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POTENTIAL OF LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR MULTIELEMENTAL ANALYSIS OF BIOLOGICAL MATERIALS

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ABSTRACT:

The performance, problems and promise of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for the elemental analysis of biological matrices are briefly reviewed.

1. INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) has become established as a sensitive method for elemental and isotopic analysis during the last decade [1-3]. The great expansion in the user-base has opened a market for alternative sample introduction methods to the conventional pneumatic nebulization (PN) of aqueous sample solutions. Of the alternatives, laser ablation (LA) of solid samples is one of the most attractive because it offers a number of analytical advantages, including little or no sample preparation; rapid sample throughput; relatively low background levels; relatively low levels of water-related spectral interferences; good detection limits and wide dynamic range; and the possibility of spatially-resolved analysis. Owing to the matrix-dependence of the ablation process, the major difficulty lies in obtaining accurate and precise concentration data.

Since its introduction by Gray [4], LA-ICP-MS has received considerable attention for the analysis of rocks [5,7], soils [8], sediments [9], metals [10], and even plastics [11]. However, it is only recently that any attention has been given to the pros and cons of the analysis of biological materials by this method. In this work, these aspects are reviewed and prospects for development indicated.

2. LASER SYSTEMS

Pulses from a ruby [4] or Nd:Yttrium aluminium garnet [12] laser are usually used for sample ablation. The sample sits on a platform within a glass cell. Typically, the platform, which may be viewed by video camera, is movable under computer control to allow an unablated surface to be presented to successive laser pulses. Either giant (Q-switched) or freerunning (N mode) pulses may be employed, but the former are typically used on more modern systems for maximum sensitivity. The Q-swiched pulses are relatively short (μs to ns), while N mode pulses are relatively long (ms); thus the power densities associated with the former are relatively high.

The incident laser pulses cause heating of the sample surface and material erupts at high velocity. Some of the vapour and aerosol generated is swept to the central channel of the ICP by a suitable flow of argon, typically about 0.8 L/min, a value similar to that typically used in PN.

Owing mainly to greater ablated mass, response (count rate at a given mass) increases with increasing laser energy (in either laser mode), which is set empirically to give adequate responses across the mass range. Optimization is time-consuming and tedious, and need not detains us here. Readers interested in this are directed to two recent publications [13,14].

3. LITERATURE ON BIOLOGICAL ANALYSIS

In a paper that was mainly concerned with a comparison of the capabilities of instrumental neutron activation analysis to those of ICP-MS, Ward *et al* [15] reported concentrations of V, Fe, Mn, Ni, Co, Cu, Zn, As, Se, Sr, Mo, Cd and Pb in National Institute of Standards and Technology (NIST) Standard Reference Material 1577 Bovine Liver determined by LA-ICP-MS. A disc of sample was prepared by mixing 0.96 g of dried material with 0.24 g of Elvesite 2013 (a carbonaceous binder) in a tungsten mill. The resulting powder was pressed in an aluminium cup (usually used in x-ray fluorescence). Pressing of the cup to 10 tonnes produced a disc of about 3 cm diameter and of height 3 mm. A disc of the Canadian reference material TORT-1 Lobster Hepatopancreas was similarly prepared for use as a calibration

standard.

The sample and standard were ablated with five N mode shots (0.35 J) per integration. Individual elemental sensitivities based on the certified concentrations in TORT-1 were used to calculate the concentrations in NIST 1577. Reasonable accuracies but poor precisions were obtained compared to PN-ICP-MS or certified concentrations.

This simple approach to calibration was applied to the determination of a wider range of elements in various biological materials by the author and colleagues (9, 14, 16). Fourteen elements - Al, P, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba and Pb - were determined in Japanese National Institute of Environmental Studies Certified Reference Materials (CRMs) number 1 (Pepper Bush) and number 7 (Tea Leaves) and eight elements were determined in International Atomic Energy Agency CRM All milk powder (9). The concentration data of the milk analysis are reproduced in Table 1.

TABLE I. Analysis of IAEA CRM All Milk Powder. Adapted from ref (9). Concentrations, mean (standard deviation), in µg/g dry mass.

Element	m/z	LA-ICP-MS	Certified
Na	23	5150(920)	4420(330)
Mg	24	1150(230)	1100(80)
Al	27	2.8(1.8)	1.3*
P	31	10700(2460)	9100(1020)
K	39	17210(2870)	17200(1000)
Mn	55	0.26(0.13)	0.377(0.081)
Fe	57	1.3(0.5)	3.65(0.76)
Zn	66	77.4(18)	38.9(2.3)

*Non-certified value

Successful multielemental analyses of plant materials - NIST SRMs 1571 Orchard Leaves and NIST 1573 Tomato Leaves - have also been reported (14). The feasibility of multielemental analysis of diverse biological matrices - hair, mixed diet and milk powder - was published only this year (16). Reasonable accuracies were obtained, but were inferior to those obtained by conventional PN-ICP-MS. Precisions too, were tipically poorer than those obtained by the conventional approach.

4. PERFORMANCE AND ANALYTICAL DIFFICULTIES

As noted in the introduction, a number of advantages are anticipated with the use of LA-ICP-MS and these are substantially met in practice. Depending on the matrix, direct ablation of the solid sample may be possible. Otherwise no more than ball-milling with an appropriate binder and pressing into a pellet is required.

Sample throughput equals or exceeds that obtained with sample introduction by PN. As sample interchange is simple and rapid, and the ablation cell may be rapidly purged, less time need be spent than is typically necessary with PN, were rinsing of the spray-chamber to avoid memory effects may take two minutes or more.

Background levels are low, as are memory effects. However, with the ruby system used by the author Q-switched pulses, particularly of high energy (> 0.5 J) typically produce a rapid expansion of gas in the cell to torch line which can re-suspend particles deposited on the tube linings, leading to high counts in 'blank' spectra obtained with data acquisition following ablation of an inert material such as Teflon™.

The relatively low water-loading of the plasma with LA leads to relatively low levels of water-related polyatomic interferences compared to those observed with PN (14). However, the analytical advantage of this depends upon the sensitivity obtained, and in practice this advantage may not be as great as it appears at first sight. Moreover, the relative inaccuracy of the technique inhibits the assessment of the magnitude of this effect.

Detection limits compare favourably to those obtained with PN. Although the latter may be lower by say two orders of magnitude, with PN 100-fold dilutions are typically necessary to reduce the dissolved solids content to acceptable levels. Thus in practice detection limits, or rather quantitation limits, obtained with LA are excellent. Table 2 shows multielement detection limits based on line equivalent background and sensitivities obtained from the analysis of NIST SRM 1549 (milk powder).

TABLE II. Detection limits for the analysis of NIST 1549 milk powder (values are concentrations in µg/g dry mass). Data adapted from ref (9).

Element	Detection limit	Element	Detection limit
Na	10.2	K	51
Mg	0.28	Mn	0.03
Al	0.01	Fe	0.04
P	58	Zn	1.5

A linear dynamic range of at least five orders of magnitude has also been demonstrated (9).

Difficulties in analysis relate to the matrix-dependence of the ablation process. In the studies of the analysis of biological materials cited, matrix-matched standards were employed, This or similar approaches to calibration have been widely used. However, the use of SRMs for calibration suffers a number of difficulties. A suitable matrix may not be available or may not be well-characterized. Certainly it is improbable that several well-characterized and suitable matrices will be available. Routine consumption of SRMs is also expensive.

For practical analysis a problem arises if the element of interest is not certified in the standard or is certified at a trace level, which will not, owing to sensitivity, provide a reliable calibration.

However, at high laser energies or repetition rates, saturation, an overabundance of counts, may occur at a particular m/z, either in the sample or in the standard analysis. This may be tolerated if the element affected is not of analytical interest or if an alternative isotope (m/z) is available. The number and mode of laser shots may be chosen to give high responses, response to background or response to noise ratios, but too high an ablation rate may also lead to deposition on the cell walls and associated gas lines, thus giving rise to memory effects or blockage of the torch injector tip or both. All these effects are detrimental to analytical performance. Moreover, if the ICP is completely overloaded with sample material the ionization process will be disturbed and no reliable analysis will then be possible.

A problem sometimes encountered is poor laser-sample coupling. For example, in the analysis of milk powder (9, 16), graphite is typically added to the mix prior to ball-milling. For a given laser pulse the pressed mix ablates better than pressed milk powder alone.

To improve accuracy internal standardisation on an element whose concentration is known in the sample is possible, but this necessitates a separate analysis by an independent technique. The element chosen for internal standardsation should ideally be homogeneously distributed in the sample and standard, and present sufficient sensitivity for reliable calibration.

To improve precision, internal standardisation between replicates (based on the response of a particular isotope) may be used. This may be done independently of internal standardisation to improve accuracy as described in the previous paragraph. Such a procedure corrects for effects such as differences in laser output between one data acquisition and the next.

5. PROSPECTS

The feasibilty of semiquantitative multielemental analysis of biological materials by LA-ICP-MS has been shown by the recent studies outlined above. A number of developments in this field may be expected, including, among others, studies of:

(1) the use of artificial biological standards in place of SRMs for calibration purposes;

(2) the microprobe capability inherent in the technique (17);

(3) the feasibility of the determination of isotope ratios (of which there is very little work to date);

(4) the addition of molecular gases, such as N_2, to the argon plasma for improved performance, particularly increased sensitivity (this has been shown to be feasible in PN-ICP-MS (18)).

Important would be novel methods to improve both accuracy and precision to enable LA-ICP-MS to provide fully quantitative analysis and thereby greatly increase the value of the technique. Already, however, the method shows great promise and is an additional tool in the armoury of the analyst.

6. REFERENCES

1. **DATE, A.R. & GRAY, A.L.**;Applications of Inductively Coupled Plasma Mass Spectrometry, Blackie and Son Ltd., Glasgow, 1989.
2. **GRAY, A.L.**; "The ICP as an ion

source-origins, achievements and propects", Spectrochim. Acta,40B(10-12): 1525-37, 1985.
3. **DURRANT, S.F.**; "Inductively coupled plasma-source mass spectrometry: the first decade", Braz. J. Vac. Appl., 10(1): 33-38, 1991.
4. **GRAY, A.L.**; "Solid sample introduction by laser ablation for inductively coupled plasma source mass spectrometry"; Analyst, 110(5):551-56, 1985.
5. **IMAI, N.**; "Quantitative analysis of original and powdered rocks and mineral inclusions by LA-ICP-MS"; Anal. Chim. Acta, 235(2):381-391, 1990.
6. **VAN HEUZEN, A.A.**; Analysis of solids by laser ablation - inductively coupled plasma mass spectrometry (LA-ICP-MS) -I. Matching with a glass matrix"; Spectrochim. Acta 46B(14): 1803-1817, 1991.
7. **PEARCE, N.J.G., PERKINS, W.T., ABELL, I., DULLER, G.A.T. & FUGE, R.**; "Mineral microanalysis by laser ablation inductively coupled plasma mass spectrometry"; J. Anal. At. Spectrom. 7(1):53-57, 1992.
8. **DURRANT, S.F. & WARD, N.I.**; "Rapid multielemental analysis of Chinese reference soils by laser ablation inductively coupled plasma-source mass spectrometry", Fres. J. Anal. Chem. 345:512-517, 1993.
9. **DURRANT, S.F.**; "Multielemental analysis of environmental matrices by laser ablation inductively coupled plasma mass spectrometry", Analyst 117:1585-1592, 1992.
10. **DURRANT, S.F.**; "Inorganic analysis of solids by laser ablation inductively coupled plasma-source mass spectrometry", Braz. J. Vac. Appl. 10(1):39-43, 1991.
11. **MARSHALL, J., FRANKS, J., ABELL, J. & TYE, C.**; "Determination of trace elements in solid plastic materials by laser ablation-inductively coupled plasma mass spectrometry", J. Anal. At. Spectrom. 6(2):145-150, 1991.
12. **ARROWSMITH, P.**; "Laser ablation of solids for elemental analysis by inductively coupled plasma mass spectrometry", Anal. Chem. 59(10):1437-1444, 1987.
13. **ABELL, I.D.**; "Performance benefits of optimisation of laser ablation sampling for ICP-MS" in Applications of Plasma Source Mass Spectrometry, Holland, G., Eaton, A.N. (eds), Roy. Soc. Chem., Cambridge, pp. 209-217, 1991.
14. **WARD; N.I., DURRANT, S.F. & GRAY, A.L.**; "Analysis of biological standard reference materials by laser ablation inductively coupled plasma mass spectrometry", J. Anal. At. Spectrom., 7(7):1139-1146, 1992.
15. **WARD, N.I., ABOU-SHAKRA, F.R. & DURRANT, S.F.**; "Trace elemental content of biological materials: a comparison of NAA and ICP-MS analysis", Biol. Tr. El. Res. 26-27:177-187, 1990.
16. **DURRANT, S.F. & WARD, N.I.**; "Laser ablation - inductively coupled plasma-mass spectrometry (LA-ICP-MS) for the multielemental analysis of biological materials: a feasibilty study", Food Chemistry 49(3):317-323, 1994.
17. **HUANG, Y., SHIBATA, Y. & MORITA, M.**; "Microlaser ablation-inductively coupled plasma mass spectrometry. 1. Instrumentation and performance of micro laser ablation system", Anal. Chem. 65(21):2999-3003, 1993.
18. **DURRANT, S.F.**; "Alternatives to all-argon plasmas in inductively coupled plasma mass spectrometry (ICP-MS): an overview", Fres. J. Anal. Chem. 347:389-392, 1993.