

MULTIELEMENTAL ANALYSES OF TREE RINGS BY
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

G.S. Hall*, D.K. Yamaguchi**, T.M. Rettberg***

*Department of Chemistry, Rutgers,
The State University of New Jersey,
New Brunswick, N.J. 08903, USA

**Mountain Research Station and Institute of
Arctic and Alpine Research (INSTAAR),
University of Colorado, Boulder, Co. 80309, USA

**VG Instruments Inc., Danvers, Ma., 01923, USA

Received 19 September 1990

Accepted 27 September 1990

Inductively coupled plasma mass spectrometry (ICP-MS) was evaluated for major, minor, trace, and ultra-trace elemental analyses of individual tree rings. The samples were obtained from an old-growth Douglas fir (*Pseudotsuga menziesii*) growing 15 km northeast of Mount St. Helens volcano, Washington, USA and from trees at various other North American sites. Samples were brought into solution by microwave digestion in sealed Teflon vessels. Eighty percent of elements from Li to U had detection limits in the solid (wood) below 8.0 ng g^{-1} (parts per billion, ppb). When selected element concentrations in the Mount St. Helens samples are plotted against time, two anomalous peaks occur at A.D. 1478 and 1490 that closely correlate with past eruptions of the volcano. These preliminary results show that ICP-MS is a rapid and sensitive analytical method for multielemental analyses of individual tree rings.

* To whom correspondence should be addressed.

INTRODUCTION

Elemental analyses of tree rings have various application such as examining pollution histories¹ and as palaeoclimatic indicators². Previously INAA³, ICP-AES⁴, PIXE-PIGE⁵, EDXRF⁶, and TIMS⁷ have been used to determine elemental concentrations in tree rings. However, none of these methods can be used to determine more than 30 elements in an individual ring. The ideal analytical method for tree-ring analyses would have the following properties:

- fast sample throughput,
- the ability to determine isotopes and to do isotope dilution,
- the ability to determine major, minor, trace, and ultra-trace elements during a single analysis,
- minimum operator intervention,
- the ability to determine more than 60 elements,
- the ability to analyze small samples, and
- minimum matrix effects.

Pioneering experiments by Gray et al.⁸ demonstrated the feasibility of extracting and mass analyzing ions from a direct current argon plasma (DCAP). Additional experiments by Houk et al.⁹ showed that lower detection limits could be obtained using an inductively coupled argon plasma (ICAP). Subsequently, the combined experiments led to the development of a very sensitive (sub parts per trillion, ppt, in solution) technique, inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS can meet the requirements outlined above for multielemental analyses of individual tree rings.

Recent applications of ICP-MS¹⁰⁻¹² in the physical sciences prompted us to evaluate the technique for

routine multielemental analyses of individual tree rings. The introduction of a new generation of spectrometers (VG Plasma Quad PQ2 Plus Turbo) with low ppt solution detection limits, further stimulated our interest in the technique. The objective of this study was to determine if ICP-MS is suitable for multielemental analyses of individual tree rings.

EXPERIMENTAL

Samples

Evaluation of ICP-MS was performed on a Douglas-fir (*Pseudotsuga menziesii*) stump wedge obtained from the forest 15 km northeast of Mount St. Helens (MSH) volcano, Washington, USA. The site was impacted by the fallout of 90 cm of tephra ("volcanic ash") Wn in A.D. 1479-1480, and by the fallout of about 10 cm of tephra set X during the A.D. 1482-1510 interval¹³⁻¹⁵. The tree rings were dated accurately using standard dendrochronological methods¹⁶. Additional tree rings analyzed included ponderosa pine, giant sequoia, bristlecone pine, and white oak from various North American sites. Individual rings were separated using a stainless steel razor blade; consequently some samples showed Ni contamination.

Approximately 0.250 g of each ring was transferred to a CEM Teflon digestion vessel and 3 ml of ultrapure (Ultrax) HNO₃ was added. Each vessel was sealed and placed in a CEM microwave oven for dissolution. Samples were digested for 10 min at 20% power. After allowing vessels to cool to room temperature, they were vented to release digestion gases (CO₂, NO). These

samples were again subjected to microwave digestion for 15 min at 30% power. After dissolution, vessel contents were quantitatively transferred to tared acid-washed polyethylene bottles. Subsequently, samples were gravimetrically diluted to 10 g using high purity water obtained from a Millipore purification system. Digested tree-ring solutions were then aspirated into the ICP-MS. A 30 sec sample equilibration time was allowed before data acquisition started. A one minute rinse with dilute HNO_3 was used between samples to reduce memory effects.

Solution detection limits were determined by analyzing the procedural blank 5 times as an unknown sample and multiplying the resulting standard deviations by 3. More realistic detection limits for the solid wood were determined by multiplying solution detection limits by 40 (0.250 g wood digested and diluted to 10 g with H_2O).

To validate the sample preparation method and the ICP-MS analysis, National Institute of Standards and Technology (NIST) SRM 1575 (pine needles) were carried through the same procedure. A blank containing Ultrex HNO_3 was also carried through the procedure to determine detection limits and to use for blank subtraction during data analysis.

Instrumental

For data acquisition and analysis, we used a VG Instruments PlasmaQuad PQ2 Plus ICP-MS (VG Elemental, Winsford, Cheshire, UK) with dual-mode detection¹⁰ in the jump/scanning mode. Instrument operating parameters are summarized in Table 1. The spectrometer was calibrated with aqueous standards prepared from NIST stock

TABLE 1

PlasmaQuad operating parameters

Plasma	
Forward rf power	1400 W
Reflected rf power	<10 W
Coolant flow (Ar)	13 l min ⁻¹
Nebuliser flow (Ar)	1 l min ⁻¹
Spray chamber temperature	Controlled at 10±0.2 °C
Nebuliser	Meinhard concentric
Sample uptake rate	0.7 ml min ⁻¹
Sampling depth	12 mm beyond load coil
Mass spectrometer	
Sampler, nickel	1.0 mm orifice (Nicone)
Skimmer, nickel	0.75 mm orifice (Nicone)
Interface operating pressure	1.9 mbar
Analyser pressure	2.5×10 ⁻⁶ mbar
Data acquisition	
Mass range	6.02 to 249.14 amu
Number of channels	4096
Dwell time (µs)	320
Run time	65.5 s
Collector type	Dual mode
Skipped mass regions	
Pulse counting	11.50-22.50, 27.50-28.50, 29.50-30.50, 31.50-33.50, 34.50-41.50, 79.50-80.50
Analog	13.50-22.50, 39.40-41.50 70.00-249.10

standards. The following elements were used to generate the instrument response curve using ¹¹⁵In as an internal standard: ⁹Be, ²⁴Mg, ⁵⁹Co, ¹¹⁵In, ²⁰⁸Pb, and ²³⁸U. The response curve was used in the semi-quantitative data analysis mode to determine the concentrations of 65 elements from Li to U. Rare-earth element (REE) concentrations were determined more accurately using external calibration.

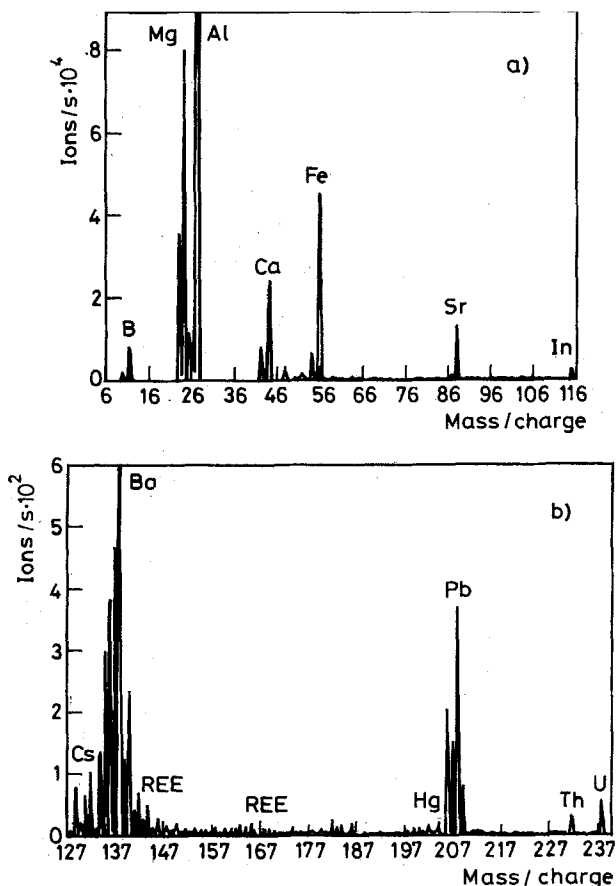


Fig. 1. ICP-MS spectra of 1490 Mount St. Helens tree ring: (a) 6.02-127.00 amu, and (b) 128.00-238.00 amu. Some peaks are marked for clarity

RESULTS AND DISCUSSION

A typical mass spectrum of a tree ring is presented in Fig. 1. Element concentrations in the standard pine needles were within 15-20% of certified values. This level of agreement was excellent considering the instrument was calibrated with 6 elements to cover the

TABLE 2
ICP-MS tree-ring detection limits (DL) in
semiquantitative mode

Element	Mass	*DL, ng g ⁻¹	Element	Mass	*DL, ng g ⁻¹
Li	7	558.48	Sb	121	1.08
Be	9	20.16	Te	128	4.60
B	11	16.68	Cs	133	1.84
Na	23	14.08	Ba	138	1.88
Mg	24	10.76	La	139	1.20
Al	27	88.28	Ce	140	1.44
Ca	44	1435.92	Pr	141	1.04
Sc	45	7.80	Nd	146	7.68
Ti	47	51.48	Sm	152	4.36
V	51	1.28	Eu	153	1.72
Cr	52	8.36	Gd	158	2.00
Mn	55	11.80	Tb	159	0.36
Fe	57	512.36	Dy	163	1.64
Co	59	5.08	Ho	165	1.56
Ni	60	17.64	Er	166	3.16
Cu	63	0.84	Tm	169	0.84
Zn	66	10.36	Yb	172	1.96
Ga	69	3.64	Lu	175	0.48
Ge	72	3.96	Hf	178	2.28
As	75	2.20	Ta	181	0.60
Se	77	23.52	W	182	2.56
Rb	85	1.40	Re	187	1.40
Sr	88	2.84	Os	192	2.28
Y	89	1.96	Ir	193	1.28
Zr	90	3.12	Pt	195	1.92
Nb	93	2.12	Au	197	0.56
Mo	98	0.56	Hg	202	1.20
Ru	102	4.16	Tl	205	0.80
Pd	106	0.48	Pb	208	1.76
AG	109	4.80	Bi	209	0.40
Cd	111	7.44	Th	232	0.56
In	115	1.32	U	238	0.92
Sn	120	6.40			

*Based on 0.250 g of wood with a dilution factor of 40.

mass range 6.02 to 249.14 amu. After external calibration, REE concentrations in the pine needles were within 0.5-1% of certified values.

Wood detection limits for the solid wood are summarized in Table 2. These detection limits are quite

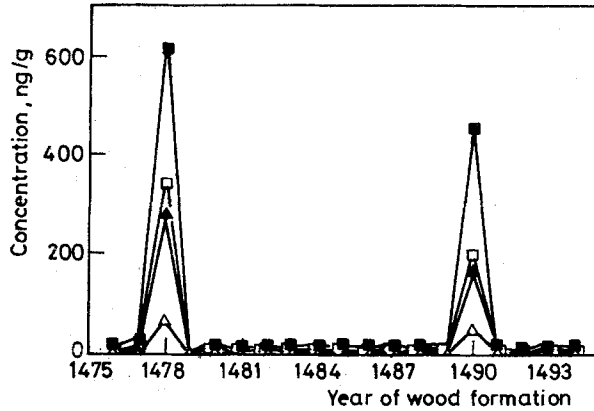


Fig. 2: Selected rare-earth elements, Ce (■), Nd (□), La (▲), and Sm (△) in Mount St. Helens tree rings

impressive even after a 40 fold dilution. However, our reported detection limits can be improved by using a "cleaner blank" and by cleaning the sampler and skimmer. Such low detection limits would be useful when individual tree rings of 10-30 mg are obtained from 4.5 mm diameter tree cores.

The concentrations of selected REE in MSH tree rings are plotted against time in Fig. 2. These data are the first reported concentrations of REE in tree rings. Two anomalous peaks at A.D. 1478 and 1490 closely correlate with the Wn and X tephra eruptions. Other REE (Gd, Lu, Tm etc.) showed similar peaks. However, it is puzzling that the 1478 chemical anomaly predates the possible 1479-80 interval of the Wn eruption by one year. High concentrations of Mn, Cu, Zn, and Ca in tree rings from giant sequoia correlated with forest fire dates. Concentrations of Na, Mn, Zn, and Rb in white oak (Hubbard Brook, N.H., USA) tree rings were correlated with acid rain.

These preliminary results show that ICP-MS, combined with microwave digestion, is an excellent analytical technique for individual tree-ring analysis. Major (Mg, P, etc.), minor (Na, Ca, etc.), trace (Mn, Cu, etc.), and ultra-trace (Sm, Cs, etc.) elements can be determined simultaneously during a single analytical run. This is because of the 8-order linear dynamic range of and because of the dual-mode detection capability of the spectrometer. The semi-quantitative mode is advantageous because it does not require that the analyst know which elements might be significant in a sample. Results therefore are not biased by a preconceived notion of what is present in a sample. Also, since data are collected for all elements, they can be re-inspected at a later date to evaluate other interesting features in the data. For example, because we did not know which elements would show responses to tephra eruptions, we analyzed all elements from Li to U.

ICP-MS is an excellent method for the determination of Pb in tree rings. All four isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb) were detected in our samples. By comparing the isotopic ratios of Pb in tree rings with ratios from anthropogenic sources, pollution chronologies can be constructed.

We have also evaluated laser ablation ICP-MS to measure elemental concentrations in solid wood. The technique shows promise if the spectrometer is calibrated with a standard that has a matrix similar to a tree ring.

Superior detection limits, rapid sample throughput, multielemental analysis, simple spectra, and ease of operation make ICP-MS the method of choice for individual tree-ring analysis. We have adopted the techni-

que for routine elemental analyses of many different kinds of tree rings for applications in acid rain, archaeology, and volcanic history.

*

We thank G. Gibson of VG Instruments Inc. for arranging access to the ICP-MS. This research was supported by NSF grant RII-8506643.

REFERENCES

1. E.A. Bondietti, C.F. Baes, S.B. McLaughlin, Can. J. For. Res., 19 (1989) 586.
2. R. Ramesh, S.K. Bhattachara, K. Goplan, Nature, 317 (1985) 802.
3. R. Tout, W. Gilboy, N. Spyrou, J. Radioanalytical Chem., 37 (1977) 705.
4. H. Matusiewicz, R. Barnes, Anal. Chem., 57 (1985) 406.
5. G.S. Hall, Nucl. Instr. Methods in Physics Research, B49 (1990) 60.
6. L.E. MacLauchlan, M.R. Cackette, J.M. D'Auria, J.H. Borden, Can. J. For. Res., 17 (1987) 1124.
7. R. Holtzman, Environ. Sci. Tech., 4 (1970) 314.
8. A.L. Gray, Proc. Soc. Anal. Chem., 11 (1974) 182.
9. R.S. Houk, V.A. Fassel, D.G. Flesch, H.J. Svec, A.L. Gray, C.E. Taylor, Anal. Chem., 52 (1980) 2283.
10. R.C. Hutton, A.N. Eaton, R.M. Gosland, Appl. Spect., 44 (1990) 238.
11. J.K. Friel, C.S. Skinner, Analyst, 115 (1990) 269.

12. L.K. Olson, J.A. Caruso, F.L. Fricke, Appl. Spect., 44 (1990) 716.
13. D.K. Yamaguchi, Geology, 13 (1985) 554.
14. D.R. Mullineaux, Bull. Volcanol., 48 (1986) 17.
15. D.K. Yamaguchi, Ph.D. dissertation, University of Washington, Seattle, Wa., USA, (1986).
16. M.A. Stokes, T.L. Smiley, *An Introduction to Tree-Ring Dating*, Univ. Chicago Press, Chicago, Il. USA, (1968).