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Inductively Coupled Plasma Mass Spectrometry; The Ideal Tool for Trace Element Fingerprinting of Forensic Materials?

Steve Shuttleworth

Steve Shuttleworth –
Product Specialist

11/20/08



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Forensic Analysis and Elemental Fingerprinting

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- Trace element fingerprinting allows the analyst to discriminate between samples.
- Analysis permits a determination of whether an association exists between a recovered fragment and a source of known origin.
- It's key to understand the sources of elemental variation arising from the sample and also from the analysis technique.

VARIAN Available Techniques CONFIDENTIAL



AA



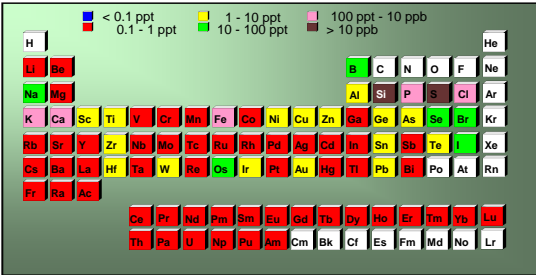
ICP-OES



ICP-MS

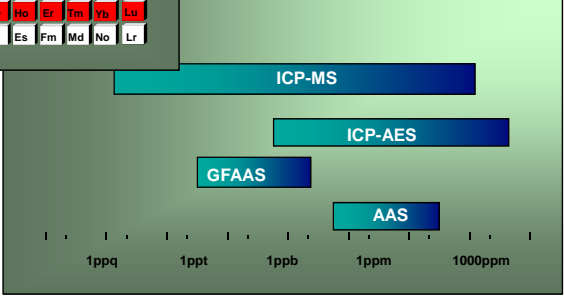
VARIAN Characteristics of ICP-MS CONFIDENTIAL

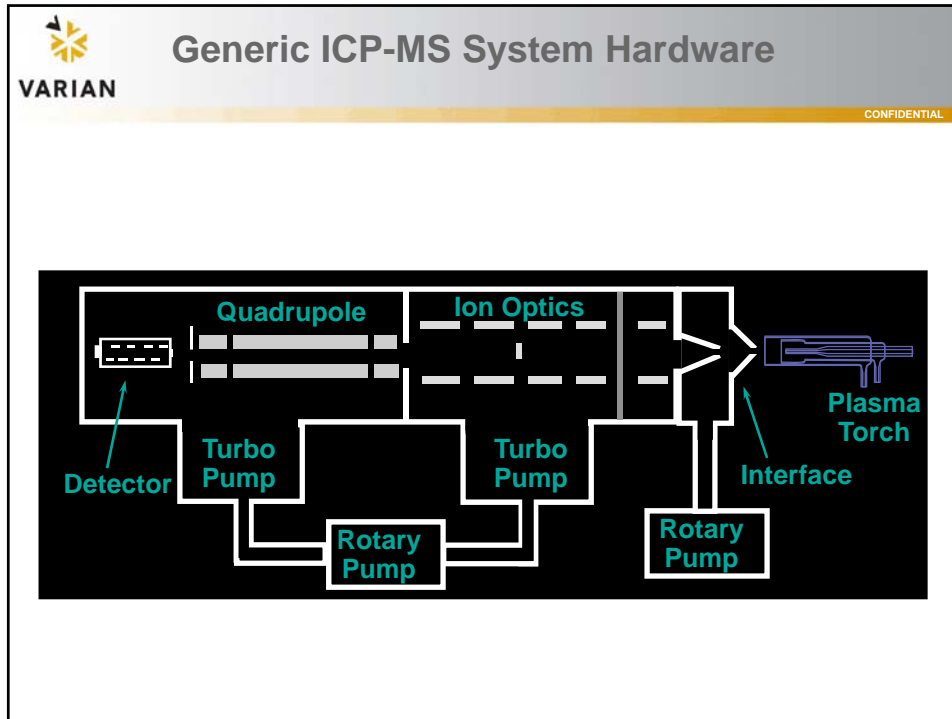
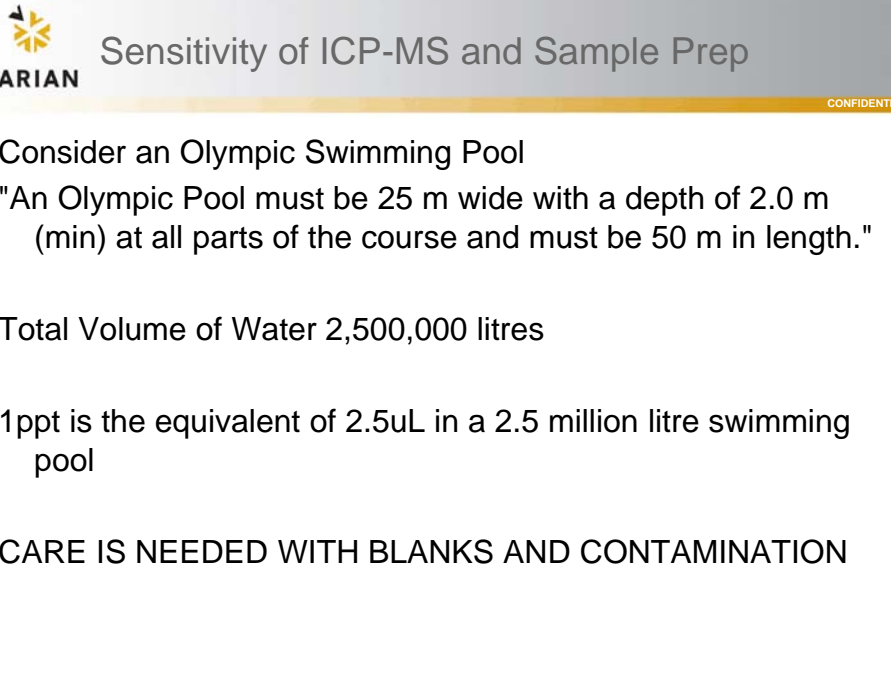
■ < 0.1 ppt
■ 0.1 - 1 ppt
■ 1 - 10 ppt
■ 10 - 100 ppt
■ 100 ppt - 10 ppb
■ > 10 ppb



Elemental Range

Dynamic Range



Sensitivity of ICP-MS and Sample Prep

Consider an Olympic Swimming Pool
 "An Olympic Pool must be 25 m wide with a depth of 2.0 m (min) at all parts of the course and must be 50 m in length."

Total Volume of Water 2,500,000 litres

1ppt is the equivalent of 2.5uL in a 2.5 million litre swimming pool

CARE IS NEEDED WITH BLANKS AND CONTAMINATION

Clean Practices for ICP-MS Sample Prep

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- No Glassware
- Always wear gloves
- Wash All Vessels Prior To Use (5% nitric 24-48 hrs)
- Optima Grade Acid For Sample Prep
- Trace Metal Grade Acid For Cleaning
- 18 M Ohm DI Water For All Dilutions

Forensic Applications: Gunshot Residue Analysis

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Application Note 00406
Determination of Antimony, Barium and Lead in Gunshot Residues using the Varian 810-MS
Mudong Wang
Varian, Inc.

Introduction
Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has become one of the most popular and powerful analytical techniques for a very wide range of trace element determination. ICP-MS combines high sensitivity, low detection limits, wide analytical range, multi-element capability (over 70 elements), and the ability to perform both semi-quantitative and fully quantitative analysis.
Varian's patented 80 degree ion mirror ion optical provides unsurpassed efficiency of transfer of ions from the interface to the main analyzer. It enables the Varian ICP-MS to achieve a sensitivity of more than 1000 million (10⁸) which, maintaining excellent (100%) T flow. The Varian 810-MS can be upgraded to the Varian 810-MS, which includes Varian's unique patented gradient interference management system, the Collision Reaction Interface (CRI). The CRI reduces interferences for elements such as As, Se, Cr, V and Fe, thus permitting lower detection limits.
This application note demonstrates the ability of the Varian 810-MS to directly determine the concentrations of Sb, Ba and Pb in gunshot residue (GSR) collection swab solutions.

Instrumentation
The GSR analysis was carried out using the Varian 810-MS system and all experimental work was performed in a routine analytical laboratory, not under "clean-room" conditions. The Varian 810-MS is designed for ease of use, and all operations are fully controlled by the Varian ICP-MS expert software.
The ICP-MS expert software provides one-step instrument setup and optimization. With the auto-setup routine supplied with the software, the instrument can be automatically tuned to optimal analysis conditions. Typical method parameters and instrument settings used for the GSR analysis are listed in Table 1. A total sampling time, including the rinse and sample uptake delay, it around two minutes per sample.

Materials and Reagents
High-purity nitric acid (Ultrapure[®], Merck, Kilsyth, Victoria, Australia) and deionized water (18 MΩ cm¹, Millipore Milli-Q, Billerica, MA, USA) were used for the solution preparations. All labware, new or used, was thoroughly cleaned by acid washing and rinsing, and the clean containers were left filled with 1N HNO₃ until use.
Five calibration solutions, containing antimony, barium and lead at concentration levels of 1 µg/L, 5 µg/L, 10 µg/L, 20 µg/L, and 50 µg/L, were prepared by diluting a 100 µg/L multi-element stock solution (ICP-MS, Hospital Products, St. Leonards, NSW, USA) with 1N HNO₃. An internal standard solution, containing 20 µg/L of ¹¹⁵Sn, ¹¹³In, ¹¹⁵Tl, ¹¹³Bi and ²⁰⁸Pb, was prepared by diluting a 100 µg/L internal standard stock (ICP-MS, Hospital Products, St. Leonards, NSW, USA) with 1N HNO₃. Internal standardization is commonly used in ICP-MS to compensate for any variations in the sample introduction system. In this work, the internal standard was automatically added to the nebulizer

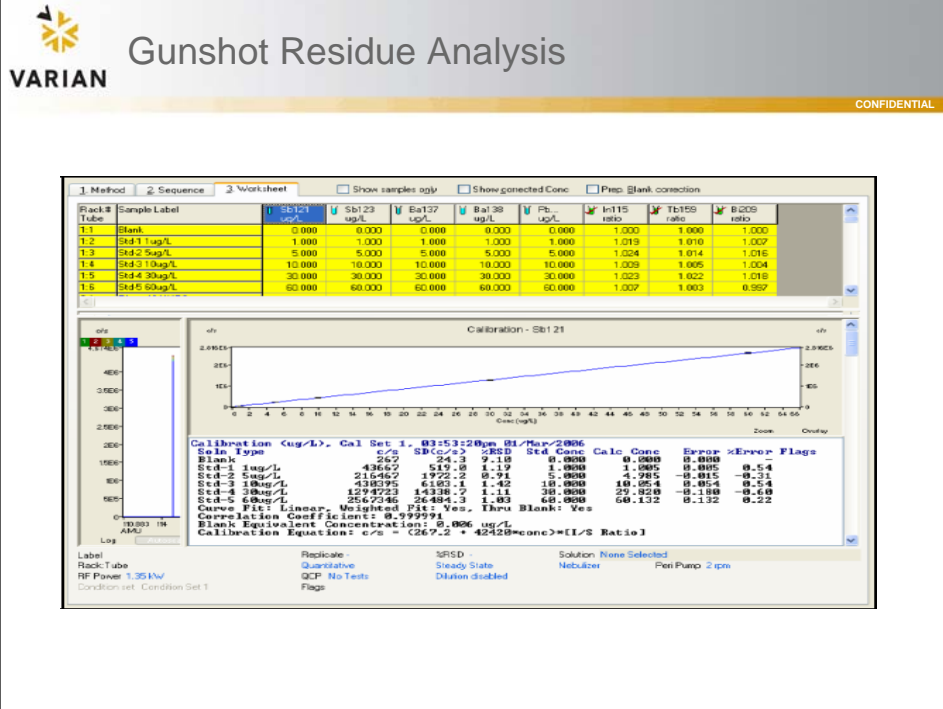
Table 1. Typical instrument conditions for the GSR analysis

Gas Flow Parameters	Instrument Parameters	Setting
Carrier Gas	Plasma Flow	14.5
Makeup Gas	Nebulizer Flow	0.80
Sample Nebulization	Sample Flow	0.80
	RF Power (W)	1.55
	Sampling Depth (mm)	8.0
	Ramp Rate (µg/L)	0.10
	Sample Dilution Ratio	6.00
Ion Optics (V)	RF Ion Mirror Volt	150
	Shield Gas Flow (L/min)	1.50
	Carrier Gas	250
	Makeup Gas	20
	Makeup Gas	20
	Internal Ion Filter	On
	Intercept Lens	Off
	Intercept Lens	Off
	Magnifier	Off
	Peak Mapping	On
	Scan Mode	Peak Mapping
	Scan Rate (cps)	25
	Integration	25
	Integration	5

• GSR swabs taken from the hand and rifle.

• Samples were analyzed for antimony, barium and lead

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Gunshot Residue Analysis

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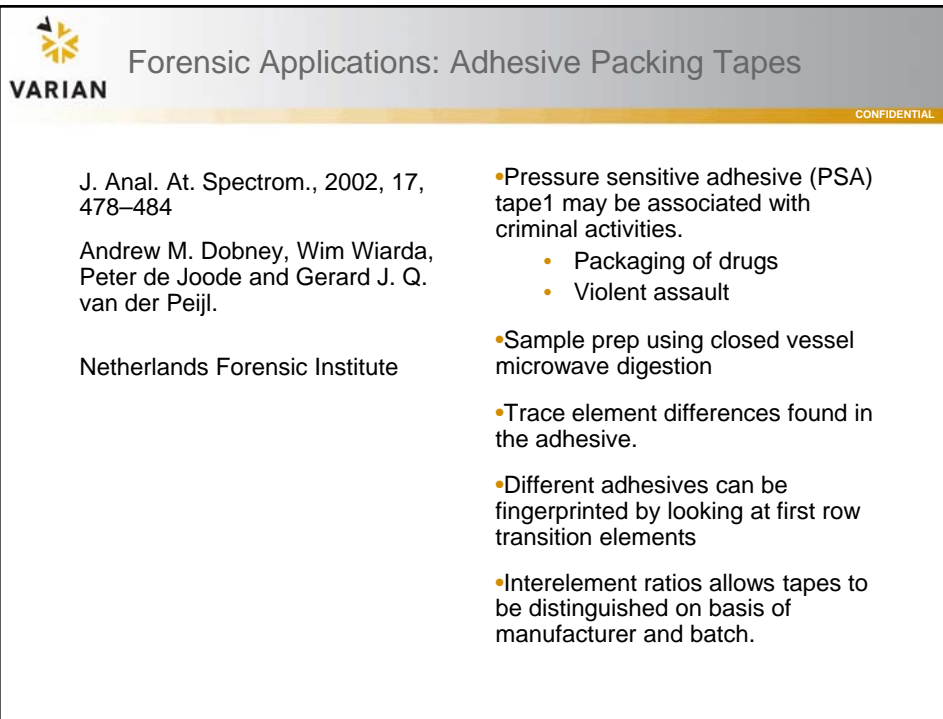
Rack#	Sample Label	U Sb121 ug/L	U Sb123 ug/L	U Ba127 ug/L	U Ba138 ug/L	U Pb ug/L	U In115 ratio	U Tb155 ratio	U Bi209 ratio
1.1	Blank	0.000	0.000	0.000	0.000	0.000	1.000	1.000	1.000
1.2	Std1 1ug/L	1.000	1.000	1.000	1.000	1.000	1.013	1.010	1.007
1.3	Std2 5ug/L	5.000	5.000	5.000	5.000	5.000	1.024	1.014	1.015
1.4	Std3 10ug/L	10.000	10.000	10.000	10.000	10.000	1.029	1.005	1.004
1.5	Std4 30ug/L	30.000	30.000	30.000	30.000	30.000	1.023	1.022	1.018
1.6	Std5 60ug/L	60.000	60.000	60.000	60.000	60.000	1.007	1.003	0.997

Calibration - Sb121

Cal Set 1: 0.353520pm 01/May/2006

Sample	Conc	SD	SSD	Std Conc	Calc Conc	Error	%Error	Flags
Blank	56.9	24.3	9.18	0.000	0.000	0.000	0.000	-
Std-1	1.0	5.19	1.12	1.000	1.000	0.000	0.000	0.54
Std-2	5.0	17.22	0.91	5.000	4.985	-0.015	-0.31	
Std-3	10.0	6.183	1.42	10.000	10.004	0.004	0.04	
Std-4	30.0	14.38	1.11	30.000	29.920	-0.080	-0.27	
Std-5	60.0	24.84	1.83	60.000	60.132	0.132	0.22	

Curve Fit: Linear, Weighted Fit: Yes, Thru Blank: Yes
 Correlation Coefficient: 0.99991
 Blank Equivalent Concentration: 0.006 ug/L
 Calibration Equation: $y = 0.99991x + 0.006$



Forensic Applications: Adhesive Packing Tapes

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J. Anal. At. Spectrom., 2002, 17, 478-484

Andrew M. Dobney, Wim Wiarda, Peter de Joode and Gerard J. Q. van der Peijl.

Netherlands Forensic Institute

- Pressure sensitive adhesive (PSA) tape1 may be associated with criminal activities.
 - Packaging of drugs
 - Violent assault
- Sample prep using closed vessel microwave digestion
- Trace element differences found in the adhesive.
- Different adhesives can be fingerprinted by looking at first row transition elements
- Interelement ratios allows tapes to be distinguished on basis of manufacturer and batch.



Forensic Analysis: Analysis of Glass

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Forensic glass analysis by ICP-MS: a multi-element assessment of discriminating power via analysis of variance and pairwise comparisons

Douglas C. Duckworth,^a Shelby J. Martin,^a Charles S. Bayne,^{ab} Robert D. Kocsis,^c Sharyn Mouton^d and Joel R. Abusalt^{de}

^aChemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6175, USA

^bComputer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6148 USA. E-mail: bayne@ornl.gov Fax: 606 574 1517; Tel: 606 574 9314

^cForensic Science Research Unit, FBI Laboratory, FBI Academy, Quantico, VA 22135, USA

^dInternational Forensic Research Institute, Florida International University, Department of Chemistry, University Park, Miami, FL 33199, USA. E-mail: abusalt@fiu.edu

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Glass fragments from 81 automobile side windows were collected and analyzed by the FBI Laboratory using ICP-AES in 1991. The FBI selected elements (Al, Ba, Ca, Fe, Mg, Mn, Na, Si and Ti) to use for discrimination among the glass samples. This multi-element discrimination showed a significant improvement in the discrimination variance over using only refractive index (RI) measurements. Oak Ridge National Laboratory (ORNL) recently analyzed fragments from 76 of the original side window fragments using inductively coupled plasma mass spectrometry (ICP-MS). The ICP-MS analysis revealed 41 elements using a detection limit ranging from 10 to 5000 pg g⁻¹. The 41 elements were used to create a 41-element discriminative analysis and with single isotopes (Si, Al) and various due to isotopic measurements (Na, S). The between-window ratio (BW = Na/Si, S/Al) affected a measure of the variance within the population in that in the analytical measurement, providing a first approximation of the discriminating power of each element. Florida International University applied the RI measurement on 75 variable glass fragments. These RI measurements along with ICP-MS and ICP-AES elemental analysis were used to assess the potential of all possible pairs of the 75 glass that had a complete set of measurements. The pairwise comparisons used Taylor's F_{0.95} method to compare RI and element-to-element discrimination potential of ICP-AES and ICP-MS for analyzing glass in forensic casework.

Introduction
The goal of a forensic examination of glass is to determine if an association between a suspect's fragment and a fragment of glass from a particular vehicle is reasonable. This goal is achieved when an association is found in the best of quality of the techniques used to distinguish between the glass specimens. Refractive index (RI) can be measured with sufficient accuracy to distinguish between most forensic glass. However, RI is not a reliable method to distinguish between glass samples in forensic laboratories as this method requires a very small amount of glass sample in manufacturing and is widely accepted in the forensic community and the laboratory system as good evidence of an association.¹ Recently, multielement analysis is being used to distinguish between glasses of different origin where the use of RI alone fails. Multielement analysis, refractive index and mass spectrometry (ICP-MS) are used to identify and compare the analysis of glass fragments. The available elemental analysis of forensic glass fragments is reviewed in this paper.² The use of ICP-MS for forensic glass analysis is discussed in this paper.³ The use of ICP-MS for forensic glass analysis is discussed in this paper.³ The use of ICP-MS for forensic glass analysis is discussed in this paper.³

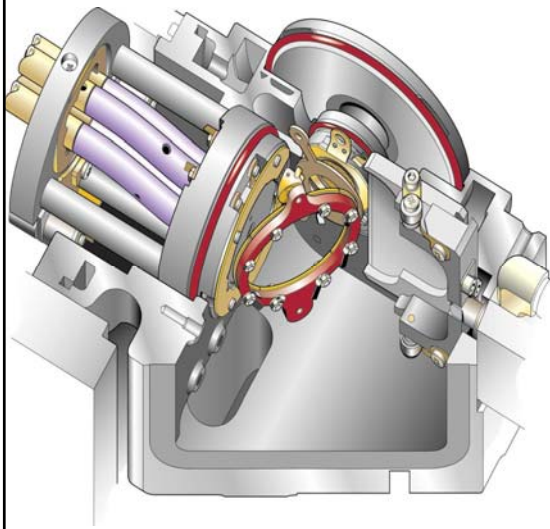
ICP-MS
ANALYSIS
FOCUS

- Broken glass may be associated with criminal activities.
- Small fragments of glass are easily transported on clothing
- Samples were crushed, then digested with a HF, HCl, HNO₃ mix on a hotplate
- 45 Elements were identified as being useful differentiators
- A limitation of ICP-MS noted as being a requirement for sequential dilutions – Varian has addressed this with its current design of ICP-MS.



Varian's Ion Optics Design – the 90 Degree Ion Mirror

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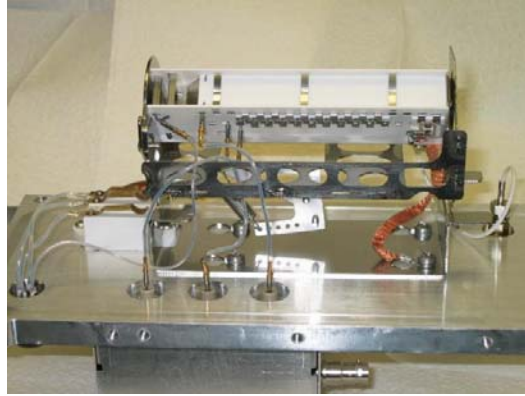
- Ions reflected & focused at 90° by parabolic electrostatic field produced by patented ion mirror
- No scanning of applied voltages is required
- Focuses analyte ions into the mass analyzer at unrivaled efficiency (> 80% from simulation studies)
- Provides Highest Sensitivity coupled with low backgrounds



Optimized Detector Design

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All-digital extended range detector with patented electronic readout

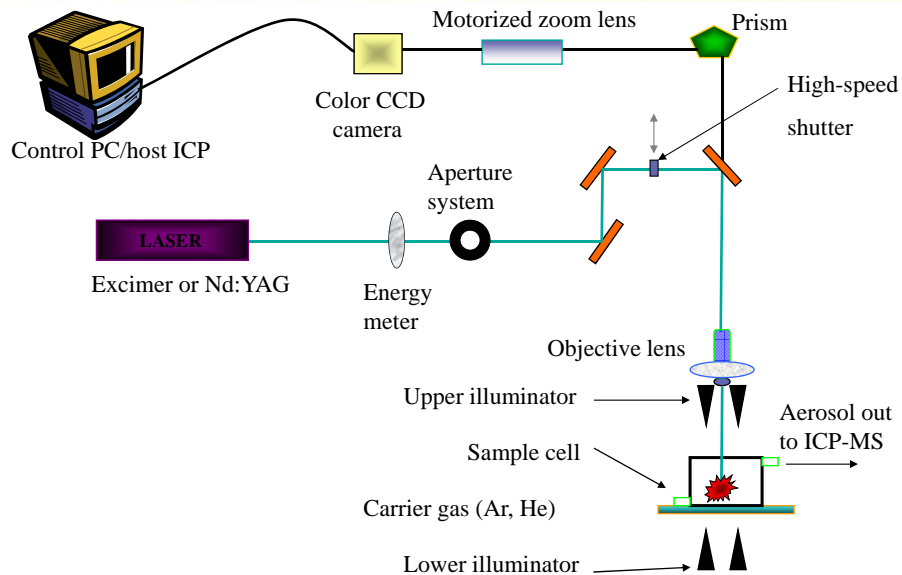


- **9 orders of dynamic, linear range with no need for cross calibrations**
- Simplifies analysis and results in less need to dilute over range samples
- All digital design extends detector lifetime.



Laser Ablation Sample Introduction

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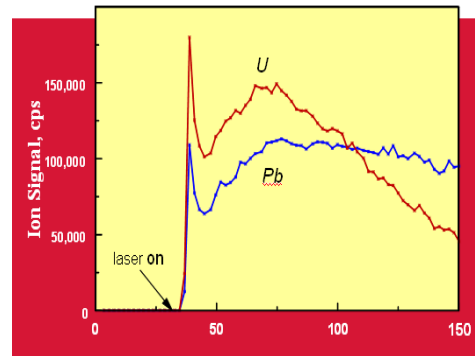




Laser Ablation For Solid Samples

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- Minimal Sample Prep
- Spatially Resolved Analysis
- Laser Induced Fractionation Can Provide Additional Evidence of Whether Samples Come From The Same Source



Conclusions

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- ICP-MS provides wide elemental coverage, wide dynamic range and high throughput.
- Different sample introduction techniques such as laser ablation permit direct analysis of solids
- ICP-MS now more robust and easy to use
- **The Ideal Tool for Trace Element Fingerprinting of Forensic Materials**



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