04	P	—
*	10	—	—		—
*	11	—	—		—
*	12	—	—		—
*	13	—	—		—
*	14	—	—		—
*	15	—	—		—
*	16	—	—		—
*	17	—	—		—
*	18	—	—		—
*	19	—	—		—
*	20	—	—		—

Curve Fit: Y=aX+[blank]

Y = 6.129E+003*X +1.497E+002

X = 1.632E-004*Y -2.442E-002

Min Conc: 0.00

Standard Addition Calibration at 0, 5 and 10ppb for Zn

Analyte measured at mass 66. High Power Cool Plasma maintains high energy to ensure good ionization even for poorly ionized elements

Sample is very volatile and must be analyzed at very low flow rate. Special Volatile Organics Torch

Analytical Approaches (5)

- Complex high-solids samples
- Can only be analyzed directly after dilution
  - Require dilution in an appropriate solvent
- Analytical conditions are selected as appropriate for the bulk solvent used.

  - Photoresist - normally supplied as a 30% resin
    - typically diluted 1:10 in NMP, PGMEA or ethyl lactate

  - Liquid Crystal
    - typically diluted 1:10 in a 1:1 mixture of methoxypropanol/ butylacetate

BEC Summary in Organic Samples

Element	Mass number	Acetone	IPA	ZS50	NMP	PGMEA
Torch		Volatile	Organic	Organic	Organic	Organic
Sample tube ID(mm)		0.16	0.2	0.3	0.3	0.3
Uptake rate(uL/min)		40	100-150	200-300	200-300	200-300
Li	7	0.5				
Na	23	190	1550	900	60	89
Mg	26	3	88	24	29	69
Al	27	15	32	6	230	180
K	39	33	160		240	94
Ca	40	21	130	60	280	510
Cr	52	4	10	32	550	100
Mn	55	21		1	220	68
Fe	56	94	13	46	4200	370
Co	59					820
Ni	60	2		16	730	210
Cu	63	110		126	580	160
Zn	64	24		47	2400	350
Zn	66	24		65	4900	480
Pb	208	10		2		27
*ZS-50(Nippon Zeon ltd.)Butyl acetate/Methoxy propanol=1/1)						
* Nebulizer: Quartz Concentric(Self aspiration)						Units - ppt

Organic Sample Analysis by Agilent 7500 ICP-MS - Summary

- New hardware and applications developments have extended the use of ShieldTorch ICP-MS into the analysis of almost all organic sample types

- Organic resistant sample introduction hardware is available

- High Power Cool Plasma gives
  - high energy to decompose complex organic samples
  - complete removal of plasma and carbon-based polyatomics under a single set of conditions
  - high sensitivity and low background for all elements typically required by the semiconductor industry

Conclusions

- Organic solvent analysis is a simple application on ICP-MS, provided
    - the correct hardware is selected (Pt cones, robust generator, extra MFC)
    - suitable sample introduction system is used (nebulizer, o-rings)
    - plasma conditions are optimized as appropriate (correct power for matrix)
    - oxygen addition is used to decompose carbon matrix
- Simple and complex organic matrices can be analyzed routinely
- Cool plasma is a highly effective technique for the removal of plasma and matrix interferences in organic solvents, and is easy to optimize, sensitive, stable and safe